Theory of Coarse-Graining
Vol 2: Continuum descriptions

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Contents

"What a scientist tries to do essentially is to select a certain domain, a certain aspect, or a certain detail, and see if that takes its appropriate place in a general scheme which has form and coherence; and, if not, to seek further information which would help him to do that."

Subramanian Chandrasekhar in *"The Works of the Mind"*, p.176, edited by Robert B. Heywood, University of Chicago Press, 1947.

Preface

1

Dynamics in the averages flavour

1.1 Introduction

In this chapter, we present the derivation of the fundamental dynamic equation of non-equilibrium statistical mechanics for isolated systems that describe the tendency towards equilibrium of the *averages* of the CG variables. In the next Chapter, we will consider the evolution of the full probability of the CG variables.

1.2 The objective of coarse-graining

The main objective of the Theory of Coarse-Graining is to obtain a dynamical description of a system with much less information than the one given in the microscopic level. This is achieved by constructing dynamic equations for the time dependent averages of the CG variables. The CG variables change in time because the microscopic state of the system changes in time as shown in (**??**). Of course, because we do not know with certainty the initial microstate of the system, we do not know the actual value of the relevant variable at a given time with certainty. Therefore, it makes sense to take the average of the CG variables over initial conditions

$$a(t) \equiv \langle A \rangle_t = \int dz\, \hat{A}(\mathcal{U}_t z)\rho_0(z) \tag{1.2.1}$$

where $\rho_0(z)$ is the probability distribution over initial conditions. For simplicity, we understand $\int dz$ as a sum over microstates in a macrocanonical setting. Equivalently, we may write the average as

$$a(t) = \int dz\, \hat{A}(z)\rho_0(\mathcal{U}_{-t} z) = \int dz\, \hat{A}(z)\rho_t(z) \tag{1.2.2}$$

where we have used a change of variables $z \rightarrow \mathcal{U}_{-t} z$ with unit Jacobian, and (**??**). Therefore, the time dependent average over initial conditions is equal to the average of the CG variables with the real ensemble that is solution of the Liouville equation. By analogy with Quantum Mechanics Eqs. (1.2.1) may be called the Heisenberg representation for

the average where the phase function is evolving, whereas (1.2.2) may be called the Schrodinger representation in which the ensemble is evolving in time.

The time derivative of the average of the CG variables is given by

$$\frac{d}{dt}a(t) = \int dz\hat{A}(z)\partial_t\rho_t(z) = -\int dz\hat{A}(z)i\mathcal{L}\rho_t(z) = \int dz\rho_t(z)i\mathcal{L}\hat{A}(z) \qquad (1.2.3)$$

where we have used the Liouville's equation (**??**). Of course, (1.2.3) is not a proper dynamic equation for $a(t)$ because the right hand side is not a function of $a(t)$ and this equation is not a *closed* differential equation for the averages. How to close this equation? Imagine for a moment that the solution of the Liouville's equation $\rho_t(z)$ could be very well approximated by a time-dependent relevant ensemble $\overline{\rho}_t(z)$ of the form (**??**) corresponding to the value of the average $a(t)$

$$\overline{\rho}_t(z) = \rho_N^0 \frac{\exp\{-\lambda(t)\hat{A}(z)\}}{Z(\lambda(t))} \qquad (1.2.4)$$

The conjugate variables $\lambda(t)$ are adjusted in such a way that the relevant ensemble does produce the correct macroscopic averages

$$a(t) = \int dz\hat{A}(z)\overline{\rho}_t(z) \qquad (1.2.5)$$

Because the connection between the averages and the conjugate variables is one to one, the relevant ensemble $\overline{\rho}_t(z)$ is fully determined by the average values $a(t)$. If we are allowed to approximate the real ensemble $\rho_t(z)$ by the relevant ensemble (1.2.4), this is

$$\rho_t(z) \approx \overline{\rho}_t(z) \qquad (1.2.6)$$

we obtain after introducing (6.7.2) into (1.2.3)

$$\frac{d}{dt}a(t) = \int dz\overline{\rho}_t(z)i\mathcal{L}\hat{A}(z) \qquad (1.2.7)$$

The right hand side of this equation is now a function of the averages through the relevant ensemble and, therefore, (1.2.7) is a closed equation for the averages.

Unfortunately, the real ensemble is not well approximated by the relevant ensemble in general. At later times, equations of the form (1.2.7) only capture the *reversible* part of the dynamics and all the interesting dissipative processes are eliminated in this approximation. What do we mean by this? Consider the time-dependent entropy function which is the result of evaluating the entropy (**??**) of the given level of description at the value of the average $a(t)$. If we take the time derivative we obtain

$$\frac{d}{dt}S(t) = \frac{\partial S}{\partial a}[a(t)]\frac{d}{dt}a(t) = -\lambda(t)\int dz\hat{A}(z)i\mathcal{L}\overline{\rho}_t(z) = \int dzi\mathcal{L}\overline{\rho}_t(z) = -\frac{d}{dt}\int dz\overline{\rho}_t(z) = 0$$
$$(1.2.8)$$

where we have used the chain rule, (**??**), (1.2.7), the form of the relevant ensemble (**??**)

and, in the last identity, that the relevant ensemble is normalized. Therefore, the dynamic equation (1.2.7) does not produce any increase of the entropy function and can be termed a reversible equation.

Despite of its shortcomings, the approximation (6.7.2) suggests the procedure in order to obtain closed equations for the averages. We may write the real ensemble as the sum of two contributions

$$\rho_t(z) = \overline{\rho}_t(z) + \delta\rho_t(z) \tag{1.2.9}$$

The term $\delta\rho_t(z)$ is known as the non-relevant part. If we could express the non-relevant part $\delta\rho_t(z)$ in terms of the relevant part $\overline{\rho}_t(z)$ we would solve the problem because then, the real ensemble $\rho_t(z)$ would be expressed in terms of the averages $a(t)$ on which the relevant ensemble depends. The main tenet of the Theory of Coarse-Graining is that one can fully express the real ensemble $\rho_t(z)$ in terms of the relevant ensemble at *present and past times*. That this can be achieved at all is shown by the following simple argument.

Assume that at the initial time the initial ensemble (to be used as initial condition of the Liouville's equation) is of the relevant type (**??**), this is

$$\rho_0(z) = \overline{\rho}_0(z) \tag{1.2.10}$$

The solution (**??**) of the Liouville's equation takes then the form

$$\rho_t(z) = \exp\{-i\mathcal{L}t\}\overline{\rho}_0(z) \tag{1.2.11}$$

We can then make use of the following trivial mathematical identity

$$\rho_t(z) = \overline{\rho}_t(z) - \int_0^t dt' \frac{d}{dt'} \left[\exp\{-i\mathcal{L}(t - t')\}\overline{\rho}_{t'}(z)\right] \tag{1.2.12}$$

This identity can be easily proved by performing explicitly the time integral of the full time derivative. Equivalently

$$\rho_t(z) = \overline{\rho}_0(\mathcal{U}_{-t}z) = \overline{\rho}_t(z) - \int_{t_0}^t dt' \frac{d}{dt'}\overline{\rho}_{t'}(\mathcal{U}_{t-t'}z) \tag{1.2.13}$$

Note that in this simple expression we have already written the solution $\rho_t(z)$ of the Liouville's equation with initial condition $\overline{\rho}_0(z)$ in terms of the relevant ensemble at previous times. Because the relevant ensemble depends on the averages $a(t)$ of the CG variables, *(1.2.12) gives the solution of the Liouville's equation in terms of the path history of the CG variables*, under the sole assumption that the ensemble is relevant at the initial time. We could use now this equation to obtain a closed equation for the averages. We do not follow this route now but instead, we will follow the method of projection operators based on the Kawasaki-Gunton projector. It should be mentioned that (1.2.13) gives, in the Markov approximation, the same dynamic equations as the projection operator method. Projection operators are not essential to the Theory of Coarse-Graining, only a convenient tool. The essential concept is that of relevant ensemble.

1.3   The method of projection operators

In the projection operator approach, the main idea is to express the relevant ensemble as the effect of a projection operator acting on the real ensemble, this is

$$\overline{\rho}_t(z) = \mathcal{P}_t \rho_t(z) \tag{1.3.1}$$

Obviously, this projector depends on time. The actual form of the projector requires the specification of further properties. In particular, we will demand that the time derivative and the projector commute when applied onto the real ensemble

$$\mathcal{P}_t \partial_t \rho_t(z) = \partial_t \mathcal{P}_t \rho_t(z) \tag{1.3.2}$$

This property will be a crucial one in the derivation of a closed equation. By using (1.3.1) into (1.3.2) we obtain

$$\mathcal{P}_t \partial_t \rho_t(z) = \partial_t \overline{\rho}_t(z) \tag{1.3.3}$$

Because the relevant ensemble depends on the actual values of the averages of the CG variables, we have by the chain rule that

$$\partial_t \overline{\rho}_t(z) = \frac{\partial \overline{\rho}_t}{\partial a(t)}(z)\dot{a}(t) = \frac{\partial \overline{\rho}_t}{\partial a(t)}(z)\text{Tr}[\hat{A}\partial_t \rho_t] \tag{1.3.4}$$

This equation can be expressed in operator form as

$$\partial_t \overline{\rho}_t(z) = \tilde{\mathcal{P}}_t \partial_t \rho_t(z) \tag{1.3.5}$$

where the operator is given by [?]

$$\tilde{\mathcal{P}}_t[\cdots] = \frac{\partial \overline{\rho}_t}{\partial a(t)}(z)\text{Tr}[\hat{A}\cdots] \tag{1.3.6}$$

and we use the symbol Tr introduced in (??) to denote a sum over microstates. This projector (1.3.6), therefore, takes the time derivative of the real ensemble and transforms it into the time derivative of the relevant ensemble. Unfortunately, the operator (1.3.6) does not satisfy (1.3.2) $\overline{\rho}_t = \tilde{\mathcal{P}}_t \rho_t$ and we need to modify this projector. A hint is given by the fact that the simplest projection that would transform any ensemble $\eta(z)$ into a relevant ensemble is of the form

$$\tilde{\tilde{\mathcal{P}}}\eta(z) = \overline{\rho}_t(z)\text{Tr}[\eta] \tag{1.3.7}$$

We aim at combining (1.3.6) and (1.3.7) in order to construct an operator that fulfill the following properties After some inspection, a projector fullfiling (1.3.2) is the Kawasaki-Gunton projector [?],[?]. It has the following form, acting on an arbitrary probability density $\eta(z)$ in phase space

$$\mathcal{P}_t \eta(z) = \overline{\rho}_t(z)\text{Tr}[\eta] + \frac{\partial \overline{\rho}_t}{\partial a(t)}(z)\text{Tr}\left[(\hat{A} - a(t))\eta\right] \tag{1.3.8}$$

This is the explicit expression of the operator $\mathcal{P}_t$ satifying the two conditions (1.3.1), (1.3.2). We have been referred to this operator as a projector, and we have to prove that it is, in fact a projector. Note that when we apply the operator (1.3.8) onto the relevant ensemble we get

$$\mathcal{P}_t \overline{\rho}_t(z) = \overline{\rho}_t(z) \tag{1.3.9}$$

suggesting that this operator is a projector. Indeed, an explicicit calculation shows that it satisfies $\mathcal{P}_t \mathcal{P}_{t'} = \mathcal{P}_t$ for all t, t'. When $t = t'$ this property shows that $\mathcal{P}_t$ is idempotent.

The projector $\mathcal{P}_t$ acts on probability densities or ensembles. It is convenient to introduce an adjoint projector $\mathcal{P}_t^\dagger$ that acts on phase functions. It is defined through

$$\text{Tr}\left[\hat{F}\mathcal{P}_t \rho_t\right] = \text{Tr}\left[\rho_t \mathcal{P}_t^\dagger \hat{F}\right] \tag{1.3.10}$$

The explicit form of the adjoint projector $\mathcal{P}_t^\dagger$ is

$$\mathcal{P}_t^\dagger \hat{F}(z) = \text{Tr}[\overline{\rho}_t \hat{F}] + (\hat{A}(z) - a(t))\text{Tr}\left[\frac{\partial \overline{\rho}_t}{\partial a(t)} \hat{F}\right] \tag{1.3.11}$$

We will denote the average of a phase function with respect to the relevant ensemble by

$$\langle \hat{F} \rangle^{a(t)} \equiv \text{Tr}[\overline{\rho}_t \hat{F}] \tag{1.3.12}$$

The notation emphasizes the fact that this average depends parametrically on the averages $a(t)$ through the relevant ensemble. The Kawasaki-Gunton projector (1.3.11) is expressed in terms of the averages (1.3.12) as

$$\mathcal{P}_t^\dagger \hat{F}(z) = \langle \hat{F} \rangle^{a(t)} + (\hat{A}(z) - a(t))\frac{\partial}{\partial a(t)}\langle \hat{F} \rangle^{a(t)} \tag{1.3.13}$$

Note that the projector takes any phase function $\hat{F}(z)$ and transforms it into a linear combination of the CG variables $\hat{A}(z)$. In particular, when applied on the CG variables it leaves them invariant

$$\mathcal{P}_t^\dagger \hat{A}(z) = \hat{A}(z) \tag{1.3.14}$$

Summary of properties of the projectors $\mathcal{P}_t, \mathcal{P}_t^\dagger$

We collect the main properties of the projectors considered so far

- They are linear operators.

- They project the real ensemble and its time derivative into the relevant ensemble and its time derivatives, respectively

$$\mathcal{P}_t \rho_t(z) = \overline{\rho}_t(z) \tag{1.3.15}$$
$$\mathcal{P}_t \partial_t \rho_t(z) = \partial_t \overline{\rho}_t(z) \tag{1.3.16}$$

- They leave invariant the relevant ensemble and CG variables, respectively

$$\mathcal{P}_t \overline{\rho}_t(z) = \overline{\rho}_t(z) \qquad\qquad \mathcal{Q}_t \overline{\rho}_t(z) = 0 \qquad\qquad (1.3.17)$$
$$\mathcal{P}_t^\dagger \hat{A}(z) = \hat{A}(z) \qquad\qquad \mathcal{Q}_t^\dagger \hat{A}(z) = 0 \qquad\qquad (1.3.18)$$

- They are projectors, because for all t, t'

$$\mathcal{P}_t \mathcal{P}_{t'} = \mathcal{P}_t \qquad\qquad \mathcal{P}_t^\dagger \mathcal{P}_{t'}^\dagger = \mathcal{P}_{t'}^\dagger \qquad\qquad (1.3.19)$$

- The complementary projectors $\mathcal{Q}_t = 1 - \mathcal{P}_t$, $\mathcal{Q}_t^\dagger = 1 - \mathcal{P}_t^\dagger$ satisfy

$$\mathcal{Q}_t \mathcal{P}_t = \mathcal{P}_t \mathcal{Q}_t = 0. \qquad\qquad \mathcal{Q}_t \mathcal{Q}_{t'} = \mathcal{Q}_t \qquad\qquad (1.3.20)$$
$$\mathcal{Q}_t^\dagger \mathcal{P}_t^\dagger = \mathcal{P}_t^\dagger \mathcal{Q}_t^\dagger = 0. \qquad\qquad \mathcal{Q}_{t'}^\dagger \mathcal{Q}_t^\dagger = \mathcal{Q}_t^\dagger \qquad\qquad (1.3.21)$$

- They are adjoint, meaning that

$$\mathcal{P}_t(\overline{\rho}_t \hat{F})(z) = \overline{\rho}_t(z) \mathcal{P}_t^\dagger \hat{F}(z)$$
$$\mathcal{Q}_t(\overline{\rho}_t \hat{F})(z) = \overline{\rho}_t(z) \mathcal{Q}_t^\dagger \hat{F}(z) \qquad\qquad (1.3.22)$$

- $\mathcal{P}_t^\dagger$ is self-adjoint with respect to the relevant ensemble

$$\mathrm{Tr}[\overline{\rho}_t \hat{F} \mathcal{P}_t^\dagger G] = \mathrm{Tr}[\overline{\rho}_t \hat{G} \mathcal{P}_t^\dagger \hat{F}] \qquad \mathrm{Tr}[\overline{\rho}_t \hat{F} \mathcal{Q}_t^\dagger \hat{G}] = \mathrm{Tr}[\overline{\rho}_t \hat{G} \mathcal{Q}_t^\dagger \hat{F}] \qquad (1.3.23)$$

The proofs of these properties are presented in appendix 25.

1.4   The exact transport equation

After having introduced the Kawasaki-Gunton projector we now use it in order to derive a closed equation for the averages $a(t)$ of the relevant variables. As a previous step, let us consider the time derivative of the non-relevant part $\delta\rho_t$ which is defined through (1.2.9). It is given by

$$\partial_t \delta\rho_t(z) = \partial_t \rho_t(z) - \partial_t \overline{\rho}_t(z) \qquad\qquad (1.4.1)$$

Next, use the Liouville equation (**??**) and the property (1.3.16) of the projector to write

$$\begin{aligned}
\partial_t \delta\rho_t(z) &= -i\mathcal{L}\rho_t(z) - \mathcal{P}_t \partial_t \rho_t(z) \\
&= -i\mathcal{L}\delta\rho_t(z) - i\mathcal{L}\overline{\rho}_t(z) - \mathcal{P}_t i\mathcal{L}\rho_t(z) \\
&= -i\mathcal{L}\delta\rho_t(z) - i\mathcal{L}\overline{\rho}_t(z) + \mathcal{P}_t i\mathcal{L}\overline{\rho}_t(z) + \mathcal{P}_t i\mathcal{L}\delta\rho_t(z) \qquad\qquad (1.4.2)
\end{aligned}$$

This brings the final form

$$\partial_t \delta\rho_t(z) = -\mathcal{Q}_t i\mathcal{L}\delta\rho_t(z) - \mathcal{Q}_t i\mathcal{L}\overline{\rho}_t(z) \qquad\qquad (1.4.3)$$

which is an inhomogeneous linear differential equation for $\delta\rho_t(z)$ where the inhomogeneous term is $-\mathcal{Q}_t i\mathcal{L}\overline{\rho}_t(z)$. This differential equation (1.4.3) has the following formal solution

$$\delta\rho_t(z) = \mathcal{U}(t,0)\delta\rho_0(z) - \int_0^t dt'\mathcal{U}(t,t')\mathcal{Q}_{t'}i\mathcal{L}\overline{\rho}_{t'}(z) \tag{1.4.4}$$

where we have introduced the following evolution operator

$$\mathcal{U}(t,t') = \exp_+\left\{\int_{t'}^t dt''(-\mathcal{Q}_{t''}i\mathcal{L})\right\} \tag{1.4.5}$$

Here, the time ordered exponential $\exp_+$ is further discussed in Appendix 1.12. Its explicit definition is

$$\mathcal{U}(t,t') = \sum_{n=0}^{\infty}\int_{t'}^t dt_1\int_{t'}^{t_1} dt_2\cdots\int_{t'}^{t_{n-1}} dt_n(-\mathcal{Q}_{t_1}i\mathcal{L})\cdots(-\mathcal{Q}_{t_n}i\mathcal{L}) \tag{1.4.6}$$

and satisfies

$$\frac{d}{dt}\mathcal{U}(t,t') = -\mathcal{Q}_t i\mathcal{L}\mathcal{U}(t,t') \tag{1.4.7}$$

We may check by simple differentiation that the solution of (1.4.3) is (1.4.4), by using (1.4.7) and the fact that if two functions of time have the same derivatives at all times and they coincide at the initial time, they are the same function. Because at the initial time the solution (1.4.4) gives the correct answer $\delta\rho_0(z)$, we are certain that (1.4.4) is the solution of (1.4.3).

We will always assume that the initial distribution function $\rho_0(z)$ is of the relevant type. We already made this assumption in (1.2.10). This assumption is equivalent to $\delta\rho_0(z) = 0$ and we have the solution of (1.4.3) as

$$\delta\rho_t(z) = -\int_0^t dt'\mathcal{U}(t,t')\mathcal{Q}_{t'}i\mathcal{L}\overline{\rho}_{t'}(z) \tag{1.4.8}$$

Finally, from (1.2.9) and (1.4.8) we have

$$\rho_t(z) = \overline{\rho}_t(z) - \int_0^t dt'\mathcal{U}(t,t')\mathcal{Q}_{t'}i\mathcal{L}\overline{\rho}_{t'}(z) \tag{1.4.9}$$

This equation shows that the solution $\rho_t(z)$ of the Liouville equation can be fully expressed in terms of the relevant ensemble $\overline{\rho}_t(z)$. Note that the projector $\mathcal{Q}_t$ depends on the relevant ensemble. Because the relevant ensemble is fully determined by the average values of the CG variables, (1.4.9) states that the real ensemble $\rho_t(z)$ is fully determined by the history of the averages $a(t)$ of the CG variables, provided that at the initial time the ensemble is of the relevant type. The averages $a(t)$ are themselves fixed by $\rho_t(z)$ itself, so (1.4.9) should be understood as an equation for $\rho_t(z)$. Of course, (1.4.9) is just the solution (1.2.11) of Liouville's equation with initial condition of the relevant type, in

a very disguised form.

We can now derive a closed dynamical equation for the average of the CG variables. By using in (1.2.3) the decomposition (1.4.9) of the real ensemble, we obtain

$$\frac{d}{dt}a_\mu(t) = \text{Tr}[\overline{\rho}_t i\mathcal{L}\hat{A}_\mu] - \int_0^t dt' \text{Tr}\left[(i\mathcal{L}\hat{A}_\mu)\mathcal{U}(t,t')\mathcal{Q}_{t'}i\mathcal{L}\overline{\rho}_{t'}\right] \tag{1.4.10}$$

We need a number of results in order to put this equation in a nicer form. First, we note

$$\mathcal{Q}_{t'}i\mathcal{L}\overline{\rho}_{t'} = -\mathcal{Q}_{t'}\overline{\rho}_{t'}i\mathcal{L}\hat{A}_\nu\lambda_\nu(t') = -\overline{\rho}_{t'}\mathcal{Q}_{t'}^\dagger i\mathcal{L}\hat{A}_\nu\lambda_\nu(t') \tag{1.4.11}$$

where we have moved the relevant ensemble to the left with the help of (1.3.22). Next, we introduce the adjoint of the projected evolution operator which is defined as

$$\text{Tr}\left[\hat{F}\mathcal{U}(t,t')\hat{G}\right] = \text{Tr}\left[\hat{G}\mathcal{U}^\dagger(t,t')\hat{F}\right] \tag{1.4.12}$$

The explicit form of this operator is

$$\mathcal{U}^\dagger(t,t') = \sum_{n=0}^\infty \int_{t'}^t dt_1 \int_{t'}^{t_1} dt_2 \cdots \int_{t'}^{t_{n-1}} dt_n (i\mathcal{L}\mathcal{Q}_{t_n}^\dagger)\cdots(i\mathcal{L}\mathcal{Q}_{t_1}^\dagger) \tag{1.4.13}$$

where now the ordering in time of the projection operators is opposite of (6.8). Then we use (1.4.11), (1.4.12) and write finally (1.4.10) in the form

$$\frac{d}{dt}a_\mu(t) = \text{Tr}[\overline{\rho}_t i\mathcal{L}\hat{A}_\mu] + \int_0^t dt' \text{Tr}\left[\overline{\rho}_{t'}(\mathcal{Q}_{t'}^\dagger i\mathcal{L}\hat{A}_\nu)\mathcal{U}^\dagger(t,t')i\mathcal{L}\hat{A}_\mu\right]\lambda_\nu(t') \tag{1.4.14}$$

We introduce now the **reversible drift** $v_\mu(a(t))$ and the **memory kernel** $D_{\mu\nu}(t,t')$ as

$$v_\mu(a(t)) \equiv \text{Tr}[\overline{\rho}_t i\mathcal{L}\hat{A}_\mu]$$
$$D_{\mu\nu}(t,t') = \text{Tr}\left[\overline{\rho}_{t'} J_\nu(t',t')J_\nu(t,t')\right] \tag{1.4.15}$$

The memory kernel is given by the correlation of the **projected current**, defined as

$$J_\nu(t,t') = \mathcal{Q}_{t'}^\dagger\mathcal{U}^\dagger(t,t')i\mathcal{L}\hat{A}_\mu \tag{1.4.16}$$

In terms of these quantities, the equation of motion for the averages (1.4.14) is

$$\frac{d}{dt}a_\mu(t) = v_\mu(a(t)) + \int_0^t dt' D_{\mu\nu}(t,t')\frac{\partial S}{\partial a_\nu}(a(t')) \tag{1.4.17}$$

where we have used (**??**). We recognize the first term as the purely reversible term (1.2.7) that arises when the real ensemble can be approximated with the relevant ensemble. As (1.4.17) is exact, irreversibility should arise from the second term alone. The second term is extremely involved because $D(t,t')$ depends on the whole path of the average $a(t')$ for $t' < t$ through the relevant ensemble $\overline{\rho}_t$, the projector $\mathcal{Q}_t$, and the evolution operator $\mathcal{U}(t,t')$. Therefore, although (1.4.17) is a *closed* equation for the average of the

CG variables, it is a formal equation arising from a rewriting of $\exp\{i\mathcal{L}t\}$. In addition its history dependence makes it very difficult to handle.

Antisymmetric form for the reversible drift

When we explicitly display the dynamic invariants, we may write the reversible drift term in a particularly interesting form. If we single out the energy in the relevant ensemble, it has the form

$$\overline{\rho}_a(z) = \frac{\exp\{-\beta\hat{H}(z) - \lambda_\nu\hat{A}_\nu\}}{Z(\beta,\lambda)} \tag{1.4.18}$$

From the definition (1.4.16) we have

$$\begin{aligned}
v_\mu(a) &= \mathrm{Tr}\left[\overline{\rho}_a i\mathcal{L}\hat{A}_\mu\right] = \mathrm{Tr}\left[\overline{\rho}_a\{\hat{A}_\mu,\hat{H}\}\right] \\
&= \mathrm{Tr}\left[\overline{\rho}_a\frac{1}{\beta}\{\hat{A}_\mu,\beta\hat{H} + \lambda_\nu\hat{A}_\nu\}\right] - \mathrm{Tr}\left[\overline{\rho}_a\{\hat{A}_\mu,\hat{A}_\nu\}\right]\frac{\lambda_\nu}{\beta} \\
&= -\frac{1}{\beta}\mathrm{Tr}\left[\{\hat{A}_\mu,\overline{\rho}_a\}\right] - \mathrm{Tr}\left[\overline{\rho}_a\{\hat{A}_\mu,\hat{A}_\nu\}\right]\frac{\lambda_\nu}{\beta}
\end{aligned} \tag{1.4.19}$$

The first term vanishes because, on partial integration

$$\mathrm{Tr}\left[\{\hat{A}_\mu,\overline{\rho}_a\}\right] = \mathrm{Tr}\left[\frac{\partial\hat{A}_\mu}{\partial z}\cdot J\cdot\frac{\partial\overline{\rho}_a}{\partial z}\right] = -\mathrm{Tr}\left[\frac{\partial^2\hat{A}_\mu}{\partial z\partial z} : J\overline{\rho}_a\right] = 0 \tag{1.4.20}$$

Therefore,

$$v_\mu(a) = -\mathrm{Tr}\left[\overline{\rho}_a\{\hat{A}_\mu,\hat{A}_\nu\}\right]\frac{\lambda_\nu}{\beta} \tag{1.4.21}$$

We introduce the antisymmetric matrix

$$V_{\mu\nu}(a) \equiv \frac{1}{\beta}\mathrm{Tr}[\overline{\rho}_a\{\hat{A}_\mu,\hat{A}_\nu\}] \tag{1.4.22}$$

and write finally the reversible drift term in the exact form

$$v_\mu(a) = V_{\mu\nu}(a)\lambda_\nu(a) \tag{1.4.23}$$

1.5   The Markovian approximation

The transport equation (1.4.17) is an exact equation that has been obtained under the assumption that the initial ensemble is of the relevant type. No approximations have been taken so far. Of course, it is a purely formal equation of extreme complexity and, as such, is completely untractable. The Markovian approximation, that we will consider now, transforms the integro-differential equation (1.4.17) into an ordinary differential

equation in which the time derivative $\dot{a}(t)$ in the left hand side depends only on the values of $a(t)$ at the present time alone. Let us see how this happens.

The memory kernel $D_{\mu\nu}(t,t')$ is expected to decay and vanish for $|t-t'| > \tau_{\mathrm{mic}}$ where τ_{mic} is a characteristic relaxation time (in general, every element μ,ν of the memory kernel will have a characteristic correlation time, so for the sake of the argument, choose for τ_{mic} the largest one, and beyond τ_{mic} all kernels have decayed). Typically, the evolution of the average at time t will depend on the history of the previous values of $a(t')$ in the interval $\tau_{\mathrm{mic}} < t' \leq t$. The Markovian assumption relies on the assumption that the CG variables $a(t)$ vary in a time scale τ_a which is much larger than the time scale τ_{mic} in which the memory decays, $\tau_a \gg \tau_{\mathrm{mic}}$. For all practical purposes, in the time interval $\tau_{\mathrm{mic}} < t' \leq t$, *the CG variables are dynamical invariants, i.e. conserved quantities.*
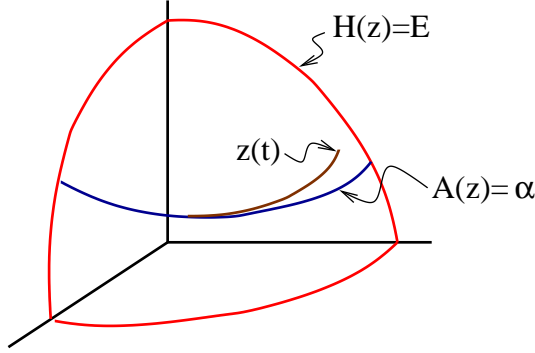
Figure 1.1: Cartoon of phase space. The evolution of the microstate z_t takes place on the submanifold of constant energy $H(z) = E$. In general, if the initial microstate satisfies $\hat{A}(z) = a$, the further evolution will be such that, in general, $\hat{A}(z_t) \neq a$. However, given that the time scale of the CG variables is very large, we have $\hat{A}(z_t) \approx a$ during long times (long compared to the decay time τ_{mic} of the correlations of $i\mathcal{L}\hat{A}$).

If this is true, then we are allowed to substitute *all instances* where $a(t')$ appears in (1.4.17) with $a(t)$. For example

$$\frac{\partial S}{\partial a}(a(t')) \approx \frac{\partial S}{\partial a}(a(t)) \tag{1.5.1}$$

This implies

$$\frac{d}{dt}a_\mu(t) = v_\mu(a(t)) + \left[\int_0^t dt' D_{\mu\nu}(t,t')\right] \frac{\partial S}{\partial a_\nu}(a(t)) \tag{1.5.2}$$

Within the same spirit, we may substitute $a(t')$ by $a(t)$ in the projected current $J_\mu(t,t')$ entering the memory kernel $D_{\mu\nu}(t,t')$. Because the only place where the average $a(t')$ appears is within the projector $\mathcal{Q}^\dagger_{t'}$, the approximation is just to replace $\mathcal{Q}^\dagger_{t_m}$ by $\mathcal{Q}^\dagger_t$. In

this way, the projected current (1.4.16) becomes

$$
\begin{aligned}
J_\mu(t,t') &= \mathcal{Q}_{t'}^\dagger \sum_{n=0}^\infty \int_{t'}^t dt_1 \int_{t'}^{t_1} dt_2 \cdots \int_{t'}^{t_{n-1}} dt_n (i\mathcal{L}\mathcal{Q}_{t_n}^\dagger)\cdots(i\mathcal{L}\mathcal{Q}_{t_1}^\dagger)i\mathcal{L}\hat{A}_\mu \\
&\approx \mathcal{Q}_t^\dagger \sum_{n=0}^\infty \int_{t'}^t dt_1 \int_{t'}^{t_1} dt_2 \cdots \int_{t'}^{t_{n-1}} dt_n (i\mathcal{L}\mathcal{Q}_t^\dagger)^n i\mathcal{L}\hat{A}_\mu \\
&= \mathcal{Q}_t^\dagger \sum_{n=0}^\infty (i\mathcal{L}\mathcal{Q}_t^\dagger)^n i\mathcal{L}\hat{A}_\mu \int_{t'}^t dt_1 \int_{t'}^{t_1} dt_2 \cdots \int_{t'}^{t_{n-1}} dt_n \\
&= \mathcal{Q}_t^\dagger \sum_{n=0}^\infty (i\mathcal{L}\mathcal{Q}_t^\dagger)^n i\mathcal{L}\hat{A}_\mu \frac{1}{n!}(t-t')^n \\
&= \mathcal{Q}_t^\dagger \left[\sum_{n=0}^\infty \frac{1}{n!}(t-t')^n (i\mathcal{L}\mathcal{Q}_t^\dagger)^n \right] i\mathcal{L}\hat{A}_\mu
\end{aligned}
\tag{1.5.3}
$$

By using the definition of the exponential operator the final form for the projected current is

$$
J_\mu(t,t') \approx \mathcal{Q}_t^\dagger \exp\{(t-t')i\mathcal{L}\mathcal{Q}_t^\dagger\} i\mathcal{L}\hat{A}_\mu
\tag{1.5.4}
$$

Finally, with the change of variables $\tau = t - t'$ the time integral of the memory kernel that appears in (1.5.2) becomes

$$
\int_0^t dt' D_{\mu\nu}(t,t') = \int_0^t d\tau \,\mathrm{Tr}\left[\overline{\rho}_t(\mathcal{Q}_t^\dagger i\mathcal{L}\hat{A}_\nu)\mathcal{Q}_t^\dagger \exp\{i\mathcal{L}\mathcal{Q}_t^\dagger \tau\}i\mathcal{L}\hat{A}_\mu\right]
\tag{1.5.5}
$$

Observe that the relevant ensemble and the projector depend on the state average $a(t)$. Therefore, we introduce the **dissipative matrix** as

$$
D_{\mu\nu}(a(t)) = \int_0^t dt' D_{\mu\nu}(t,t')
\tag{1.5.6}
$$

The dissipative matrix is given in terms of a **Green-Kubo** formula

$$
D_{\mu\nu}(a) = \int_0^{\Delta t} dt \left\langle J_\nu^a(0) J_\mu^a(t) \right\rangle^a
\tag{1.5.7}
$$

as a time integral of a correlation function. We will discuss the reason for setting the upper limit of integration to Δt below. In this expression, the average with the relevant ensemble $\overline{\rho}_a(z)$ corresponding to the particular values a of the averages is

$$
\langle \cdots \rangle^a = \mathrm{Tr}\left[\overline{\rho}_a \cdots\right]
\tag{1.5.8}
$$

and we have introduced the **projected current** in the form

$$
J_\mu^a(t) = \mathcal{Q}_a^\dagger \exp\{i\mathcal{L}\mathcal{Q}_a^\dagger t\} i\mathcal{L}\hat{A}_\mu
\tag{1.5.9}
$$

where the projector $\mathcal{Q}_a^\dagger$ is just $\mathcal{Q}_t^\dagger$ at the particular $a(t) = a$, compare with (1.5.4). The notation with the superscript a conveys the idea that the projected current depends on the actual average a of the CG variables.

The projected current (1.5.9) can also be written in the form

$$J_\mu^a(t) = \exp\{\mathcal{Q}_a^\dagger i\mathcal{L}t\}\mathcal{Q}_a^\dagger i\mathcal{L}\hat{A}_\mu \qquad (1.5.10)$$

as can be seen by the Taylor expansion of the exponential operator. In this form, it is obvious that the projected current is a total time derivative, given by

$$J_\mu^a(t) = \frac{d}{dt}\tilde{A}_\mu(t) \qquad (1.5.11)$$

where $\tilde{A}_\mu(t) = \exp\{\mathcal{Q}_a^\dagger i\mathcal{L}t\}\hat{A}_\mu$.

Alternatively, we can also write the dissipative matrix (1.5.7) as

$$D_{\mu\nu}(a) = \int_0^{\Delta t} dt \left\langle \tilde{J}_\nu^a(0)\tilde{J}_\mu^a(t) \right\rangle^a \qquad (1.5.12)$$

where now the projected current is defined as

$$\tilde{J}_\mu^a(t) = \exp\{i\mathcal{L}\mathcal{Q}_a^\dagger t\}\mathcal{Q}_a^\dagger i\mathcal{L}\hat{A}_\mu \qquad (1.5.13)$$

which is, in principle, different from (1.5.9). Both forms (1.5.7) and (1.5.12) are mathematically equivalent. The first form (1.5.7) will be useful to illustrate the plateau problem (see below) whereas the second form (1.5.12) is more suited to discuss the approximation of the projected dynamics with the real dynamics, below.

The plateau problem

Note that in (1.5.7) we have put the upper limit of the integration to a time Δt instead of t. Recall that the memory kernel decays within the correlation time τ_{mic}. After a time τ_{mic} from the initial preparation of the system we could, in principle, extend the upper limit of the integral to infinity. However, a problem known as the **plateau problem** arises if we strictly take $\Delta t \to \infty$.

If we use (1.5.11) in (1.5.7), the dissipative matrix takes the form

$$D_{\mu\nu}(a) = \int_0^{\Delta t} dt \left\langle J_\nu(0)\frac{d}{dt}\tilde{A}_\mu(t) \right\rangle^a = \left\langle J_\nu(0)\tilde{A}_\mu(\Delta t) \right\rangle^a - \left\langle J_\nu(0)\tilde{A}_\mu(0) \right\rangle^a \qquad (1.5.14)$$

The last term vanishes because

$$\left\langle J_\nu(0)\tilde{A}_\mu(0) \right\rangle^a = \mathrm{Tr}\left[\overline{\rho}_a(\mathcal{Q}_a^\dagger i\mathcal{L}\hat{A}_\nu)\hat{A}_\mu \right] = 0 \qquad (1.5.15)$$

upon using the fact that $\mathcal{Q}_a^\dagger$ is self-adjoint with respect to the relevant ensemble and $\mathcal{Q}_a^\dagger \hat{A}(z) = 0$. Concerning the first term, even though we do not know how is the actual evolution $\tilde{A}$ of the CG variables under the projected dynamics, we expect that for sufficiently large times τ the CG variables and the projected currents become uncorrelated,

i.e.

$$\lim_{\Delta t \to \infty} \left\langle J_\nu(0)\tilde{A}_\mu(\Delta t) \right\rangle^a = \langle J_\nu(0)\rangle^a \left\langle \tilde{A}_\mu(\Delta t)\right\rangle^a = 0 \qquad (1.5.16)$$

where the term vanishes because $\langle J_\nu(0)\rangle^a = \mathrm{Tr}[\rho_a \mathcal{Q}_a^\dagger i\mathcal{L}\hat{A}_\nu] = 0$. Therefore, if we extend the upper time $\tau \to \infty$, the dissipative matrix vanishes!

As a function of Δt the dissipative matrix $D_{\mu\nu}(a)$ starts at zero at $\Delta t = 0$ and ends up at zero for $\Delta t = \infty$. The physical picture is that the projected currents, which are closely related to the time derivatives of the CG variables, evolve in two different time scales, one that is fast and oscillates rapidly on a time scale τ_{mic} and an overall slow component that decays to zero in the time scale τ_{mac} of the CG variables. It is on the longest time scale τ_{mac} that the correlation of the projected currents start to vanish. The solution to the plateau problem is then to extend Δt to be larger than τ_{mic} but not much larger, to a value in which the CG variables have still not changed appreciably. Under the bounds $\tau_{\mathrm{mic}} < \Delta t \ll \tau_{\mathrm{mac}}$, the precise value of Δt should not affect strongly the value of $D_{\mu\nu}(a)$, provided that the Markov assumption is justified. The Markov assumption, then, relies on the separation of time scales in the evolution of the projected currents.

The projected dynamics is similar to the real dynamics

The projected dynamics $\exp\{i\mathcal{L}\mathcal{Q}_a^\dagger t\}$ appearing in the dissipative matrix is problematic. If we could approximate this evolution operator with the real Hamiltonian dynamics $\exp\{i\mathcal{L}t\}$, we would simplify our lives considerably because we know how the evolution operator $\exp\{i\mathcal{L}t\}$ works on any phase function $\hat{F}(z)$, see (**??**): it simply produces the Hamiltonian dynamics

$$\exp\{i\mathcal{L}t\}\hat{F}(z) = \hat{F}(\mathcal{U}_t z) \qquad (1.5.17)$$

where $\mathcal{U}_t z$ is the solution of Hamilton's equation. From a numerical point of view Hamilton's equations could be solved through the identity

$$\exp\{\mathcal{A}t\} = \lim_{N\to\infty} [1 + \Delta t \mathcal{A}]^N, \qquad \Delta t = \frac{t}{N} \qquad (1.5.18)$$

valid for an operator $\mathcal{A}$ in a Hilbert space[1]. In a numerical setting, we fix N to a finite but large number (so that Δt is sufficiently small) and approximate the solution (1.5.17) as a succession of time steps each one involving the **infinitesimal generator**

$$[1 + i\mathcal{L}\Delta t]\,\hat{F}(z) \qquad (1.5.19)$$

By following the same route, we may now consider the action of the projected evolution operator $\exp\{i\mathcal{L}\mathcal{Q}_a^\dagger t\}$ on an arbitrary phase function $\hat{F}(z)$. The corresponding infinites-

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[1]We know that, in practice, symplectic methods are to be preferred [**?**], but we use (1.5.18) for the sake of the argument

imal generator has the following action

$$\left[1 + \Delta t i\mathcal{L}\mathcal{Q}_a^\dagger\right]\hat{F}(z) = \left[1 + \Delta t i\mathcal{L}\right]\hat{F}(z) - i\mathcal{L}\hat{A}(z)\frac{\partial}{\partial a}\left\langle\hat{F}\right\rangle^a \qquad (1.5.20)$$

We recognize in the two first terms the infinitesimal updating of a phase function due to the Hamiltonian dynamics. The last bit involves the average with the relevant ensemble and complicates strongly the calculation of the projected dynamics. In order to use the projected dynamics, at each time step we would need to compute an average with respect to the relevant ensemble! This is completely unfeasible. In addition, the projected dynamics suffers from other problems too. It can be shown that it is not unitary, does not conserve volume in phase space, and it does not produce stationary correlations.

The way out of this blind alley is to realize in (1.5.20) that the projected dynamics is very similar to the real Hamiltonian dynamics, differing in terms which are of order $i\mathcal{L}\hat{A}$ and formally small. During the time scale in which correlations need to be computed, the real dynamics leads to almost conserved CG variables, $i\mathcal{L}A(z) \approx 0$. Therefore $i\mathcal{L}\hat{A}(z)$ are formally very small quantities that can be neglected in front of the Hamiltonian evolution. In this way, the projected dynamics is approximated with the real dynamics, i.e.

$$\exp\{i\mathcal{L}\mathcal{Q}_a^\dagger t\} \approx \exp\{i\mathcal{L}t\} \qquad (1.5.21)$$

and the projected current in (1.5.13) becomes

$$\tilde{J}_\mu^a(t) = \exp\{i\mathcal{L}\mathcal{Q}_a^\dagger t\}\mathcal{Q}_a^\dagger i\mathcal{L}\hat{A}_\mu \approx \exp\{i\mathcal{L}t\}\mathcal{Q}_a^\dagger i\mathcal{L}\hat{A}_\mu$$

$$= \exp\{i\mathcal{L}t\}\left[i\mathcal{L}\hat{A}_\mu(z) - \langle i\mathcal{L}\hat{A}_\mu\rangle^a - (\hat{A}_\nu(z) - a_\nu)\frac{\partial v_\mu}{\partial a_\nu}(a)\right]$$

$$= i\mathcal{L}\hat{A}_\mu(\mathcal{U}_t z) - \langle i\mathcal{L}\hat{A}_\mu\rangle^a - (\hat{A}_\nu(\mathcal{U}_t z) - a_\nu)\frac{\partial v_\mu}{\partial a_\nu}(a) \qquad (1.5.22)$$

where the reversible drift is $v_\mu(a) = \text{Tr}[\overline{\rho}_a i\mathcal{L}\hat{A}_\mu]$. The projected current $\tilde{J}_\mu^a(t)$ is now, in principle, computable with an MD simulation that gives the solution $\mathcal{U}_t z$ of Hamilton's equations with initial condition z.

The Markovian transport equation

In summary, under the Markovian approximation, the exact integro-differential transport equation (1.4.17) becomes

$$\frac{d}{dt}a_\mu(t) = v_\mu(a(t)) + D_{\mu\nu}(a(t))\frac{\partial S}{\partial a_\nu}(a(t)) \qquad (1.5.23)$$

This is a first order ordinary differential equation for the averages $a(t)$. The values of immediate future values of $a(t)$ (dictated by the time derivative of $a(t)$) are, in the Markovian approximation, given by just the present values of $a(t)$ alone.

The different objects appearing in the transport equation are the reversible drift, the

dissipative matrix, and the entropy, given in terms of microscopic expressions as

$$v_\mu(a) = \text{Tr}[\overline{\rho}_a i\mathcal{L}\hat{A}_\mu]$$

$$D_{\mu\nu}(a) = \int_0^{\Delta t} dt \text{Tr}\left[\overline{\rho}_a \left(\mathcal{Q}_a^\dagger i\mathcal{L}\hat{A}_\nu\right) \exp\{i\mathcal{L}t\} \left(\mathcal{Q}_a^\dagger i\mathcal{L}\hat{A}_\mu\right)\right] \qquad (1.5.24)$$

where the relevant ensemble $\overline{\rho}_a(z)$ is given in (1.2.4), and the explicit form of the projector $\mathcal{Q}_a^\dagger = 1 - \mathcal{P}_a^\dagger$, where the projector $\mathcal{P}_a^\dagger$ is given in (1.3.13). Finally, the entropy $S(a)$ is the result of evaluating the Gibbs-Jaynes entropy functional at the relevant ensemble, this is

$$S(a) = \mathcal{S}[\overline{\rho}_a] = -\sum_{N=0}^\infty \int dz_N \overline{\rho}_a(z_N) \ln \frac{\overline{\rho}_a(z_N)}{\rho_N^0} \qquad (1.5.25)$$

1.6 The initial ensemble revisited

We pause in this section on the issue about initial conditions. One crucial assumption in the formulation of a closed equation for the CG variables is that the initial ensemble $\rho_0(z)$ is the relevant ensemble $\overline{\rho}_{a_0}(z)$ at the initial values of the CG variables or, in other words that the irrelevant part of the ensemble vanishes $\delta\rho_0(z) = 0$. This allowed us to neglect in (1.4.4) the term $\mathcal{U}(t,0)\delta\rho_0(z)$. If we do not neglect this term, instead of the exact closed equation (1.4.10) we obtain

$$\frac{d}{dt}a_\mu(t) = \text{Tr}[\overline{\rho}_t i\mathcal{L}\hat{A}_\mu] - \int_0^t dt' \text{Tr}\left[(i\mathcal{L}\hat{A}_\mu)\mathcal{U}(t,t')\mathcal{Q}_{t'} i\mathcal{L}\overline{\rho}_{t'}\right] + \text{Tr}[i\mathcal{L}\hat{A}_\mu \mathcal{U}(t,0)\delta\rho_0] \tag{1.6.1}$$

In the Markovian approximation, if the initial ensemble is not of the relevant type instead of (1.5.23) we obtain

$$\frac{d}{dt}a_\mu(t) = v_\mu(a(t)) + D_{\mu\nu}(a(t))\frac{\partial S}{\partial a_\nu}(a(t)) + \text{Tr}[i\mathcal{L}\hat{A}_\mu \mathcal{U}(t,0)\delta\rho_0] \qquad (1.6.2)$$

This equation is not closed because the last term is not an explicit function of the averages $a(t)$. In order to construct this term we *need* to know and provide the specific form of the initial ensemble, and then perform the trace average in order to predict the evolution of $a(t)$. We offer now several arguments that allow one to neglect this ugly term. The first argument relies in the intuitive idea that almost any initial ensemble $\rho_0(z)$ evolving under a dynamics in which the CG variables are slow, will equilibrate in a time scale τ_{mic} towards the quasi-equilibrium ensemble in which the CG variables are considered dynamic invariants. This quasi-equilibrium ensemble is the relevant ensemble, in much the same way as the canonical ensemble is the equilibrium ensemble when the only dynamic invariant is the Hamiltonian. After this time scale, we expect $\mathcal{U}(t,0)\rho_0(z) \simeq \overline{\rho}_a(z) \simeq \mathcal{U}(t,0)\overline{\rho}_a(z)$, which implies $\mathcal{U}(t,0)\delta\rho_0(z) \simeq 0$ for $t > t_c$. Note that the initial ensemble term in (1.6.2) can be written as

$$\text{Tr}[i\mathcal{L}\hat{A}_\mu \mathcal{U}(t,0)\delta\rho_0] = \text{Tr}[i\mathcal{L}\hat{A}_\mu \mathcal{U}(t,0)\mathcal{Q}\rho_0] = \text{Tr}[\rho_0 J_\mu^a(t)] \qquad (1.6.3)$$

this is, it is the average with respect to the initial ensemble of the projected current. Therefore, the time scale τ_{mic} in which this average decays to zero is related to the time scale of the projected current.

It seems, therefore, plausible that when the Markov approximation is a good approximation, and the projected currents evolve in time scales much shorter than the CG variables, we may neglect the initial condition term $\mathrm{Tr}[\rho_0 J_\mu^a(t)]$ after a time τ_{mic}, irrespective of the actual value of the initial ensemble $\rho_0(z)$, because, in this view, any initial ensemble will relax, within this time scale towards the relevant ensemble $\overline{\rho}_a(z)$. This plausibility argument has no rigor and cannot be considered as a proof. However, it has the taste of a "physical justification" for the selection of the relevant ensemble as the initial ensemble.

Alternatively, one could take an "epistemological justification" of the assumption that the initial ensemble is of the relevant form. We are constructing a transport equation that, in the Markovian approximation, has the structure of a first order ordinary differential equation for the average $a(t)$. These kind of equations require for its solution the initial value of the average of the CG variables. Therefore, implicit in the use an validity of the very transport equation is that we have access to the initial values of the averages of the CG variables. Otherwise the equation is useless. Should we have some means of accessing additional information beyond the averages of the CG variables, we should probably include it in the description because they may have measurable and detectable effects. Therefore, the most honest way of specifying the initial ensemble is through the MaxEnt principle where the known information is given by the averages of the CG variables at the initial time. This is, of course, the relevant ensemble. In that sense, the transport equation (1.5.23) (without the initial condition term) gives the more honest prediction for the averages at later times under the information about the averages at the initial time. If it turns that the equation gives predictions not in accord to observations (from real experiments or simulations) and we cannot blame the Markovian approximation, this means that we are missing some crucial aspect of the problem which is not reflected in our selection of CG variables.

1.7   The First and Second Laws

The Markovian transport equations (1.5.23) encode the First and Second Laws of Thermodynamics as we show in this section.

The First Law

Recall that we include the dynamic invariants in the list of CG variables. In this section, we consider what form the transport equations (1.5.23) take when we make explicit the dynamic invariants. For simplicity, we assume that the only dynamic invariants of the system are the number of particles $\hat{N}(z)$ and the Hamiltonian $H(z)$. The transport equation (1.5.23) will become, explicitly

$$
\frac{d}{dt}N = v_N + D_{NN}\frac{\partial S}{\partial N} + D_{NE}\frac{\partial S}{\partial E} + D_{Na}\frac{\partial S}{\partial a}
$$
$$
\frac{d}{dt}E = v_E + D_{EN}\frac{\partial S}{\partial N} + D_{EE}\frac{\partial S}{\partial E} + D_{Ea}\frac{\partial S}{\partial a}
$$
$$
\frac{d}{dt}a(t) = v_a + D_{aN}\frac{\partial S}{\partial N} + D_{aE}\frac{\partial S}{\partial E} + D_{aa}\frac{\partial S}{\partial a} \tag{1.7.1}
$$

The microscopic conservation of the number of particles $i\mathcal{L}\hat{N}(z_N) = 0$ and the energy $i\mathcal{L}\hat{H}(z_N) = 0$ implies that all the reversible drift terms and dissipative matrix elements with a subindex N or E vanish identically. The resulting transport equations are

$$
\frac{d}{dt}N = 0
$$
$$
\frac{d}{dt}E = 0
$$
$$
\frac{d}{dt}a = v_a + D_{aa}\frac{\partial S}{\partial a} \tag{1.7.2}
$$

It is apparent that the total number of particles and the energy are conserved (as it should) and the dynamics of a happens at constant values of N, E. For this reason, we may regard the above set of equations as a reflection of the First Law of thermodynamics that tells us that energy is conserved (and obviously, the number of particles). In fact, not only energy, but any other dynamic invariant that may exist in the problem.

The Second Law

Let us write down the dynamic equations (1.7.2) will all the components of the CG variables

$$
\frac{d}{dt}a_\mu(t) = v_\mu(a(t)) + D_{\mu\nu}(a(t))\frac{\partial S}{\partial a_\nu}(a(t)) \tag{1.7.3}
$$

when we understand that there is an implicit dependence on the dynamic invariants in the reversible drift and dissipative matrix. We have already seen in (1.2.8) that the first term does not contribute to the rate of entropy. Note that we may decompose the

dissipative matrix into its symmetric and antisymmetric parts

$$D_{\mu\nu} = D_{\mu\nu}^S + D_{\mu\nu}^A, \qquad D_{\mu\nu}^S = \frac{1}{2} \left[D_{\mu\nu} + D_{\nu\mu} \right], \qquad D_{\mu\nu}^A = \frac{1}{2} \left[D_{\mu\nu} - D_{\nu\mu} \right] \qquad (1.7.4)$$

Therefore we have

$$\frac{d}{dt} S(a(t)) = \frac{\partial S}{\partial a_\mu}(a(t)) D_{\mu\nu}^S(a(t)) \frac{\partial S}{\partial a_\mu}(a(t)) \qquad (1.7.5)$$

The antisymmetric contribution to the dissipative matrix does not contribute to the entropy production because we take the trace of the product of a symmetric and an antisymmetric matrix, which always vanishes. We will show below that the symmetric part of the dissipative matrix $D_{\mu\nu}^S(a(t))$ is positive semidefinite. This implies that the evolution of the averages of the CG variables $a(t)$ is such that

$$\frac{d}{dt} S(a(t)) \geq 0 \qquad (1.7.6)$$

Because the entropy is a never decreasing function of time, this implies that the evolution of the averages $a(t)$ is such that makes the entropy larger and larger until a maximum is reached, this is

$$a^{\text{eq}} = \lim_{t \to \infty} a(t) \qquad (1.7.7)$$

The equilibrium state predicted by the transport equations (1.5.2) will be, therefore, the state that maximizes the entropy of the given level of description, this is

$$\frac{\partial S}{\partial a}(a^{\text{eq}}) = 0 \qquad (1.7.8)$$

The dissipative matrix is positive definite

We now show that indeed the dissipative matrix is positive definite. The correlations of the projected currents are not stationary correlations. This is easily seen

$$\left\langle \tilde{J}_\nu(\tau + \Delta\tau) \tilde{J}_\mu(\Delta\tau) \right\rangle^a = \text{Tr} \left[\rho_a \left(\exp\{i\mathcal{L}(\tau + \Delta\tau)\} \tilde{J}_0 \right) \left(\exp\{i\mathcal{L}\Delta\tau\} \tilde{J}_0 \right) \right]$$

$$= \text{Tr} \left[\tilde{J}_0 \exp\{-i\mathcal{L}\Delta\tau\} \left(\rho_a \exp\{i\mathcal{L}(\tau + \Delta\tau)\} \tilde{J}_0 \right) \right]$$

$$= \text{Tr} \left[\left(\exp\{-i\mathcal{L}\Delta\tau\} \rho_a \right) \tilde{J}_0 \exp\{i\mathcal{L}\tau\} \tilde{J}_0 \right] \qquad (1.7.9)$$

If the relevant ensemble was invariant under the real dynamics, $\exp\{-i\mathcal{L}\Delta\tau\}\rho_a = \rho_a$ then we would have the stationarity condition

$$\left\langle \tilde{J}_\nu(\tau + \Delta\tau) \tilde{J}_\mu(\Delta\tau) \right\rangle^a = \left\langle \tilde{J}_\nu(\tau) \tilde{J}_\mu(0) \right\rangle^a \qquad (1.7.10)$$

for any $\Delta\tau$. However, $\exp\{-i\mathcal{L}\Delta\tau\}\rho_a \neq \rho_a$. Nevertheless, because the relevant ensemble depends on the microscopic state only through the CG variables and the CG variables

are assumed to vary slowly in the time scale of the correlation of projected currents, we may approximate

$$\exp\{-i\mathcal{L}\Delta\tau\}\rho_a(z) = \rho_a(z)(1 - i\mathcal{L}\hat{A}_\mu(z)\tau\lambda_\mu + \cdots) \approx \rho_a(z) \qquad (1.7.11)$$

for times $\Delta\tau$ within the decay time of the memory kernel. Of course, this is consistent with neglecting third order terms in $i\mathcal{L}\hat{A}$ and with the Markovian approximation. Therefore, the correlation in the dissipative matrix is approximately stationary. Now, an interesting property of stationary correlations is that its infinite time integral is always positive. This is the Wiener-Kinchine theorem that we sketch in Appendix 1.12 and that states that for a stationary auto-correlation function $\langle \hat{B}(t)\hat{B}(t')\rangle = C(t - t')$, the time integral is positive

$$\int_{-\infty}^{+\infty} dt\langle \hat{B}\hat{B}(t)\rangle \geq 0 \qquad (1.7.12)$$

We will use this result to show that the symmetric part of the dissipative matrix is, within the Markovian approximation, a positive definite matrix.

To this end, let us now consider the symmetric part $D_{\mu\nu}^S(a)$ of the dissipative matrix (1.5.24), which is

$$D_{\mu\nu}^S(a) \equiv \frac{1}{2}\left[D_{\mu\nu}(a) + D_{\nu\mu}(a)\right] = \frac{1}{2}\int_0^{\Delta t} dt\mathrm{Tr}\left[\overline{\rho}_a\left(\mathcal{Q}_a^\dagger i\mathcal{L}\hat{A}_\nu\right)\exp\{i\mathcal{L}\tau\}\left(\mathcal{Q}_a^\dagger i\mathcal{L}\hat{A}_\mu\right)\right]$$
$$+ \frac{1}{2}\int_0^{\Delta t} dt\mathrm{Tr}\left[\overline{\rho}_a\left(\mathcal{Q}_a^\dagger i\mathcal{L}\hat{A}_\mu\right)\exp\{i\mathcal{L}\tau\}\left(\mathcal{Q}_a^\dagger i\mathcal{L}\hat{A}_\nu\right)\right]$$
$$(1.7.13)$$

The last integral can be written, under the assumption that the relevant ensemble is quasi-stationary, as

$$\int_0^{\Delta t} dt\mathrm{Tr}\left[\overline{\rho}_a\left(\mathcal{Q}_a^\dagger i\mathcal{L}\hat{A}_\mu\right)\exp\{i\mathcal{L}t\}\left(\mathcal{Q}_a^\dagger i\mathcal{L}\hat{A}_\nu\right)\right]$$
$$= \int_0^{\Delta t} dt\mathrm{Tr}\left[\overline{\rho}_a\left(\left(\mathcal{Q}_a^\dagger i\mathcal{L}\hat{A}_\nu\right)\exp\{-i\mathcal{L}t\}\mathcal{Q}_a^\dagger i\mathcal{L}\hat{A}_\mu\right)\right]$$
$$= \int_{-\tau}^0 dt\mathrm{Tr}\left[\overline{\rho}_a\left(\left(\mathcal{Q}_a^\dagger i\mathcal{L}\hat{A}_\nu\right)\exp\{i\mathcal{L}t\}\mathcal{Q}_a^\dagger i\mathcal{L}\hat{A}_\mu\right)\right] \qquad (1.7.14)$$

where we have performed a change of variables in the last equality. Then (1.7.13) becomes

$$D_{\mu\nu}^S(a) = \frac{1}{2}\int_{-\tau}^\tau dt\mathrm{Tr}\left[\overline{\rho}_a\left(\mathcal{Q}_a^\dagger i\mathcal{L}\hat{A}_\nu\right)\exp\{i\mathcal{L}t\}\left(\mathcal{Q}_a^\dagger i\mathcal{L}\hat{A}_\mu\right)\right] \qquad (1.7.15)$$

If we left and right contract the above matrix with an arbitrary vector v_μ we obtain

$$v_\mu D_{\mu\nu}^S(a)v_\nu = \frac{1}{2}\int_{-\tau}^\tau dt'\mathrm{Tr}\left[\overline{\rho}_a B_a \exp\{-i\mathcal{L}t'\}B_a)\right] \qquad (1.7.16)$$

where the phase function $B_a(z) = v_\mu \mathcal{Q}_a^\dagger i \mathcal{L} \hat{A}_\mu(z)$. The quadratic form (1.7.16) is therefore the integral from $\pm\tau$ of a quasi-stationary time correlation function. If we have a clear separation of time scales, in the time of the decay of the correlation the correlation itself is stationary and we may extend τ to very large values, in such a way that (1.7.16) falls in the form of the Wiener-Kinchine theorem (1.7.12). Therefore, under these assumptions

$$v_\mu D_{\mu\nu}^S(a) v_\nu \geq 0 \tag{1.7.17}$$

for all vectors v and the symmetric part of the dissipative matrix is positive definite.

1.8 Dynamics of averages under external forcing

We now consider the averages flavour in the presence of external forcing. We review the steps done in Chapter 1 in the absence of external forcing and pinpoint the steps where differences arise.

The objective is to find a closed equation for the averages $a(t)$ of the CG variables $\hat{A}(z)$ computed with the solution $\rho_t(z)$ of the Liouville's equation (??). In the list of CG variables we introduce the unperturbed Hamiltonian $H_0(z)$. To obtain the evolution equation for the averages of the CG variables, one introduces the relevant ensemble $\overline{\rho}_t(z)$ which is fixed by the values of the averages $a(t)$ according to the Maximum Entropy Principle and has the usual form given in (1.2.4), (1.2.5). This relevant ensemble is, presumably, a good approximation to the real ensemble, and it makes sense to perform a perturbation of the form (1.2.9). One convenient way to do this perturbation is by introducing the Kawasaki-Gunton projector (1.3.8) and its adjoint (1.3.11). Eqs (1.4.1)-(1.4.3) are unaltered, except that now the equation for the non-relevant part (1.4.3) involves the time-dependent Liouville operator, this is

$$\partial_t \delta\rho_t(z) = -\mathcal{Q}_t i \mathcal{L}_t \delta\rho_t(z) - \mathcal{Q}_t i \mathcal{L}_t \overline{\rho}_t(z) \tag{1.8.1}$$

This results into a redefinition of the evolution operator of the projected dynamics in (1.4.5) that now reads

$$\mathcal{U}(t, t') = \exp_+ \left\{ -\int_{t'}^{t} dt'' \mathcal{Q}_{t''} i \mathcal{L}_{t''} \right\} \tag{1.8.2}$$

where now, not only the projector $\mathcal{Q}_t$ is time-dependence, but also the Liouville operator is time-dependent due to the external forcing. Eqs (1.4.1)-(1.4.9) remain unchanged in the presence of external forcing.

We need the action of the Liouville operator on the unperturbed Hamiltonian, which is given by

$$i\mathcal{L}_t \hat{H}^0(z) = -\frac{\partial \hat{H}}{\partial z}(z, \phi_t) \cdot J \cdot \frac{\partial \hat{H}^0}{\partial z} = i\mathcal{L}_0 \hat{H}^0(z) - \phi_t \frac{\partial C}{\partial z}(z) J \frac{\partial \hat{H}^0}{\partial z}(z)$$

$$= -\phi_t \frac{\partial C}{\partial z}(z) J \frac{\partial \hat{H}^0}{\partial z}(z) = -\phi_t \{C, \hat{H}^0\}(z) \tag{1.8.3}$$

1.9   Microscopic Reversibility on CG

We now explore the consequences of the fact that the microscopic Hamiltonian dynamics is time reversible. To this end, we will assume that the CG variables have the parity (**??**) under the reversal of momentum. All the CG variables that we will encounter in this book have this well-defined parity under time reversal. Obviously, the Hamiltonian satisfies

$$\hat{H}(\epsilon z_N) = \hat{H}(z_N) \tag{1.9.1}$$

Let us consider the time reversal properties of the partition function

$$\begin{aligned}
Z(\lambda) &= \sum_{N=0}^{\infty} \int dz_N \rho_N^0 \exp\{-\lambda_\mu(a)\hat{A}_\mu(z_N)\} \\
&= \sum_{N=0}^{\infty} \int dz_N \rho_N^0 \exp\{-\lambda_\mu(a)\hat{A}_\mu(\epsilon z_N)\} \\
&= \sum_{N=0}^{\infty} \int dz_N \rho_N^0 \exp\{-\varepsilon_\mu \lambda_\mu(a)\hat{A}_\mu(z_N)\}
\end{aligned} \tag{1.9.2}$$

where in the second equality we have considered the change of variables $z \to \epsilon z$ that has unit Jacobian. Then we have

$$Z(\lambda) = Z(\varepsilon \lambda) \tag{1.9.3}$$

The averages with respect to the relevant ensemble are obtained as

$$a_\mu(\lambda) = -\frac{\partial Z(\lambda)}{\partial \lambda_\mu} \tag{1.9.4}$$

and, therefore, they satisfy the following symmetry

$$a_\mu(\varepsilon \lambda) = \varepsilon_\mu a_\mu(\lambda) \tag{1.9.5}$$

that just reflects the parity (**??**) of the CG variables. As a consequence of all the above, the relevant ensemble satisfies

$$\begin{aligned}
\overline{\rho}_a(\epsilon z_N) &= \frac{\rho_N^0}{Z(\lambda)} \exp\{-\lambda_\mu(a)\hat{A}_\mu(\epsilon z_N)\} \\
&= \frac{\rho_N^0}{Z(\varepsilon \lambda)} \exp\{-\varepsilon_\mu \lambda_\mu(a)\hat{A}_\mu(z_N)\} = \overline{\rho}_{\varepsilon a}(z_N)
\end{aligned} \tag{1.9.6}$$

The entropy, which is just the result of evaluating the Gibbs-Jaynes entropy at the relevant ensemble, will inherit from the relevant ensemble the property

$$S(\varepsilon a) = S(a) \tag{1.9.7}$$

and the conjugate variables satisfy

$$\lambda_\mu(\varepsilon a) = \frac{\partial}{\partial a_\mu} S(\varepsilon a) = \varepsilon_\mu \frac{\partial}{\partial a_\mu} S(a) = \varepsilon_\mu \lambda_\mu(a) \tag{1.9.8}$$

which could also be inferred from (1.9.5).

We consider next the symmetry properties of the reversible drift and dissipative matrix in the (1.5.2). As these quantities both involve the time derivative of the CG variables, let us first consider the symmetry properties of those. First, let us apply the Liouville operator on both sides of (??)

$$i\mathcal{L}[\hat{A}_\mu(\epsilon z_N)] = i\mathcal{L}[\varepsilon_\mu \hat{A}_\mu(z_N)] = \varepsilon_\mu i\mathcal{L}\hat{A}_\mu(z_N) \tag{1.9.9}$$

Let us consider the left hand side of this equation

$$i\mathcal{L}[\hat{A}_\mu(\epsilon z_N)] = \frac{\partial \hat{H}}{\partial z}(z_N) J \frac{\partial}{\partial z}[\hat{A}_\mu(\epsilon z_N)]$$

$$= \frac{\partial \hat{H}}{\partial z}(z_N) J \epsilon \frac{\partial \hat{A}_\mu}{\partial z}(\epsilon z_N) \tag{1.9.10}$$

$$= -\frac{\partial \hat{H}}{\partial z}(z_N) \epsilon J \frac{\partial \hat{A}_\mu}{\partial z}(\epsilon z_N) \tag{1.9.11}$$

$$= -\frac{\partial \hat{H}}{\partial z}(\epsilon z_N) J \frac{\partial \hat{A}_\mu}{\partial z}(\epsilon z_N) \tag{1.9.12}$$

$$= -[i\mathcal{L}\hat{A}_\mu](\epsilon z_N) \tag{1.9.13}$$

In (1.9.10) we have used the chain rule, in (1.9.11) we have used the anticommutativity (??) and in (1.9.12) we have used

$$\frac{\partial}{\partial z}\hat{H}(z_N) = \frac{\partial}{\partial z}\hat{H}(\epsilon z_N) = \epsilon \frac{\partial \hat{H}}{\partial z}(\epsilon z_N) \tag{1.9.14}$$

which is equivalent to

$$\epsilon \frac{\partial}{\partial z}\hat{H}(z_N) = \frac{\partial \hat{H}}{\partial z}(\epsilon z_N) \tag{1.9.15}$$

In summary, from (1.9.12) and (1.9.9) we have

$$i\mathcal{L}\hat{A}_\mu(\epsilon z_N) = -\varepsilon_\mu i\mathcal{L}\hat{A}_\mu(z_N) \tag{1.9.16}$$

The reversible drift term defined in (1.4.16), when evaluated at εa is

$$v_\mu(\varepsilon a) = \sum_{N=0}^{\infty} \int dz_N \bar{\rho}_{\varepsilon a}(z_N) i\mathcal{L}\hat{A}_\mu(z_N) = \sum_{N=0}^{\infty} \int dz_N \bar{\rho}_a(\epsilon z_N) i\mathcal{L}\hat{A}_\mu(z_N) \tag{1.9.17}$$

$$= \sum_{N=0}^{\infty} \int dz_N \bar{\rho}_a(z_N) i\mathcal{L}\hat{A}_\mu(\epsilon z_N) = -\varepsilon_\mu v_\mu(a) \tag{1.9.18}$$

This equation tells us that if all the variables are even $\varepsilon_\mu = 1$ and then, necessarily the reversible drift term vanishes in this case. This important result shows that the appearance of reversible terms is linked to the time reversal properties of the CG variables.

Now, consider the dissipative matrix given in (1.5.24). We aim at obtaining its parity properties. Consider

$$
\begin{aligned}
D_{\mu\nu}(\varepsilon a) &= \int_0^\infty d\tau \mathrm{Tr}[\overline{\rho}_{\varepsilon a} \mathcal{Q}_{\varepsilon a}^\dagger i\mathcal{L}\hat{A}_\nu \exp\{i\mathcal{L}\tau\} \mathcal{Q}_{\varepsilon a}^\dagger i\mathcal{L}\hat{A}_\mu] \\
&= \int_0^\infty d\tau \sum_{N=0}^\infty \int dz_N \overline{\rho}_{\varepsilon a}(z_N) \mathcal{Q}_{\varepsilon a}^\dagger i\mathcal{L}\hat{A}_\nu(z_N) \exp\{i\mathcal{L}\tau\} \mathcal{Q}_{\varepsilon a}^\dagger i\mathcal{L}\hat{A}_\mu(z_N)] \\
&= \int_0^\infty d\tau \sum_{N=0}^\infty \int dz_N \overline{\rho}_{\varepsilon a}(\epsilon z_N) \mathcal{Q}_{\varepsilon a}^\dagger i\mathcal{L}\hat{A}_\nu(\epsilon z_N) \exp\{i\mathcal{L}\tau\} \mathcal{Q}_{\varepsilon a}^\dagger i\mathcal{L}\hat{A}_\mu(\epsilon z_N)]
\end{aligned}
$$

$$(1.9.19)$$

where in the last equality we have made a change of variables from $z \to \epsilon z$, that has unit Jacobian. We explore the parity of the projected current

$$
\begin{aligned}
\mathcal{Q}_{\varepsilon a}^\dagger i\mathcal{L}\hat{A}_\nu(\epsilon z_N) &= i\mathcal{L}\hat{A}_\nu(\epsilon z_N) - v_\nu(\varepsilon a) - (\hat{A}_\nu(\epsilon z_N) - \varepsilon a_\nu)\frac{\partial v_\nu}{\partial a_\nu}(\varepsilon a) \\
&= -\varepsilon_\nu \left[i\mathcal{L}\hat{A}_\nu(z_N) - v_\nu(a) - (\hat{A}_\nu(z_N) - a_\nu)\frac{\partial v_\nu}{\partial a_\nu}(a) \right]
\end{aligned}
$$

$$(1.9.20)$$

On the other hand

$$
\exp\{i\mathcal{L}\tau\} \mathcal{Q}_{\varepsilon a}^\dagger i\mathcal{L}\hat{A}_\mu(\epsilon z_N) = -\varepsilon_\mu \exp\{-i\mathcal{L}\tau\} \mathcal{Q}_a^\dagger i\mathcal{L}\hat{A}_\mu(z_N) \tag{1.9.21}
$$

Therefore,

$$
\begin{aligned}
D_{\mu\nu}(\varepsilon a) &= \int_0^\infty d\tau \varepsilon_\mu \varepsilon_\nu \mathrm{Tr}[\overline{\rho}_a \mathcal{Q}_a^\dagger i\mathcal{L}\hat{A}_\nu \exp\{-i\mathcal{L}\tau\} \mathcal{Q}_a^\dagger i\mathcal{L}\hat{A}_\mu] \\
&= \int_0^\infty d\tau \varepsilon_\mu \varepsilon_\nu \mathrm{Tr}[\overline{\rho}_a \mathcal{Q}_a^\dagger i\mathcal{L}\hat{A}_\mu \exp\{i\mathcal{L}\tau\} \mathcal{Q}_a^\dagger i\mathcal{L}\hat{A}_\nu]
\end{aligned}
$$

$$(1.9.22)$$

where in the last equality we have used the quasistationarity of the memory kernel. So finally

$$
D_{\mu\nu}(\varepsilon a) = \varepsilon_\mu \varepsilon_\nu D_{\nu\mu}(a) \tag{1.9.23}
$$

These are the celebrated **Onsager reciprocal relations** for the dissipative matrix. They were initially obtained for near equilibrium situations when the dissipative matrix is state independent. The result (1.9.23) extends this property to far from equilibrium situations.

Note that for the symmetric and antisymmetric part of the dissipative matrix the

reciprocal relations imply

$$D^S_{\mu\nu}(\varepsilon a) = \varepsilon_\mu \varepsilon_\nu D^S_{\nu\mu}(a)$$
$$D^A_{\mu\nu}(\varepsilon a) = -\varepsilon_\mu \varepsilon_\nu D^A_{\nu\mu}(a) \tag{1.9.24}$$

Magnetic fields and rotating frames: The Onsager-Casimir relations

In Chapter **??** when we will discuss external forcing, we will see that the Hamiltonian of a system of particles interacting with external time independent magnetic and electric fields deriving from the scalar $\phi(\mathbf{r})$ and vector $\mathbf{A}(\mathbf{r})$ potentials is given by

$$\hat{H}(z) = \sum_i \frac{1}{2m} \left[\mathbf{p}_i - \frac{q}{c} \mathbf{A}(\mathbf{r}_i) \right]^2 + q\phi(\mathbf{r}_i) + V(z) \tag{1.9.25}$$

We see therefore that the Hamiltonian is invariant under the simultaneous change of the momentum *and* the vector potential. Because the magnetic field is the rotational of the vector potential $\mathbf{B} = \mathbf{\nabla} \times \mathbf{A}(\mathbf{r})$, exchanging the sign of the momenta and the magnetic field leaves the Hamiltonian invariant.

We will also see in Chapter **??** that observing a system with respect to a non-inertial frame that rotates at constant angular velocity is equivalent to have the system in an inertial frame but in the presence of a very particular form of electric and magnetic fields, given by (**??**). Therefore, the Hamiltonian is again invariant under the simultaneous change of the sign of the momentum and the sign of the angular velocity.

Therefore, the Onsager-Casimir relations in the presence of a time independent magnetic field or with respect to a frame rotating at constant angular velocity are valid, provided that we exchange also the sign of the magnetic field and the angular velocity. This is

$$D_{\mu\nu}(\varepsilon a, \mathbf{B}, \boldsymbol{\omega}) = \varepsilon_\mu \varepsilon_\nu D_{\nu\mu}(a, -\mathbf{B}, -\boldsymbol{\omega}) \tag{1.9.26}$$

1.10   Underlying symmetries and the Curie principle

[Decide if I use general symmetries or only rotation] We have introduced the rotation operator in phase space (1.10.1)

As another example of a symmetry, consider the total angular momentum that generates rotations in the sense that

$$\mathcal{T}_{\boldsymbol{\theta}} = \exp\left\{ -\boldsymbol{\theta} \cdot \{\hat{\mathbf{L}}, \cdots\} \right\} \tag{1.10.1}$$

is the rotation operator whose action on a phase space function is

$$\mathcal{T}_{\boldsymbol{\theta}} f(\mathbf{q}, \mathbf{p}) = f(\mathcal{R}_{\boldsymbol{\theta}} \mathbf{q}, \mathcal{R}_{\boldsymbol{\theta}} \mathbf{p}) \tag{1.10.2}$$

where the rotation matrix is

$$\mathcal{R}_{\boldsymbol{\theta}} = e^{\boldsymbol{\Lambda}_{\boldsymbol{\theta}}} \tag{1.10.3}$$

We will assume that the CG variables transform under the rotation operator (1.10.1) according to

$$\mathcal{T}_{\boldsymbol{\theta}} \hat{A}_{\mu}(z) = R_{\mu\nu}(\boldsymbol{\theta}) \hat{A}_{\nu}(z) \tag{1.10.4}$$

1.11   Summary

In this summary we collect the main result of this chapter with all the required definitions. We also discuss the assumptions and approximations that have been taken and discuss the scope of the theory.

The main result

We have obtained in (1.4.17) an exact formal equation for the evolution of the averages. The equation as such is useless because the memory kernel is not computable explicitly. However, the exact equation allows one to implement the Markovian approximation and to obtain the approximate equation, which is the main result of this chapter

$$\frac{d}{dt}a_{\mu}(t) = v_{\mu}(a(t)) + D_{\mu\nu}(a(t))\frac{\partial S}{\partial a_{\nu}}(a(t)) \tag{1.11.1}$$

The terms in this equation have the following definitions. The reversible drift term is given by

$$v_{\mu}(a) = \text{Tr}[\overline{\rho}_a i\mathcal{L}\hat{A}_{\mu}] \tag{1.11.2}$$

where the relevant ensemble is

$$\overline{\rho}_a(z_N) = \rho_N^0 \frac{\exp\{-\lambda(t)\hat{A}(z_N)\}}{Z(\lambda)} \tag{1.11.3}$$

The partition function is

$$Z(\lambda) = \text{Tr}\left[\rho_N^0 \exp\{-\lambda(t)\hat{A}(z_N)\}\right] \tag{1.11.4}$$

The entropy is given by

$$S(a) \equiv -\Phi(\lambda) + \lambda a \tag{1.11.5}$$

where the dimensionless thermodynamic potential is

$$\Phi(\lambda) \equiv -\ln Z(\lambda) \tag{1.11.6}$$

The conjugate variables $\lambda(a)$ are functions of the average value determined by the implicit equation

$$\frac{\partial \Phi}{\partial \lambda}(\lambda) = a \qquad (1.11.7)$$

which is nothing else that the requirement that the average of the CG variables with the relevant ensemble with λ gives the value a. The derivative of the entropy, in turn, is given by

$$\frac{\partial S}{\partial a}(a) = \lambda(a) \qquad (1.11.8)$$

Finally, the dissipative matrix is defined as

$$D_{\mu\nu}(a) = \int_0^T d\tau \left\langle \tilde{J}_\tau \tilde{J}_0 \right\rangle^a \qquad (1.11.9)$$

where the projected current, also referred to random force is

$$\tilde{J}_\tau(z_N) \equiv \exp\{i\mathcal{L}\tau\} \left[i\mathcal{L}\hat{A}(z_N) - v(a) - (\hat{A}(z_N) - a)\frac{\partial v}{\partial a}(a) \right] \qquad (1.11.10)$$

Assumptions and approximations

A number of assumptions and approximations are involved in the derivation of the transport equation (1.11.1). We have used Classical Mechanics with a time-independent conserved Hamiltonian and we assume that the Hamiltonian flow is mixing and reaches a unique equilibrium state. This assumption is implicit in the very use of a relevant ensemble as a reference ensemble on which to perform "perturbations", which is at the basis of the projection operator method. Recall that the list of CG variables include the dynamic invariants and that the relevant ensemble is, therefore, a generalization of the canonical ensemble. If the canonical ensemble could not be used because the system was not mixing or ergodic, there is no hope that the relevant ensemble would represent in any realistic way the overall evolution of the system.

The essential approximation is the Markovian approximation which is, in fact, a collection of related simultaneous approximations that one takes in order to go from the exact equation (1.4.17) to the approximate equation (1.11.1). In this Markovian approximation one assumes that

- The CG variables are quasi-invariants in the time scale of decay of the correlations of the projected currents which are, essentially the fluctuations of the time derivatives of the CG variables.

- The projected currents have an evolution with two separated time scales, one short time scale, associated to "collisions" or small changes, and a long time scale associated to the fact that the CG variables are not strictly constant in time.

- The projected dynamics $\exp\{i\mathcal{L}\mathcal{Q}\}$, which is uncomputable, can be substituted by the real dynamics $\exp\{i\mathcal{L}\}$ which can be computed from MD simulations.

Note that the projected current is "of order $i\mathcal{L}\hat{A}$", and then the dissipative matrix is of order $(i\mathcal{L}\hat{A})^2$. By approximating the projected dynamics with the real dynamics we are neglecting terms which are of order $(i\mathcal{L}\hat{A})^3$ in the dissipative matrix. Admittedly, this procedure is not very rigorous. After all, if we can neglect third order terms why not neglecting second order terms like the one involving the dissipative matrix in front of the reversible term $v_\mu(a)$ in the transport equation, which is itself of first order in $i\mathcal{L}\hat{A}$? Of course, if we do that, then the resulting equation is (1.2.7) which we have seen that does not produce any entropy increase. It seems that keeping up to second order is just what is necessary to have physically reasonable equations.

- The relevant ensemble is almost invariant under the evolution, and the correlation of the projected forces is stationary. As a result, a lax use of the Wiener-Kinchine theorem suggest that the symmetric part of the dissipative matrix is positive definite.

It is clear that the Markovian approximation is, from a mathematical point of view, a mess. This lack of mathematical rigour is only compensated by the extreme usefulness of their physical consequences.

Scope

The equation (1.11.1) is a cornerstone of Non-Equilibrium Statistical Mechanics. It describes the evolution of the averages $a(t)$ of the CG variables. These are averages over initial conditions or, equivalently, averages with the solution of the Liouville's equation. The initial conditions are drawn from the least biased (in the sense of the Principle of Maximum Entropy) microscopic ensemble $\rho_0(z)$ which is compatible with the macroscopic information given by the initial value $a(0)$ of the averages of the CG variables.

The transport equation describes the ulterior evolution towards the equilibrium value $a_{\text{eq}} = \langle\hat{A}\rangle_{\text{eq}}$. Nowhere in the theory it is assumed that the initial value $a(0)$ should be close to the final value a_{eq} and the theory describes arbitrarily large departures from equilibrium. During the evolution, entropy always increase according to the Second Law and the final equilibrium state a_{eq} is the one that maximizes the entropy.

The transport equation does not allow to study stationary non-equilibrium states. The reason is that at the most microscopic level the system is isolated and described by a Hamiltonian which is time-independent. In this book, we regard stationary states as very long lived states of an otherwise decaying systems (until running out of external energy supply). Externally forced systems will be consider in Chapter **??**.

An equation for averages is useful when the realization of each trajectory of the CG variables starting from different initial condition is similar or, in other words, when fluctuations are small. The reason is that if different trajectories are very different, having the average is not very informative.

1.12   Appendix

In this appendix we discuss the time ordered exponential and the Wiener-Kinchine theorem.

The time ordered exponential

Consider an evolution equation for an ensemble of the form

$$\partial_t \rho_t(z) = \mathcal{A}_t \rho_t(z) \tag{1.12.1}$$

where $\mathcal{A}_t$ is an operator that depends parametrically on the time t. Examples of this type of equation are the Liouville's equation

$$\partial_t \rho_t(z) = -i\mathcal{L}_t \rho_t(z) \tag{1.12.2}$$

when the Liouville operator $i\mathcal{L}_t$ is assumed to depend explicitly in time, due to the presence of time-dependent terms in the Hamiltonian. Another example is the evolution equation (1.4.3).

We seek for a formal solution of this equation. To this end we integrate over a time interval to get, with $t > 0$

$$\rho_t(z) = \rho_0(z) + \int_0^t dt_1 \mathcal{A}_{t_1} \rho_{t_1}(z) \tag{1.12.3}$$

This is a recursive equation in which the function $\rho_t(z)$ is given in terms of itself at previous times. By using the same equation (1.12.3) in the right hand side of (1.12.3)

$$\rho_t(z) = \rho_0(z) + \int_0^t dt_1 \mathcal{A}_{t_1} \left[\rho_0(z) + \int_0^{t_1} dt_2 \mathcal{A}_{t_2} \rho_{t_2}(z) \right]$$

$$= \rho_0(z) + \int_0^t dt_1 (\mathcal{A}_{t_1}) \rho_0(z) + \int_0^t dt_1 \mathcal{A}_{t_1} \int_0^{t_1} dt_2 \mathcal{A}_{t_2} \rho_{t_2}(z) \tag{1.12.4}$$

This still contains the ensemble at all past times. Repeating this indefinitely we obtain formally

$$\rho_t(z) = \sum_{n=0}^{\infty} \int_0^t dt_1 \cdots \int_0^{t_{n-1}} dt_n \mathcal{A}_{t_1} \cdots \mathcal{A}_{t_n} \rho_0(z) \tag{1.12.5}$$

where only the initial ensemble appears.

We may introduce the operator

$$\exp_+ \left\{ \int_0^t dt' \mathcal{A}_{t'} \right\} = \sum_{n=0}^{\infty} \int_0^t dt_1 \cdots \int_0^{t_{n-1}} dt_n \mathcal{A}_{t_1} \cdots \mathcal{A}_{t_n} \tag{1.12.6}$$

and the formal solution of (1.12.2) is

$$\rho_t(z) = \exp_+ \left\{ \int_0^t dt' \mathcal{A}_{t'} \right\} \rho_0(z) \tag{1.12.7}$$

This operator satisfies

$$\frac{d}{dt}\exp_+\left\{\int_0^t dt'\,\mathcal{A}_{t'}\right\} = \frac{d}{dt}\sum_{n=0}^{\infty}\int_0^t dt_1\cdots\int_0^{t_{n-1}}dt_n\mathcal{A}_{t_1}\cdots\mathcal{A}_{t_n}$$

$$= \frac{d}{dt}\mathcal{A}_t\sum_{n=0}^{\infty}\int_0^t dt_2\cdots\int_0^{t_{n-1}}dt_n\mathcal{A}_{t_1}\cdots\mathcal{A}_{t_n} = \mathcal{A}_t\exp_+\left\{\int_0^t dt'\,\mathcal{A}_{t'}\right\}$$

$$(1.12.8)$$

By applying both sides of this operator equation to $\rho_0(z)$, we recover (1.12.1) thus showing that (1.12.7) is indeed a formal solution of (1.12.1)

By a suitable change of variables inside the multidimensional integrals, the time ordered exponential operator is

$$\exp_+\left\{\int_0^t dt'\,\mathcal{A}_{t'}\right\} = \sum_{n=0}^{\infty}\frac{1}{n!}\int_0^t dt_1\cdots\int_0^t dt_n T[\mathcal{A}_{t_1}\cdots\mathcal{A}_{t_n}] \qquad (1.12.9)$$

where the notation $T[\mathcal{A}_{t_1}\cdots\mathcal{A}_{t_n}]$ means that the operators are ordered from right to left as time increases. These two last identities justify the name given to the time ordered exponential operator.

The Wiener-Khinchine theorem

In this appendix we present an informal proof of the fact that the time integral of a stationary autocorrelation is positive. Introduce the Fourier transform with respect of time of the phase functions through

$$B(t) = \int_{-\infty}^{+\infty}\frac{d\omega}{2\pi}e^{i\omega t}\tilde{B}(\omega)$$

$$\tilde{B}(\omega) = \int_{-\infty}^{+\infty}de^{-i\omega t}B(t) \qquad (1.12.10)$$

and compute the following average

$$\langle\tilde{B}(\omega)\tilde{B}^*(\omega')\rangle = \int_{-\infty}^{+\infty}dt\int_{-\infty}^{+\infty}dt'e^{-i\omega t}e^{i\omega't'}\langle B(t)B(t')\rangle \qquad (1.12.11)$$

Because the correlation is stationary $\langle B(t)B(t')\rangle = C(t-t')$ we have

$$\langle\tilde{B}(\omega)\tilde{B}^*(\omega')\rangle = 2\pi\delta(\omega-\omega')\int_{-\infty}^{+\infty}d\tau e^{-i\omega\tau}\langle BB(\tau)\rangle \qquad (1.12.12)$$

When $\omega = \omega'$ the right hand side is $\langle|\tilde{B}(\omega)|^2\rangle$ and, therefore, positive. The right hand side is singular due to the Dirac delta function. But assuming that the value of the Dirac

delta function at the origin is positive, one concludes that

$$\int_{-\infty}^{+\infty} d\tau e^{-i\omega\tau}\langle BB(\tau)\rangle \geq 0 \tag{1.12.13}$$

for all ω and, in particular, for $\omega = 0$ thus giving

$$\int_{-\infty}^{+\infty} d\tau \langle BB(\tau)\rangle \geq 0 \tag{1.12.14}$$

If the singularity of Dirac delta function is bothering one, it is possible to regularize it by using, instead of the Fourier transforms (1.12.10), a transform defined as

$$\tilde{B}_T(\omega) = \int_{-T}^{+T} dt e^{-i\omega t} B(t) \tag{1.12.15}$$

For $T \to \infty$ this transform is the Fourier transform. Because we are interested in this limit, we may use Abel's theorem

$$\lim_{T\to\infty} \int_{-T}^{T} f(t)dt = \lim_{\epsilon\to+0} \int_{-\infty}^{\infty} e^{-\epsilon|t|} f(t)dt \tag{1.12.16}$$

Therefore,

$$\langle \tilde{B}_T(\omega)\tilde{B}_T^*(\omega')\rangle = \int_{-\infty}^{+\infty} dt \int_{-\infty}^{+\infty} dt' e^{-i\omega t} e^{i\omega' t'} e^{-\epsilon|t|} e^{-\epsilon|t|'} \langle B(t)B(t')\rangle \tag{1.12.17}$$

By using the stationarity $\langle B(t)B(t')\rangle = \langle B(t-t')B\rangle$ we now obtain

$$\langle \tilde{B}_T(\omega)\tilde{B}_T^*(\omega')\rangle = \int_{-\infty}^{+\infty} d\tau e^{i\omega\tau} \int_{-\infty}^{+\infty} dt' e^{-i(\omega-\omega')t'} e^{-\epsilon|t'+\tau|} e^{-\epsilon|t'|} \langle BB(\tau)\rangle \tag{1.12.18}$$

For $\omega = \omega' = 0$ this expression becomes

$$0 \leq \langle |\tilde{B}_T(0)|^2\rangle = \int_{-\infty}^{+\infty} d\tau \langle BB(\tau)\rangle \int_{-\infty}^{+\infty} dt' e^{-\epsilon|t+\tau|} e^{-\epsilon|t|} \tag{1.12.19}$$

Perform the change of variable $t' = \epsilon\tau'$ in the integral

$$\frac{1}{\epsilon} \int_{-\infty}^{+\infty} d\tau' e^{-|\tau'+\epsilon\tau|} e^{-|\tau'|} \approx \frac{1}{\epsilon} \int_{-\infty}^{+\infty} d\tau' e^{-2|\tau'|} = \frac{1}{\epsilon} \geq 0 \tag{1.12.20}$$

We conclude therefore, that the infinite time integral of a stationary autocorrelation function is always positive

$$\int_{-\infty}^{+\infty} d\tau \langle BB(\tau)\rangle \geq 0 \tag{1.12.21}$$

[Talk about the scope of transport equations for averages. They are valid if fluctuations are small]

2

Dynamic Density Functional Theory: $\hat{n}_{\mathbf{r}}$

2.1 Density functional theory

In this section, we present the Density Functional Theory (DFT) of classical fluids in a way slightly different from usual presentations [?, ?]. This should allow us to put DFT in the general framework of "entropy calculations". In the grand canonical ensemble one introduces the grand partition function as

$$
\begin{aligned}
\Xi[\phi] \;=\; & \sum_{N=0}^{\infty} \frac{\exp\{\beta\mu N\}}{N!h^{3N}} \int d\mathbf{r}_1 d\mathbf{p}_1 \cdots d\mathbf{r}_N d\mathbf{p}_N \\
& \times \;\; \exp\left\{-\beta H_N - \beta \sum_i \phi(\mathbf{r}_i)\right\}
\end{aligned}
\tag{2.1.1}
$$

where $H_N = K_N + U_N$ is the N-particle Hamiltonian, with kinetic energy $K_N = \sum_i^N p_i^2/2m$ and potential of interaction U_N between the particles, $\phi(\mathbf{r})$ is an external field, $\beta = (k_B T)^{-1}$, k_B is the Boltzmann constant, h is the Planck constant, T the temperature, and μ is the chemical potential. The grand partition function can be understood as a functional of the external field $\phi(\mathbf{r})$. The grand potential is defined in terms of the grand partition function $\Xi[\phi]$ as $\Omega[\phi] = -k_B T \ln \Xi[\phi]$, and it is itself a functional of the external field. The functional derivatives of the grand potential with respect to the external field are related to the gran canonical averages of the microscopic density operator

$$
\hat{n}_{\mathbf{r}} = \sum_i^N \delta(\mathbf{r} - \mathbf{r}_i)
\tag{2.1.2}
$$

As it is easily checked,

$$
\frac{\delta\Omega[\phi]}{\delta\phi(\mathbf{r})} = \langle \hat{n}_{\mathbf{r}} \rangle^{\phi} = n(\mathbf{r})
\tag{2.1.3}
$$

where the grand canonical average is denoted by $\langle \cdots \rangle^{\phi}$ and the functional dependence on the external field is made explicit as a superscript. The second derivatives of the grand potential lead to correlation of density fluctuations

$$\frac{\delta^2 \Omega[\phi]}{\delta\phi(\mathbf{r}_1)\delta\phi(\mathbf{r}_2)} = -\beta \left(\langle \hat{n}_{\mathbf{r}_1} \hat{n}_{\mathbf{r}_2} \rangle^{\phi} - \langle \hat{n}_{\mathbf{r}_1} \rangle^{\phi} \langle \hat{n}_{\mathbf{r}_2} \rangle^{\phi} \right) \tag{2.1.4}$$

Higher derivatives of the grand potential with respect to the external potential lead to expressions involving higher particle distributions. These many particle distributions are all functionals of the external field. Eqn. (2.1.4) shows that, being proportional to a variance, the matrix of second derivatives is definite negative and, therefore, it has a well defined inverse. At the same time, the matrix of second derivatives is, from Eqns. (22.3) and (2.1.4),

$$\frac{\delta^2 \Omega[\phi]}{\delta\phi(\mathbf{r}_1)\delta\phi(\mathbf{r}_2)} = \frac{\delta n(\mathbf{r}_1)}{\delta\phi(\mathbf{r}_2)}, \tag{2.1.5}$$

and, therefore, this matrix can be interpreted as the Jacobian matrix in functional sense of a change of variables, from the external potential to the probability density. The fact that this Jacobian is negative definite implies that its functional determinant does not vanish and the functional $n[\phi]$ can be inverted to give $\phi[n]$. In other words, there is a one to one relationship between the external potential and the one-particle distribution. This is the essence of the Density Functional Theory. The corollary of this theorem is that all many particle equilibrium distribution functions, being themselves functionals of the potential $\phi(\mathbf{r})$, are actually functionals of the one-particle distribution. In this way, at equilibrium, the actual functional form of the one-particle distribution function determines the many-particle distribution functions.

In principle, we could use n as the independent variable in the grand potential, instead of the external potential ϕ. However, note in Eqn. (22.3) that n is the derivative of $\Omega[\phi]$. As we know from the usual treatment in Thermodynamics [?] such a change of variables implies a loss of information. The correct way to proceed is to introduce the Legendre transform $\overline{\Omega}[n]$ of $\Omega[\phi]$, which is defined by

$$\overline{\Omega}[n] = \Omega[\phi[n]] - \int d\mathbf{r}\, n(\mathbf{r})\phi(\mathbf{r})[n] \tag{2.1.6}$$

The functional $\overline{\Omega}[n]$ contains exactly the same information as $\Omega[\phi]$. The Legendre transform $\overline{\Omega}[n]$ of the grand potential $\Omega[\phi]$ is called *the density functional*. By taking the functional derivative of $\overline{\Omega}[n]$, one obtains the usual connection between conjugate variables in the Legendre transform

$$\frac{\delta \overline{\Omega}[n]}{\delta n(\mathbf{r})} = -\phi(\mathbf{r}) \tag{2.1.7}$$

to be compared with Eqn. (22.3). Also, note that if we take another functional derivative with respect to the density field in Eq. (2.1.7) we obtain

$$\frac{\delta \overline{\Omega}[n]}{\delta n(\mathbf{r}_1)\delta n(\mathbf{r}_2)} = -\frac{\delta\phi(\mathbf{r}_1)}{\delta n(\mathbf{r}_2)} \tag{2.1.8}$$

which is the inverse matrix in functional sense of the matrix of correlations of the density in Eq. (2.1.4).

It is worth considering the ideal gas for which the Hamiltonian reduces to the kinetic energy term, i.e. $U_N = 0$. In this case, the grand potential can be explicitly computed with the result

$$\Omega^{\mathrm{id}}[\phi] = -k_B T \exp\{\beta\mu\} \int \frac{d\mathbf{r}}{\Lambda^3} \exp\{-\beta\phi(\mathbf{r})\} \tag{2.1.9}$$

where Λ is the thermal wavelength. Eqn. (22.3) becomes now

$$n(\mathbf{r}) = \frac{\delta\Omega^{\mathrm{id}}[\phi]}{\delta\phi(\mathbf{r})} = \frac{1}{\Lambda^3} \exp\{-\beta(\phi(\mathbf{r}) - \mu)\} \tag{2.1.10}$$

The Legendre transform (10) is easily computed with the result

$$\overline{\Omega}^{\mathrm{id}}[n] = k_B T \int d\mathbf{r} n(\mathbf{r})[\ln(\Lambda^3 n(\mathbf{r})) - 1 - \beta\mu] \tag{2.1.11}$$

In the non-ideal case for which $U_N \neq 0$, one introduces an interacting part $\Phi[n]$ to the density functional,

$$\overline{\Omega}[n] = \overline{\Omega}^{\mathrm{id}}[n] + \Phi[n] \tag{2.1.12}$$

The usual direct correlations are defined as functional derivatives of the interaction part

$$\frac{\delta^n \Phi[n]}{\delta n(\mathbf{r}_1) \cdots \delta n(\mathbf{r}_n)} = -k_B T c(\mathbf{r}_1, \cdots, \mathbf{r}_n) \tag{2.1.13}$$

For example, the first derivative of $\overline{\Omega}[n]$ in Eqn (2.1.12) leads easily to the result

$$n(\mathbf{r}) = \frac{1}{\Lambda^3} \exp\{-\beta(\phi(\mathbf{r}) + k_B T c(\mathbf{r}) - \mu)\} \tag{2.1.14}$$

which is the usual definition of the first direct distribution. The expression in terms of the second direct distribution of the fact that the functional matrices (2.1.4) and (2.1.8) are inverse of each other leads to the Ornstein-Zernike equation [**?**]. This equation allows to obtain the pair distribution function from the second direct distribution function. The Percus-Yevick (PY) and Hypernetted Chain (HNC) approximations are *models* for the direct correlation in terms of the pair distribution function to be inserted into the Ornstein-Zernike equation (leading to the Percus-Yevick and Hypernetted Chain equations, respectively) that may be solved for the pair distribution function.

The construction of the density functional $\overline{\Omega}[n]$ may be regarded as a purely mathematical transformation devoid of physical meaning. After all, all the information in $\overline{\Omega}[n]$ is exactly the same as that in $\Omega[\phi]$. But as it happens in some major advances in Physics, just rewriting the same thing in a different appearance helps in proposing approximation schemes that would otherwise be difficult to implement. In the present case, it seems to be easier to model the density functional $\overline{\Omega}[n]$ than the grand potential $\Omega[\phi]$. For example, Rosenfeld's fundamental measure theory leads to a model for $\Omega[\phi]$ that produces the PY model for hard spheres.

We advance a very simplistic model for the interacting part $\Phi[n]$ of the density functional which will play a role in the following. We propose the following linear model

$$\Phi[n] = -k_B T \int d\mathbf{r}\, n(\mathbf{r}) F(\mathbf{r}) \tag{2.1.15}$$

where $F(\mathbf{r})$ is some function, independent of the density field. The prediction of this simplistic model is that the direct correlation function is just $c^{(1)}(\mathbf{r}) = F(\mathbf{r}$ and, because $F(\mathbf{r})$ is assumed to be independent of the density field, higher order direct correlations vanish. In order to have a mininum of realism, we should model $F(\mathbf{r}) = c_{\mathrm{eq}}^{(1)}(\mathbf{r})$ in such a way that, at least, the equilibrium density profile is correctly described. This simplistic model takes $c_{\mathrm{eq}}^{(1)}(\mathbf{r})$ or, equivalently, $n^{\mathrm{eq}}(\mathbf{r})$ as *input* and, therefore, its predictive power, as compared with much more realistic models for $\Phi[n]$ already available[?],[?], is deceptively limited. Nevertheless, for the discussion to come it will play an important role.

The proposed model is, therefore

$$
\begin{aligned}
\overline{\Omega}[n] &= k_B T \int d\mathbf{r}\, n(\mathbf{r})[\ln(\Lambda^3 n(\mathbf{r})) - 1 - \beta\mu] \\
&\quad - k_B T \int d\mathbf{r}\, n(\mathbf{r}) c_{\mathrm{eq}}^{(1)}(\mathbf{r}) \\
&= k_B T \int d\mathbf{r}\, n(\mathbf{r}) \left[\ln \frac{n(\mathbf{r})}{n^{\mathrm{eq}}(\mathbf{r})} - 1\right]
\end{aligned} \tag{2.1.16}
$$

3

Dynamic Density Functional Theory: $c_{\mathbf{r}}$

In the derivation of the dynamic equation (**??**) for $\hat{n}_{\mathbf{r}}$ we have assumed implicitly that the sum in the definition (22.3) was over all the atoms labeled with index i in the system. However, the above derivation remains *exactly the same* when $\hat{n}_{\mathbf{r}}$ is interpreted as the concentration field of a collection of colloidal particles. Of course, the different nature of the physical system (molecular fluid or colloidal suspension) will be reflected in the particular form for $\mathbf{D}(\mathbf{r}, \mathbf{r}', t)$ and $\overline{\Phi}[n]$. In what follows we show how the DDFT obtained with projection operators accommodate several recent proposals for DDFT in colloidal suspensions.

3.1   The system

In this Chapter we consider a colloidal system. In order to keep the discussion simple, we will assume that we have N_C colloidal solid spheres interacting with a collection of N_S solvent atoms. Both the spheres and the atoms are assumed to be structureless and, therefore, the microscopic state of the system is characterized by the position and momentum of the center of mass of each particle. The macrocanonical phase space for this system is the collection of all the phase spaces with N_S atoms and N_C spheres with varying values of N_S, N_C.

The Hamiltonian has the form

$$\hat{H}(z) = \sum_i^{N_C} \frac{\mathbf{P}_i^2}{2M} + \sum_i^{N_S} \frac{\mathbf{p}_i^2}{2m} + V(q, R) \qquad (3.1.1)$$

where $\mathbf{p}_i$ is the momentum of the i-th atom, $\mathbf{P}_i$ is the momentum of the i-th colloidal sphere, m is the mass of the atoms, M the mass of the spheres, and $V(q, R)$ is the potential energy of interaction that includes the interactions between all the particles.

3.2   The CG variables

We choose as CG variables the total number of solvent particles $\hat{N}_S(z)$, the total energy $\hat{H}(z)$, and the concentration field $\hat{c}_{\mathbf{r}}(z)$ of the colloidal particles. The concentration is defined as

$$\hat{c}_{\mathbf{r}}(z) = \sum_{i}^{N_C} \delta(\mathbf{q}_i - \mathbf{r}) \tag{3.2.1}$$

where $\mathbf{q}_i$ is the position of the center of mass of the i-th colloidal sphere. We will consider that the macroscopic information that we have available are the averages of the relevant variables. Therefore, we will be discussing the canonical flavor summarized in Sec. 1.11. The relevant ensemble (1.11.3) now takes the form

$$\overline{\rho}(z) = \frac{\rho^0}{Z[\alpha, \beta, \lambda]} \exp\left\{-\alpha N_S - \beta \hat{H}(z) - \int d\mathbf{r}\lambda(\mathbf{r})\hat{c}_{\mathbf{r}}(z)\right\}$$

$$Z[\alpha, \beta, \lambda] = \sum_{N_S=0}^{\infty} \sum_{N_C=0}^{\infty} \rho^0 \int dz_{N_S} dz_{N_C} \exp\left\{-\alpha N_S - \beta \hat{H}(z) - \sum_{i=1}^{N_C} \lambda(\mathbf{q}_i)\right\} \tag{3.2.2}$$

where now the reference density is

$$\rho^0 = \frac{1}{N_C! N_S! h^{3(N_C + N_S)}} \tag{3.2.3}$$

on due account of the indistinguishability of the atoms and spheres.

The connection between the conjugate variables and the averages is given by (1.11.7) that in the present case is

$$\frac{\partial \Phi}{\partial \alpha}[\alpha, \beta, \lambda] = \overline{N}_S$$

$$\frac{\partial \Phi}{\partial \beta}[\alpha, \beta, \lambda] = E$$

$$\frac{\delta \Phi}{\delta \lambda(\mathbf{r})}[\beta, \lambda] = c(\mathbf{r}) \tag{3.2.4}$$

3.3   The relevant ensemble and the entropy

The entropy (**??**) of this level of description is now

$$S[\overline{N}_S, \overline{E}, c] = -\Phi[\alpha, \beta, \lambda] + \alpha \overline{N}_S + \beta \overline{E} + \int d\mathbf{r}\lambda(\mathbf{r})c(\mathbf{r}) \tag{3.3.1}$$

Here, $\alpha, \beta, \lambda(\mathbf{r})$ are understood as functions of the averages $\overline{N}_S, \overline{E}, c(\mathbf{r})$. The following bit of the entropy

$$F[\alpha, \beta, n] = \Phi[\alpha, \beta, \lambda] - \alpha \overline{N}_S \int d\mathbf{r} \lambda(\mathbf{r}) n(\mathbf{r}) \tag{3.3.2}$$

is the free energy functional of this level of description

3.4   The reversible drift

The time derivative of the CG variables are

$$i\mathcal{L}\hat{c}_{\mathbf{r}}(z) = \hat{\mathbf{J}}_{\mathbf{r}}(z) = \sum_i^{N_C} \mathbf{v}_i \delta(\mathbf{q}_i - \mathbf{r}) \tag{3.4.1}$$

The drift term $v_\mu(t)$ in Eq. (1.11.2) vanishes now, as it involves a Gaussian momentum integral of a velocity. Alternatively, note that all the CG variables $\mathcal{H}_N(z), \hat{c}_{\mathbf{r}}(z)$ are even under time reversal. Therefore, according to Eq. (1.9.18) the resulting drift term should vanish.

3.5   The dissipative matrix

The projected current (1.11.10) simplifies to

$$\mathcal{Q}_t i\mathcal{L} A_\mu \quad \rightarrow \quad \mathcal{Q}_t i\mathcal{L}\hat{n}_{\mathbf{r}} = \nabla \cdot \hat{\mathbf{J}}_{\mathbf{r}}(z) \tag{3.5.1}$$

The dissipative matrix (1.11.9) becomes now

$$\mathcal{D}_{\mu\nu} \rightarrow \nabla_{\mathbf{r}} \nabla_{\mathbf{r}'} \mathbf{D}(\mathbf{r}, \mathbf{r}', t) \tag{3.5.2}$$

where $\nabla_{\mathbf{r}} = \frac{\partial}{\partial \mathbf{r}}$ and the diffusion tensor is given by the Green-Kubo formula

$$\mathbf{D}(\mathbf{r}, \mathbf{r}', t) = \int_0^{\Delta t} dt' \mathrm{Tr}[\overline{\rho}_t \hat{\mathbf{J}}_{\mathbf{r}'} \hat{\mathbf{J}}_{\mathbf{r}}(t')] \tag{3.5.3}$$

Note that this non-local transport coefficient depends on time t only through the actual value of $n(\mathbf{r}, t)$ on which it depends functionally (through the conjugate fields β, λ appearing in the relevant ensemble $\overline{\rho}_t$).

3.6   The transport equation

The final dynamic equation (1.11.1) for the density field is given by

$$\partial_t n(\mathbf{r}, t) = -\nabla_{\mathbf{r}} \mathbf{J}(\mathbf{r}, t) \tag{3.6.1}$$

where we have introduced the average current as

$$\mathbf{J}(\mathbf{r}, t) \equiv \int d\mathbf{r}' \mathbf{D}(\mathbf{r}, \mathbf{r}', t) \nabla_{\mathbf{r}'} \frac{\delta S[E, n]}{\delta n(\mathbf{r}', t)} \tag{3.6.2}$$

where we have performed an integration by parts. This is a closed dynamic equation for the evolution of the concentration field. Note that this equation satisfies the conservation of the average number of colloidal particles,

$$\overline{N}_C = \int d\mathbf{r} c(\mathbf{r}, t) \tag{3.6.3}$$

3.7   Models and Approximations

We will restrict now the discussion to a dilute colloidal suspension.

The entropy functional in this case

Volver aquí después de hacer boundary conditions

The dissipative matrix

For a dilute colloidal suspension, the current correlation may be computed in an approximated way as follows. We assume that the positions evolve much slower than the velocities of the colloidal particles so we can approximate

$$
\begin{aligned}
\mathbf{D}(\mathbf{r}, \mathbf{r}') &= \int_0^\infty dt \mathrm{Tr}[\overline{\rho}_t \hat{\mathbf{J}}_{\mathbf{r}'} \hat{\mathbf{J}}_{\mathbf{r}}(t')] \\
&= \int_0^\infty dt \sum_i \sum_j \mathrm{Tr}[\overline{\rho}_t \mathbf{v}_i \mathbf{v}_j(t) \delta(\mathbf{r} - \mathbf{r}_i) \delta(\mathbf{r}' - \mathbf{q}_j(t))] \\
&\approx \int_0^\infty dt \sum_i \sum_j \mathrm{Tr}[\overline{\rho}_t \mathbf{v}_i \mathbf{v}_j(t) \delta(\mathbf{r} - \mathbf{q}_i) \delta(\mathbf{r}' - \mathbf{q}_j)] \tag{3.7.1}
\end{aligned}
$$

In addition, we may assume that velocities and positions are statistically independent, and in the dilute limit, the correlations of velocities of different particles vanish. In this way,

$$
\begin{aligned}
\mathbf{D}(\mathbf{r}, \mathbf{r}') &\approx \int_0^\infty dt \sum_i \sum_j \mathrm{Tr}[\overline{\rho}_t \mathbf{v}_i \mathbf{v}_j(t)] \mathrm{Tr}[\overline{\rho}_t \delta(\mathbf{r} - \mathbf{q}_i) \delta(\mathbf{r}' - \mathbf{q}_j)] \\
&\approx \sum_i \sum_j \delta_{ij} D_0 \mathbf{1} \mathrm{Tr}[\overline{\rho}_t \delta(\mathbf{r} - \mathbf{r}_i) \delta(\mathbf{r}' - \mathbf{q}_j)] \\
&= D_0 \mathbf{1} n(\mathbf{r}, t) \delta(\mathbf{r}' - \mathbf{r}) \tag{3.7.2}
\end{aligned}
$$

where we have introduced the diffusion coefficient D_0 through the usual Green-Kubo expression

$$D_0 = \frac{1}{3} \int_0^\infty dt \mathrm{Tr}[\overline{\rho}_t \mathbf{v}_i \cdot \mathbf{v}_i(t)] \tag{3.7.3}$$

By inserting this form (3.7.2) into Eq. (??) we arrive at the equation proposed by Marconi and Tarazona [?]

$$\partial_t n(\mathbf{r}, t) = \nabla_\mathbf{r} D_0 n(\mathbf{r}, t) \nabla_\mathbf{r} \frac{\delta \overline{\Phi}[n]}{\delta n(\mathbf{r}, t)} \tag{3.7.4}$$

At finite colloidal concentration, hydrodynamic interactions mediated by the solvent flow play an important role for the dynamics [?]. Two different strategies have been employed to incorporate those in DDFT. We show now that both strategies fall within our general class of DDFT.

The first and simplest strategy was proposed in Ref. [?]. Here, on a phenomenological level, the diffusion coefficient D_0 occurring in the standard DDFT in Eq. (3.7.4) was replaced by a density-dependent long-time self-diffusion $D_s(\phi_c)$ where ϕ_c denotes the volume fraction of the colloids. For hard-sphere colloids, the function $D_s(\phi_c)$ is known from equilibrium long-time dynamics, see e.g. Ref. [?] for an empirical fitting formula. The following approximation for the diffusion tensor was used

$$\mathbf{D}(\mathbf{r}, \mathbf{r}', t) = D_s(\overline{\phi}_c(\mathbf{r}))\mathbf{1} n(\mathbf{r}, t) \delta(\mathbf{r}' - \mathbf{r}) \tag{3.7.5}$$

Here, $\overline{\phi}_c(\mathbf{r})$ is a weighted packing fraction gained from the inhomogeneous packing fraction $\phi_c(\mathbf{r})$ by convoluting the latter with the normalized volume function of a sphere [?].

As a second strategy, the standard DDFT was generalized [?, ?] to include hydrodynamic interactions between the particles explicitly using the approach of Archer and Evans [?]. The form proposed in Refs. [?, ?] fits into the framework of our general equation (??) if the diffusion tensor $\mathbf{D}(\mathbf{r}, \mathbf{r}', t)$ is approximated as

$$\mathbf{D}(\mathbf{r}, \mathbf{r}', t) = D_0 k_B T \rho^{(2)}(\mathbf{r}, \mathbf{r}', t) \omega_{12}(\mathbf{r} - \mathbf{r}') \tag{3.7.6}$$

Here, $\rho^{(2)}(\mathbf{r}, \mathbf{r}', t)$ is the two-particle density in nonequilibrium and the distinct hydrodynamic tensor $\omega_{12}(\mathbf{r} - \mathbf{r}')$ couples the velocity of a particle at position $\mathbf{r}$ to the force exerted from another particle at position $\mathbf{r}'$. The latter can be further approximated by the Oseen or Rotne-Prager expression [?].

3.8 Discussion

The dynamic equation for the concentration of the colloidal particles has very much the same structure as the continuity equation for a simple liquid. However, we should stress that despite the formal structural appearance, the underlying dynamics is very different. This dynamics reflects in the particular form of the entropy functional and the form of the dissipative matrix.

We also expect that the Markovian approximation will be fully respected in the

present level of description because the colloidal particles move much slowly that the solvent atoms. Of course, what we have to compare is the time scale of the concentration of colloidal particles with the time scale of correlation of the current (3.4.1).

4

Diffusion in mixtures: $n_{\mathbf{r}}^{\alpha}$

4.1   The system

In this Chapter we consider a mixture of M different species. Each specie is in a fluid state and diffuse in the rest of species. The mixture is not reacting chemically. We will discuss in a later chapter how to deal with reactive mixtures. The microscopic state of the sytem is given by

$$z \to \mathbf{q}_{i_\alpha}, \mathbf{p}_{i_\alpha}, \quad i_\alpha = 1, \cdots, N_\alpha, \quad \alpha = 1, \cdots M \tag{4.1.1}$$

Here $\mathbf{q}_{i_\alpha}, \mathbf{p}_{i_\alpha}$ are the position and momenta of the i-th atom of specie α, and there are N_α atoms of specie α and M species. The total number of particles in the system is

$$N = \sum_{\alpha}^{M} N_\alpha \tag{4.1.2}$$

The Hamiltonian of the system is given by

$$\hat{H}(z) = \sum_{\alpha}^{M} \sum_{i_\alpha}^{N_\alpha} \frac{\mathbf{p}_{i_\alpha}^2}{2m_\alpha} + \frac{1}{2} \sum_{\alpha,\beta}^{M} \sum_{i_\alpha}^{N_\alpha} \sum_{j_\beta}^{N_\beta} \phi^{\alpha\beta}(|\mathbf{q}_{i_\alpha} - \mathbf{q}_{j_\beta}|) \tag{4.1.3}$$

where we have assumed a pair-wise potential of interaction, although this is not essential in the following.

We assume periodic boundary conditions as a way of mimicking an infinite system. We do not include external confining potentials like hard-walled containers. Of course, in an experimental situation we need to include the container. This induces notable differences with unconfined systems. We will consider diffusing mixtures in confined space in a later chapter.

The dynamic invariants of the system are the total number of particles of each specie,

the Hamiltonian (**??**), and the total momentum, defined as

$$\mathbf{P}(z) = \sum_{\alpha}^{M} \sum_{i_{\alpha}}^{N_{\alpha}} \mathbf{p}_{i_{\alpha}} \tag{4.1.4}$$

Because momentum is conserved, by choosing the center of mass reference system in which $\mathbf{P} = 0$ we have that the position of the center of mass of the system is also a conserved quantity.

4.2   The CG variables

We will describe the macroscopic state of the system by using as CG variables the number density of each specie. They are defined as

$$\hat{n}_{\mathbf{r}}^{\alpha}(z) = \sum_{i_{\alpha}}^{N_{\alpha}} \delta(\mathbf{q}_{i_{\alpha}} - \mathbf{r}) \tag{4.2.1}$$

In addition, we will include in the set of CG variables the Hamiltonian (4.1.3) but will not include the total number of particles of each species. Although these variables are dynamic invariants, they are redundant in the sense that are given from the space integrals of the number density fields, i.e.

$$N_{\alpha} = \int d\mathbf{r} \hat{n}_{\mathbf{r}}^{\alpha}(z) \tag{4.2.2}$$

As we already know, the flavor to be selected for the type of variables (4.2.1) is the canonical flavor for which we keep track of the averages of the CG variables. The time-dependent average of the number density fields phase function (4.2.1) is denoted by

$$n^{\alpha}(\mathbf{r}, t) = \text{Tr}[\rho_t \hat{n}_{\mathbf{r}}^{\alpha}] \tag{4.2.3}$$

and gives the probability of finding any one atom of species α in the vicinity of $\mathbf{r}$ at time t. Such a variable is particularly useful when we are interested in how the particles of the liquid distribute themselves in space.

4.3   The relevant ensemble and the entropy

The relevant ensemble in the canonical flavor is given by (1.11.3). The CG variable (22.3) is, in fact, a collection of phase functions that are indexed with the continuum subindex $\mathbf{r}$. For the selected CG variables (22.3), we will have a conjugate variable $\lambda(\mathbf{r})$, i.e. a

value of λ for each value of $\mathbf{r}$. The relevant ensemble (1.11.3) becomes

$$\overline{\rho}_{\{N\}}(z) = \frac{\rho^0_{\{N\}}}{Z[\beta,\lambda]} \exp\left\{-\beta\hat{H}(z) - \int d\mathbf{r}\lambda^\alpha_{\{N\}}(\mathbf{r})\hat{n}^\alpha_{\mathbf{r}}(z_N)\right\}$$

$$Z[\beta,\lambda] = \sum_{\{N\}=0}^{\infty} \rho^0 \int dz_{\{N\}} \exp\left\{-\beta\hat{H}_{\{N\}}(z) - \sum_\alpha \sum_{i_\alpha=1}^{N_\alpha} \lambda^\alpha_{\{N\}}(\mathbf{q}_{i_\alpha})\right\} \qquad (4.3.1)$$

We have introduced a multi-index notation $\{N\} = \{N_1, \ldots, N_M\}$. For example

$$\sum_{\{N\}=0}^{\infty} = \sum_{N_1=0}^{\infty} \cdots \sum_{N_M=0}^{\infty} \qquad (4.3.2)$$

The quantum indistinguishability factor is now

$$\rho^0 = \frac{1}{h^{3N}} \prod_\alpha^M \frac{1}{N_\alpha!} \qquad (4.3.3)$$

The conjugate variables and the average of the CG variables are related by (1.11.7) that in the present case becomes

$$\frac{\delta\Phi}{\delta\lambda^\alpha(\mathbf{r})}[\beta,\lambda] = n^\alpha(\mathbf{r})$$

$$\frac{\partial\Phi}{\partial\beta}[\beta,\lambda] = E \qquad (4.3.4)$$

The connection between the averages $E, n^\alpha(\mathbf{r}$ and the conjugate variables $\beta, \lambda^\alpha(\mathbf{r})$ is one to one. The entropy (??) for this level of description is given by

$$S[E,n] = -\Phi[\beta,\lambda] + \sum_\alpha^M \int d\mathbf{r}\lambda^\alpha(\mathbf{r})n^\alpha(\mathbf{r}) + \beta E \qquad (4.3.5)$$

Here, $\beta, \lambda^\alpha(\mathbf{r})$ are understood as functions of the averages $E, n^\alpha(\mathbf{r})$. The derivatives of the entropy give the conjugate variables

$$\frac{\partial S}{\partial E}[E,n] = \beta$$

$$\frac{\delta S}{\delta n^\alpha(\mathbf{r}')}[E,n] = \lambda^\alpha(\mathbf{r}) \qquad (4.3.6)$$

The following bit of the entropy

$$F[n,\beta] = \Phi[\beta,\lambda] - \sum_\alpha^M \int d\mathbf{r}\lambda^\alpha(\mathbf{r})n^\alpha(\mathbf{r}) \qquad (4.3.7)$$

is known as the (dimensionless) **free energy functional** of the mixture. It is the partial Legendre transform of the thermodynamic potential with respect to the number density fields.

Exercise: We said that total momentum is a dynamic invariant and, in principle, it should be included in the list of CG variables. Why we have not included it? Show that by including this dynamic invariant, nothing changes provided that we choose the center of mass reference system.

4.4   The reversible drift

The CG variables (4.2.1) are all even under time reversal. For this reason, according to (1.9.18) the drift term vanishes in this level of description.

4.5   The dissipative matrix

The Liouville operator on the relevant variable, $i\mathcal{L}A_\mu$, is now

$$i\mathcal{L}A_\mu \quad \rightarrow \quad i\mathcal{L}\hat{n}_{\mathbf{r}}^\alpha(z) = -\nabla\cdot\hat{\mathbf{J}}_{\mathbf{r}}^\alpha(z) \qquad (4.5.1)$$

where the current of particles of type α is defined as

$$\hat{\mathbf{J}}_{\mathbf{r}}^\alpha(z) = \sum_{i_\alpha}^{N_\alpha} \mathbf{v}_{i_\alpha}\delta(\mathbf{q}_{i_\alpha} - \mathbf{r}) \qquad (4.5.2)$$

The projected current (1.11.10) coincides with the time derivative (4.5.1), because the drift vanishes. The resulting dissipative matrix (1.11.9)

$$\mathscr{D}_{\mu\nu} \rightarrow \nabla_{\mathbf{r}}\nabla_{\mathbf{r}'}\mathbf{D}^{\alpha\beta}(\mathbf{r},\mathbf{r}',t) \qquad (4.5.3)$$

where the non-local diffusion tensor is given by the Green-Kubo formula

$$\mathbf{D}^{\alpha\beta}(\mathbf{r},\mathbf{r}',t) = \int_0^{\Delta t} dt'\,\mathrm{Tr}[\overline{\rho}_t\hat{\mathbf{J}}_{\mathbf{r}'}^\beta\hat{\mathbf{J}}_{\mathbf{r}}^\alpha(t')] \qquad (4.5.4)$$

Note that, because total linear momentum is conserved, we have that

$$\sum_\alpha^M \int d\mathbf{r}\,m^\alpha\hat{\mathbf{J}}_{\mathbf{r}}^\alpha(z) = \sum_\alpha^M m^\alpha \sum_{i_\alpha}^{N_\alpha} \mathbf{v}_{i_\alpha} = \mathbf{P} = 0 \qquad (4.5.5)$$

This identity implies the following relation for the dissipative matrix

$$\sum_\alpha^M m_\alpha \int d\mathbf{r}\,\mathbf{D}^{\alpha\beta}(\mathbf{r},\mathbf{r}',t) = 0 \qquad (4.5.6)$$

Because the CG variables have even parity under time reversal, we know that the dissipative matrix will be symmetric. In the present case, with the continuum indices $\mathbf{r}, \mathbf{r}'$ this symmetry means

$$\mathbf{D}^{\alpha\beta}(\mathbf{r}, \mathbf{r}', t) = \mathbf{D}^{\beta}(\mathbf{r}', \mathbf{r}, t) \tag{4.5.7}$$

4.6   The transport equation

The final dynamic equations (1.11.1) for the density fields is given by

$$\partial_t n^\alpha(\mathbf{r}, t) = -\nabla_{\mathbf{r}} \mathbf{J}^\alpha(\mathbf{r}, t) \tag{4.6.1}$$

where we have introduced the average current as

$$\mathbf{J}^\alpha(\mathbf{r}, t) \equiv \sum_\beta^M \int d\mathbf{r}' \mathbf{D}^{\alpha\beta}(\mathbf{r}, \mathbf{r}', t) \nabla_{\mathbf{r}'} \lambda^\beta(\mathbf{r}', t) \tag{4.6.2}$$

where the conjugate variable $\lambda^\beta(\mathbf{r}', t)$ is given by Eq. (4.3.6) evaluated at the time dependent value of $n^\alpha(\mathbf{r}, t)$. Eqs. (4.6.1) are in the form of conservation equations for each specie and, therefore, they conserve the average number of molecules of each specie, i.e.

$$\frac{d}{dt} N_\alpha = \frac{d}{dt} \int d\mathbf{r} n^\alpha(\mathbf{r}, t) = 0 \tag{4.6.3}$$

The average current of species α is given in terms of the **consitutive equation** (4.6.2) as a non-local matrix times the **thermodynamic forces** given by the derivatives of the entropy.

4.7   Models and Approximations

Up to now, the only approximation that we have taken is the Markovian approximation implicit in the use of the transport equation (1.11.1). This assumption relies on the possibility that the density field evolves in a time scale much larger than the current correlation function. This is, indeed a very strong assumption that only in very particular circumstances is expected to be satisfied by an atomic fluid. Situations in which the density evolves slowly as compared with the current may arise near liquid-solid phase transitions. In liquid phase states, we expect that the fluid moves and that changes in the density are always accompanied by currents that evolve in the same time scales. We will discuss in Chapter **??** a level of description in which, in addition to the density field, we also include the momentum field (closely related to the current of particles).

Note that the entropy functional or the density functional in principle captures the full microstructure of the fluid. Near walls, for example, allows to describe the equilibrium density field showing layering of the atoms.

In general, the calculation of $\mathbf{D}(\mathbf{r}, \mathbf{r}', t)$ is difficult because of the presence of the relevant ensemble. In order to deal with more tractable expressions, we may assume as a

first approximation that we are *near equilibrium*, in such a way that $\beta(t) \approx \beta_0, \lambda(\mathbf{r}, t) \approx 0$ and we can substitute $\overline{\rho}_t \approx \rho^{\mathrm{eq}}$, see Eq. (**??**). In this way, the kernel $\mathbf{D}(\mathbf{r}, \mathbf{r}', t)$ is just the time integral of the equilibrium current correlation tensor. In the absence of walls, we have translational and rotational invariance and $\mathbf{D}(\mathbf{r}, \mathbf{r}', t) = D(\mathbf{r} - \mathbf{r}')\mathbf{1}$. For situations far from equilibrium, we may always expand $\exp\{-\lambda A\}$ in powers of λ and compute the corresponding corrections.

5

Hydrodynamics $\hat{\rho}_{\mathbf{r}}, \hat{\mathbf{g}}_{\mathbf{r}}, \hat{e}_{\mathbf{r}}$

[Major rewritting needed!]

5.1   The system

5.2   The relevant variables

In addition to the total number of particles $\hat{N}(z)$, and Hamiltonian $\hat{H}(z)$, we describe the system with the following set

$$\hat{\rho}_{\mathbf{r}}(z) = \sum_i m_i \delta(\mathbf{r} - \mathbf{q}_i)$$

$$\hat{\mathbf{g}}_{\mathbf{r}}(z) = \sum_i \mathbf{p}_i \delta(\mathbf{r} - \mathbf{q}_i)$$

$$\hat{e}_{\mathbf{r}}(z) = \sum_i e_i \delta(\mathbf{r} - \mathbf{q}_i) \tag{5.2.1}$$

where the energy of particle i is given by

$$e_i = \frac{\mathbf{p}_i^2}{2m_i} + \phi_i + V_{ext}(\mathbf{q}_i)$$

$$\phi_i = \frac{1}{2} \sum_j \phi_{ij} \tag{5.2.2}$$

Here $\hat{\rho}_{\mathbf{r}}$ is the mass density field, $\hat{\mathbf{g}}_{\mathbf{r}}$ is the momentum density field and $\hat{e}_{\mathbf{r}}$ is the energy density field.

The averages of these phase functions with respect to the solution $\rho_t(z)$ of the Liouville

equation are denoted by

$$\rho(\mathbf{r}, t) = \int dz \rho_t(z) \hat{\rho}_{\mathbf{r}}(z)$$

$$\mathbf{g}(\mathbf{r}, t) = \int dz \rho_t(z) \hat{\mathbf{g}}_{\mathbf{r}}(z)$$

$$e(\mathbf{r}, t) = \int dz \rho_t(z) \hat{e}_{\mathbf{r}}(z) \tag{5.2.3}$$

$$\rho(\mathbf{r}, t) = \mathrm{Tr}[\overline{\rho}_t \hat{\rho}_{\mathbf{r}}]$$
$$\mathbf{g}(\mathbf{r}, t) = \mathrm{Tr}[\overline{\rho}_t \hat{\mathbf{g}}_{\mathbf{r}}]$$
$$e(\mathbf{r}, t) = \mathrm{Tr}[\overline{\rho}_t \hat{e}_{\mathbf{r}}] \tag{5.2.4}$$

because the relevant ensemble reproduces exactly the averages of the relevant variables. The above variables are assumed to be the slow variables in the system.

5.3   The relevant ensemble and the entropy

The relevant ensemble has the form

$$\overline{\rho}_t(z) = \frac{1}{Z[\nu(t), \mathbf{v}(t), \beta(t)]} \exp \left\{ - \int d\mathbf{r} \beta(\mathbf{r}, t) \left(\nu(\mathbf{r}, t) \hat{\rho}_{\mathbf{r}}(z) - \mathbf{v}(\mathbf{r}, t) \cdot \hat{\mathbf{g}}_{\mathbf{r}}(z) + \hat{e}_{\mathbf{r}}(z) \right) \right\} \tag{5.3.1}$$

Here, $\beta(\mathbf{r})\nu(\mathbf{r})$, $-\beta(\mathbf{r})\mathbf{v}(\mathbf{r})$ and $\beta(\mathbf{r})$ are the Lagrange multipliers associated to each constrain in (22.4). The particular way of writing these multipliers instead of, for example $\alpha(\mathbf{r}), \beta(\mathbf{r}), \gamma(\mathbf{r})$ is dictated by the physical meaning that $\mathbf{v}(\mathbf{r})$ and $\beta(\mathbf{r})$ will acquire in the subsequent development.

The normalization factor is the $\nu, \mathbf{v}, \beta$-dependent grand-canonical partition function defined as

$$Z[\nu(t), \mathbf{v}(t), \beta(t)] \equiv \sum_{N=0}^{\infty} \frac{1}{N! h^{3N}} \int dr_N dp_N \exp \left\{ - \sum_{i=1}^{N} \beta(\mathbf{r}_i, t) \left(m\nu(\mathbf{r}_i, t) - \mathbf{p}_i \cdot \mathbf{v}(\mathbf{r}_i, t) + e_i \right) \right\} \tag{5.3.2}$$

and the grand potential of the present level of description is

$$\Phi[\nu, \mathbf{v}, \beta] \equiv - \ln Z[\nu, \mathbf{v}, \beta] \tag{5.3.3}$$

Here, $\nu, \mathbf{v}, \beta$ are the conjugate fields of the mass, momentum and energy density, respectively, which are fixed by the condition that the averages of the relevant variables (22.4) with the relevant ensemble coincide with the averages $\rho(\mathbf{r}, t), \mathbf{g}(\mathbf{r}, t), e(\mathbf{r}, t)$ computed with the actual ensemble, solution of the Liouville equation. This condition can

be expressed as

$$\frac{\delta\Phi[\nu,\mathbf{v},\beta]}{\delta\nu(\mathbf{r},t)} = \beta(\mathbf{r},t)\rho(\mathbf{r},t)$$

$$\frac{\delta\Phi[\nu,\mathbf{v},\beta]}{\delta\mathbf{v}(\mathbf{r},t)} = -\beta(\mathbf{r},t)\mathbf{g}(\mathbf{r},t)$$

$$\frac{\delta\Phi[\nu,\mathbf{v},\beta]}{\delta\beta(\mathbf{r},t)} = \nu(\mathbf{r},t)\rho(\mathbf{r},t) - \mathbf{v}(\mathbf{r},t)\mathbf{g}(\mathbf{r},t) + e(\mathbf{r},t) \tag{5.3.4}$$

The $\nu, \mathbf{v}, \beta$ are the conjugate variables of $\rho, \mathbf{g}, e$, there is a one to one connection between these fields. Therefore, the functionals $\nu[\rho,\mathbf{g},e]$, $\mathbf{v}[\rho,\mathbf{g},e]$ and $\beta[\rho,\mathbf{g},e]$ exist and are unique.

The entropy functional of the hydrodynamic level of description is given by using the relevant ensemble (22.5) in the Gibbs-Jaynes entropy functional (**??**). Because the relevant ensemble itself depends functionally on the hydrodynamic variables the result is the entropy functional of the hydrodynamic variables. By inserting the relevant ensemble Eq.(12.4) in (**??**) and use of Eq. (22.5), we obtain the

$$S[\rho,\mathbf{g},e] = -\Phi[\nu,\mathbf{v},\beta] + \int d\mathbf{r}\beta(\mathbf{r})\left[\nu(\mathbf{r})\rho(\mathbf{r},t) - \mathbf{v}(\mathbf{r})\cdot\mathbf{g}(\mathbf{r},t) + e(\mathbf{r})\right] \tag{5.3.5}$$

where here the conjugate variables $\lambda, \mathbf{v}, \beta$ are understood as functionals of the CG variables $\rho, \mathbf{g}, e$. The entropy is related to the Legendre transform of the grand potential (up to some signs) and, therefore, we have the relations conjugate to (22.5)

$$\beta(\mathbf{r})\nu(\mathbf{r}) = \frac{\delta S[\rho,\mathbf{g},e]}{\delta\rho(\mathbf{r})}$$

$$\beta(\mathbf{r})\mathbf{v}(\mathbf{r}) = -\frac{\delta S[\rho,\mathbf{g}]}{\delta\mathbf{g}(\mathbf{r})}$$

$$\beta(\mathbf{r}) = \frac{\delta S[\rho,\mathbf{g}]}{\delta e(\mathbf{r})} \tag{5.3.6}$$

Eliminating the velocity field

We show now that both, the entropy and thermodynamic potential functionals at the hydrodynamic level, which in principle depend on three fields, do actually depend on only two of the fields. This allows to eliminate the velocity field and present the hydrodynamic functionals "in the rest frame".

In fact, it is possible to find an *explicit* expression of $\mathbf{v}$ as a function of $\rho, \mathbf{g}$. Perform the momentum integrals in Eq. (18.4) and obtain

$$\Phi[\nu,\mathbf{v},\beta] = -\ln\sum_{N=0}^{\infty}\frac{1}{N!}\int\prod_{i=0}^{N}\frac{d\mathbf{q}_i}{\Lambda^3(\mathbf{q}_i)}\exp\left\{-\sum_{j}^{N}\beta(\mathbf{r}_j,t)\left(m_j\nu(\mathbf{q}_j,t) + \phi_j - \frac{m_j\mathbf{v}^2(\mathbf{q}_j,t)}{2}\right)\right\}$$

$$\tag{5.3.7}$$

where the *local thermal wavelength* is defined as

$$\Lambda(\mathbf{q}_i) \equiv \left(\frac{h^2 \beta(\mathbf{q}_i)}{2m\pi} \right)^{\frac{1}{2}} \tag{5.3.8}$$

This shows that the function $\Phi[\nu, \mathbf{v}, \beta]$ depends on its arguments only through the combination

$$\Phi[\nu, \mathbf{v}, \beta] = \overline{\Phi}[\mu, \beta] \tag{5.3.9}$$

with

$$\mu(\mathbf{r}, t) = -\nu(\mathbf{r}, t) + \frac{\mathbf{v}^2(\mathbf{r}, t)}{2} \tag{5.3.10}$$

and where

$$\overline{\Phi}[\mu, \beta] \equiv -\ln \sum_{N=0}^{\infty} \frac{1}{N!} \int \prod_{i=0}^{N} \frac{d\mathbf{q}_i}{\Lambda^3(\mathbf{q}_i)} \exp \left\{ -\sum_j^{N} \beta(\mathbf{q}_j)(-m_j \mu(\mathbf{q}_j, t) + \phi_j) \right\} \tag{5.3.11}$$

The functional derivatives of this two variable free energy are

$$\frac{\delta \overline{F}[\mu, \boldsymbol{\lambda}, \beta]}{\delta \mu(\mathbf{r}, t)} = -\beta(\mathbf{r}, t)\rho(\mathbf{r}, t)$$

where $u(\mathbf{r}, t)$ is an energy field defined as

$$u(\mathbf{r}, t) = \frac{3}{2}\beta^{-1}(\mathbf{r}, t)n(\mathbf{r}, t) + \frac{1}{2} \int d\mathbf{r}' \phi_{\mathbf{r}\mathbf{r}'} \langle \hat{n}_\mathbf{r} \hat{n}_{\mathbf{r}'} \rangle^{\mu, \beta}$$

Therefore,

$$\beta(\mathbf{r}, t) = \frac{3n(\mathbf{r}, t)}{2k(\mathbf{r}, t)}$$

where the kinetic energy field is defined as

$$k(\mathbf{r}) = u(\mathbf{r}) - \frac{1}{2} \int d\mathbf{r}' \phi_{\mathbf{r}\mathbf{r}'} \langle \hat{n}_\mathbf{r} \hat{n}_{\mathbf{r}'} \rangle^{\mu, \beta}$$

Eq. (6.7.2) allows one to interpret $\beta(\mathbf{r}, t)$ as the inverse of a temperature field.

Then take the functional derivative of Eq. (18.4) with respect to the conjugate field $\mathbf{v}(\mathbf{r})$. Together with Eqs. (22.5), (22.5), this leads directly to the explicit form of the conjugate field $\mathbf{v}(\mathbf{r})$

$$\mathbf{v}(\mathbf{r}, t) = \frac{\mathbf{g}(\mathbf{r}, t)}{\rho(\mathbf{r}, t)}$$

and allows one to interpret the conjugate field $\mathbf{v}(\mathbf{r}, t)$ as the velocity field. Therefore, we have

$$S_{\mathrm{FHD}}[\rho, \mathbf{g}, e] = S_{\mathrm{FTD}}\left[\frac{\rho}{m}, e\right] - \int d\mathbf{r} \frac{\mathbf{g}^2(\mathbf{r})}{2\rho(\mathbf{r})}$$

This is the explicit *exact* form for the entropy at the Functional Hydrodynamic level of description. It is a non-trivial result that has a very appealing simplicity. Note that if we have good expressions for the entropy functional $S_{\mathrm{FTD}}[n, e]$, this information can be transferred directly to the hydrodynamic level. The hydrodynamic aspects of the hydrodynamic functional are simply encoded into a kinetic energy term.

The functional derivatives of Eq. (22.5) leads to

$$\lambda(\mathbf{r}, t) = -\frac{\delta \Phi^H[\rho, \mathbf{g}]}{\delta \rho(\mathbf{r}, t)} = -\frac{1}{m}\frac{\delta \Phi[n]}{\delta n(\mathbf{r}, t)} + \frac{\mathbf{v}^2(\mathbf{r}, t)}{2}$$

$$\equiv -\mu(\mathbf{r}, t) + \frac{\mathbf{v}^2(\mathbf{r}, t)}{2}$$

and to the second Eq. (22.4), as it should. We have introduced the chemical potential per unit mass in the last equation (22.5).

Galilean operator

It what follows it is convenient to introduce the Galilean operator. This operator acts of an arbitrary phase function $\hat{F}(z)$ by subtracting the velocity field from the velocity of the particles as follows

$$\mathscr{G}_t \hat{F}(\cdots, \mathbf{q}_i, \mathbf{p}_i, \cdots) = \hat{F}(\cdots, \mathbf{q}_i, \mathbf{p}_i - m_i \mathbf{v}(\mathbf{q}_i, t), \cdots)$$

The inverse operator $\mathscr{G}_t^{-1}$ is simply

$$\mathscr{G}_t^{-1} \hat{F}(\cdots, \mathbf{q}_i, \mathbf{p}_i, \cdots) = \hat{F}(\cdots, \mathbf{q}_i, \mathbf{p}_i + m_i \mathbf{v}(\mathbf{q}_i, t), \cdots)$$

Note that inside averages over phase space, the effect of the Galilean operator is as follows

$$\mathrm{Tr}[\mathscr{G}_t \hat{F}] = \mathrm{Tr}[\hat{F}]$$
$$\mathrm{Tr}[\hat{F}\hat{G}] = \mathrm{Tr}[\mathscr{G}_t \hat{F} \mathscr{G}_t \hat{G}]$$
$$\mathrm{Tr}[\hat{F}\mathscr{G}_t \hat{G}] = \mathrm{Tr}[\hat{G}\mathscr{G}_t^{-1} \hat{F}]$$

The action of the Galilean operator on the CG variables (5.2.1) is

$$\mathscr{G}_t \hat{\rho}_{\mathbf{r}}(z) = \hat{\rho}_{\mathbf{r}}(z)$$
$$\mathscr{G}_t \hat{\mathbf{g}}_{\mathbf{r}}(z) = \hat{\mathbf{g}}_{\mathbf{r}}(z) - \mathbf{v}(\mathbf{r}, t)\hat{\rho}_{\mathbf{r}}(z)$$
$$\mathscr{G}_t \hat{e}_{\mathbf{r}}(z) = \hat{e}_{\mathbf{r}}(z) - \mathbf{v}(\mathbf{r}, t)\hat{\mathbf{g}}_{\mathbf{r}}(z) + \frac{1}{2}\mathbf{v}^2(\mathbf{r}, t)\hat{\rho}_{\mathbf{r}}(z)$$

The action of the Galilean operator on the relevant ensemble gives the so called **comoving relevant ensemble** $\overline{\rho}_t^{\rm rest}(z)$

$$\overline{\rho}_t^{\rm rest}(z) \equiv \mathscr{G}_t \overline{\rho}_t(z) = \frac{\rho_N^0}{Z[\mu, \beta]} \exp\left\{ -\int d\mathbf{r}\beta(\mathbf{r}, t)\left[\hat{e}_{\mathbf{r}}(z) - \mu(\mathbf{r}, t)\hat{\rho}_{\mathbf{r}}(z)\right]\right\}$$

where we have introduced the chemical potential per unit mass as

$$\mu(\mathbf{r}, t) = -\lambda(\mathbf{r}, t) + \frac{1}{2}\mathbf{v}^2(\mathbf{r}, t)$$

Note that the averages of the relevant variables with the comoving relevant ensemble are

$$\mathrm{Tr}[\overline{\rho}_t^{\rm rest}\hat{\rho}_{\mathbf{r}}] = \rho(\mathbf{r}, t)$$
$$\mathrm{Tr}[\overline{\rho}_t^{\rm rest}\hat{\mathbf{g}}_{\mathbf{r}}] = \mathbf{g}(\mathbf{r}, t) - \rho(\mathbf{r}, t)\mathbf{v}(\mathbf{r}, t) = 0$$

$$\mathrm{Tr}[\overline{\rho}_t^{\rm rest}\hat{e}_{\mathbf{r}}] = e(\mathbf{r}, t) - \frac{\rho(\mathbf{r}, t)}{2}\mathbf{v}^2(\mathbf{r}, t) \equiv \epsilon(\mathbf{r}, t)$$

The **internal energy density field** $\epsilon(\mathbf{r}, t)$ is introduced in the last equation. The equations (5.3) show that there is a one to one connection between the conjugate variables $\mu(\mathbf{r}, t), \beta(\mathbf{r}, t)$ and the fields $\rho(\mathbf{r}, t), \epsilon(\mathbf{r}, t)$. The second equation this leads directly to the explicit form or the conjugate field $\mathbf{v}(\mathbf{r})$

$$\mathbf{g}(\mathbf{r}, t) = \rho(\mathbf{r}, t)\mathbf{v}(\mathbf{r}, t)$$

This equation allows to interpret the conjugate field $\mathbf{v}(\mathbf{r}, t)$ as the velocity field. The rest of equation show that the multipliers β, μ depend only on the density and the internal energy density $u \equiv e - \rho\mathbf{v}^2/2$.

Let us explore the consequences of a Galilean transformation on the entropy. By using (5.3) we obtain

$$S[\overline{\rho}] = -\mathrm{Tr}[\overline{\rho}(z)\ln\overline{\rho}(z)] = -\mathrm{Tr}[\mathscr{G}_t\hat{\rho}(z)\ln\{\mathscr{G}_t\hat{\rho}(z)\}] = -\mathrm{Tr}[\overline{\rho}^{\rm rest}(z)\ln\overline{\rho}^{\rm rest}(z)]$$

Because $\hat{\rho}(z)$ depends only on ρ, ϵ, we obtain that the entropy itself is a function of ρ, ϵ, this is

$$S[\rho, \mathbf{g}, e] = S^{\rm rest}[\rho, \epsilon]$$

Let us see what is the effect of the Galilean operator in the entropy functional

$$S = -\text{tr}[\overline{\rho}_t \ln \overline{\rho}_t] = -\text{tr}\left[(\mathscr{G}_t \overline{\rho}_t)\,(\mathscr{G}_t \ln \overline{\rho}_t)\right]$$

$$= \text{tr}\left[\overline{\rho}_t^{\text{rest}}\left(\mathscr{G}_t \int d\mathbf{r}\,[\lambda(\mathbf{r})\hat{\rho}_{\mathbf{r}}(z) - \beta(\mathbf{r})\mathbf{v}(\mathbf{r})\hat{\mathbf{g}}_{\mathbf{r}}(z) + \beta(\mathbf{r})\hat{e}_{\mathbf{r}}(z)]\right)\right] + \ln Z[\lambda, v, \beta]$$

$$= \text{tr}\left[\overline{\rho}_t^{\text{rest}}\left(\int d\mathbf{r}\,(\lambda(\mathbf{r},t)\hat{\rho}_{\mathbf{r}}(z) + \beta(\mathbf{r},t)\hat{e}_{\mathbf{r}}(z))\right)\right] - \int d\mathbf{r}\frac{\mathbf{g}^2(\mathbf{r},t)}{2\rho(\mathbf{r},t)}$$

The functional derivatives of entropy with respect to the relevant variables are

$$\frac{\delta \overline{S}[\rho, u]}{\delta \rho(\mathbf{r}, t)} = -\beta(\mathbf{r}, t)\mu(\mathbf{r}, t)$$

$$\frac{\delta \overline{S}[\rho, u]}{\delta u(\mathbf{r}, t)} = \beta(\mathbf{r}, t)$$

We can write the Eq. (**??**)

$$\overline{F}[\mu, \beta] = \int d\mathbf{r}\beta(\mathbf{r})\left\{u(\mathbf{r}) - \rho(\mathbf{r})\mu(\mathbf{r})\right\} - \overline{S}[\rho, u]$$

That is, the rest frame $\overline{S}$ and $\overline{F}$ are Legendre transform of each other.

5.4   The reversible drift

The time derivatives of the relevant variables are

$$i\mathcal{L}\hat{\rho}_{\mathbf{r}}(z) = -\nabla \hat{\mathbf{g}}_{\mathbf{r}}(z)$$

$$i\mathcal{L}\hat{\mathbf{g}}_{\mathbf{r}}(z) = \frac{1}{2}\sum_{kl}\mathbf{F}_{kl}\left[\delta(\mathbf{r} - \mathbf{r}_k) - \delta(\mathbf{r} - \mathbf{r}_l)\right] - \sum_i \mathbf{v}_i \mathbf{p}_i \nabla \delta(\mathbf{r} - \mathbf{r}_i)$$

$$i\mathcal{L}\hat{e}_{\mathbf{r}}(z) = \frac{1}{2}\sum_{kl}\mathbf{F}_{kl}\left[\mathbf{v}_k \delta(\mathbf{r} - \mathbf{r}_k) - \mathbf{v}_l \delta(\mathbf{r} - \mathbf{r}_l)\right] - \frac{1}{2}\sum_{ij}\mathbf{F}_{ij}\mathbf{v}_i\left[\delta(\mathbf{r} - \mathbf{r}_i) + \delta(\mathbf{r} - \mathbf{r}_j)\right] - \sum_i \mathbf{v}_i \epsilon_i \nabla \delta(\mathbf{r} - \mathbf{r}_i)$$

$$= \frac{1}{4}\sum_{ij}\mathbf{F}_{ij}(\mathbf{v}_i + \mathbf{v}_j)\left[\delta(\mathbf{r} - \mathbf{r}_i) - \delta(\mathbf{r} - \mathbf{r}_j)\right] - \sum_i \mathbf{v}_i \epsilon_i \nabla \delta(\mathbf{r} - \mathbf{r}_i)$$

By using the usual trick [**?, ?, ?**]

$$\delta(\mathbf{r} - \mathbf{r}_i) - \delta(\mathbf{r} - \mathbf{r}_j) = -\nabla \mathbf{r}_{ij}\int_0^1 d\epsilon \delta(\mathbf{r} - \mathbf{r}_j - \epsilon \mathbf{r}_{ij})$$

therefore

$$i\mathcal{L}\hat{\rho}_{\mathbf{r}}(z) = -\nabla\hat{\mathbf{g}}_{\mathbf{r}}(z)$$

$$i\mathcal{L}\hat{\mathbf{g}}_{\mathbf{r}}(z) = -\nabla\hat{\mathbf{\Sigma}}_{\mathbf{r}}(z)$$

$$i\mathcal{L}\hat{e}_{\mathbf{r}}(z) = -\nabla\hat{\mathbf{Q}}_{\mathbf{r}}(z)$$

We have defined the microscopic momentum flux tensor as $\hat{\mathbf{\Sigma}}_{\mathbf{r}}(z)$, and the energy flux vector $\hat{\mathbf{Q}}_{\mathbf{r}}(z)$ as

$$\hat{\mathbf{\Sigma}}_{\mathbf{r}}(z) \equiv \sum_i \mathbf{v}_i \mathbf{p}_i \delta(\mathbf{r} - \mathbf{r}_i) + \frac{1}{2}\sum_{ij} \mathbf{F}_{ij}\mathbf{r}_{ij} \int_0^1 d\epsilon \delta(\mathbf{r} - \mathbf{r}_j - \epsilon \mathbf{r}_{ij})$$

$$\hat{\mathbf{Q}}_{\mathbf{r}}(z) \equiv \sum_i e_i \mathbf{v}_i \delta(\mathbf{r} - \mathbf{r}_i) + \frac{1}{4}\sum_{ij}(\mathbf{v}_i + \mathbf{v}_j)\mathbf{F}_{ij}\mathbf{r}_{ij} \int_0^1 d\epsilon \delta(\mathbf{r} - \mathbf{r}_j - \epsilon \mathbf{r}_{ij})$$

We will need the effect of the Galilean operator (18.4) on these fluxes

$$S_t^{-1}\hat{\mathbf{\Sigma}}_{\mathbf{r}}(z) = \hat{\mathbf{\Sigma}}_{\mathbf{r}}(z) + \mathbf{v}(\mathbf{r},t)\hat{\mathbf{g}}_{\mathbf{r}} + \hat{\mathbf{g}}_{\mathbf{r}}\mathbf{v}(\mathbf{r},t) + \mathbf{v}(\mathbf{r},t)\mathbf{v}(\mathbf{r},t)\hat{\rho}_{\mathbf{r}}$$

$$S_t^{-1}\hat{\mathbf{Q}}_{\mathbf{r}}(z) \equiv S_t \left[\sum_i e_i \mathbf{v}_i \delta(\mathbf{r} - \mathbf{r}_i) + \frac{1}{4}\sum_{ij}(\mathbf{v}_i + \mathbf{v}_j)\mathbf{F}_{ij}\mathbf{r}_{ij} \int_0^1 d\epsilon \delta(\mathbf{r} - \mathbf{r}_j - \epsilon \mathbf{r}_{ij}) \right]$$

$$S_t^{-1}\hat{\mathbf{Q}}_{\mathbf{r}}(z) = \sum_i \frac{1}{2m}\left(\mathbf{p}_i + m\mathbf{v}(\mathbf{r}_i)\right)^2 \left(\mathbf{v}_i + \mathbf{v}(\mathbf{r}_i)\right)\delta(\mathbf{r} - \mathbf{r}_i) + \sum_i \phi_i(\mathbf{v}_i + \mathbf{v}(\mathbf{r}_i))\delta(\mathbf{r} - \mathbf{r}_i)$$

$$+ \frac{1}{4}\sum_{ij}(\mathbf{v}_i + \mathbf{v}_j)\mathbf{F}_{ij}\mathbf{r}_{ij} \int_0^1 d\epsilon \delta(\mathbf{r} - \mathbf{r}_j - \epsilon \mathbf{r}_{ij})$$

$$+ \frac{1}{4}\sum_{ij} \underbrace{(\mathbf{v}(\mathbf{r}_i) + \mathbf{v}(\mathbf{r}_j))}_{\approx 2\mathbf{v}(\mathbf{r})}\mathbf{F}_{ij}\mathbf{r}_{ij} \int_0^1 d\epsilon \delta(\mathbf{r} - \mathbf{r}_j - \epsilon \mathbf{r}_{ij})$$

$$= \hat{\mathbf{Q}}_{\mathbf{r}} + \mathbf{v}(\mathbf{r})\cdot\hat{\mathbf{\Sigma}}_{\mathbf{r}} + \mathbf{v}(\mathbf{r})\hat{e}_{\mathbf{r}} + \frac{\mathbf{v}^2(\mathbf{r})}{2}\hat{\mathbf{g}} + \mathbf{v}(\mathbf{r})\mathbf{v}(\mathbf{r})\cdot\hat{\mathbf{g}}_{\mathbf{r}} + \frac{\mathbf{v}^2(\mathbf{r})}{2}\mathbf{v}(\mathbf{r})\hat{\rho}_{\mathbf{r}}$$

Now we consider the reversible part $v_i(t)$ in Eq. (12.2). For the mass density we have

$$\partial_t \rho(\mathbf{r},t)|_{\text{rev}} = \text{Tr}[\overline{\rho}_t i\mathcal{L}\hat{\rho}_{\mathbf{r}}] = -\nabla\mathbf{g}(\mathbf{r},t)$$

where we have used Eq. (18.5) and the fact that the relevant ensemble average of $\hat{\mathbf{g}}_{\mathbf{r}}$ is precisely the momentum density field $\mathbf{g}(\mathbf{r},t)$.

On the other hand, the reversible part of the momentum density is

$$\partial_t \mathbf{g}(\mathbf{r},t)|_{\text{rev}} = \text{Tr}[\overline{\rho}_t i\mathcal{L}\hat{\mathbf{g}}_{\mathbf{r}}] = -\nabla\mathbf{\Sigma}(\mathbf{r},t)$$

where we have introduced

$$\boldsymbol{\Sigma}(\mathbf{r}, t) \equiv \text{Tr}[\overline{\rho}_t \hat{\boldsymbol{\Sigma}}_\mathbf{r}]$$

We compute this term by using the Galilean transformation

$$\boldsymbol{\Sigma}(\mathbf{r}, t) = \text{Tr}[S_t \overline{\rho}_t^{\text{rest}}(z) \hat{\boldsymbol{\Sigma}}_\mathbf{r}] = \text{Tr}[\overline{\rho}_t^{\text{rest}}(z) S_t^{-1} \hat{\boldsymbol{\Sigma}}_\mathbf{r}] = \text{Tr}\left[\overline{\rho}_t^{\text{rest}}(z) \left[\hat{\boldsymbol{\Sigma}}_\mathbf{r} + \mathbf{v}(\mathbf{r}, t)\hat{\mathbf{g}}_\mathbf{r} + \hat{\mathbf{g}}_\mathbf{r}\mathbf{v}(\mathbf{r}, t) + \mathbf{v}(\mathbf{r}, t)\mathbf{v}(\mathbf{r}, t)\hat{\rho}_\mathbf{r}\right]\right]$$
$$= \boldsymbol{\Pi}(\mathbf{r}, t) + \mathbf{v}(\mathbf{r}, t)\mathbf{v}(\mathbf{r}, t)\rho(\mathbf{r}, t)$$

where we have introduced

$$\boldsymbol{\Pi}(\mathbf{r}, t) = \text{Tr}[\overline{\rho}_t^{\text{rest}}(z) \hat{\boldsymbol{\Sigma}}_\mathbf{r}]$$

For the energy density we have

$$\partial_t e(\mathbf{r}, t)|_{\text{rev}} = \text{Tr}[\overline{\rho}_t i \mathcal{L} \hat{e}_\mathbf{r}] = -\nabla \mathbf{Q}(\mathbf{r}, t)$$

where the reversible heat flux is defined as

$$\mathbf{Q}(\mathbf{r}, t) \equiv \text{Tr}[\overline{\rho}_t \hat{\mathbf{Q}}_\mathbf{r}]$$

By using the Galilean transformation, we have

$$\mathbf{Q}(\mathbf{r}, t) = \text{Tr}[\overline{\rho}_t^{\text{rest}} S_t^{-1} \hat{\mathbf{Q}}_\mathbf{r}] = \text{Tr}\left[\overline{\rho}_t^{\text{rest}} \left(\hat{\mathbf{Q}}_\mathbf{r} + \mathbf{v}\cdot\hat{\boldsymbol{\Sigma}}_\mathbf{r} + \mathbf{v}\hat{e} + \frac{\mathbf{v}^2}{2}\hat{\mathbf{g}} + \mathbf{v}\mathbf{v}\cdot\hat{\mathbf{g}}_\mathbf{r} + \frac{\mathbf{v}^2}{2}\mathbf{v}\hat{\rho}_\mathbf{r}\right)\right]$$
$$= \mathbf{v}(\mathbf{r})\cdot\boldsymbol{\Pi}(\mathbf{r}) + \mathbf{v}(\mathbf{r})e(\mathbf{r})$$

[In summary, by collecting results we have the reversible part of the dynamics as]

5.5 The dissipative matrix

And finally we calculate the irreversible part of Eq. (12.2). The effect of the projection operator on the time derivatives of the relevant variables is

$$\mathcal{Q}_t i \mathcal{L} \hat{\rho}_\mathbf{r}(z) = 0$$
$$\mathcal{Q}_t i \mathcal{L} \hat{\mathbf{g}}_\mathbf{r}(z) = -\nabla \mathcal{Q}_t \hat{\boldsymbol{\Sigma}}_\mathbf{r}(z)$$
$$\mathcal{Q}_t i \mathcal{L} \hat{e}_\mathbf{r}(z) = -\nabla \mathcal{Q}_t \hat{\mathbf{Q}}_\mathbf{r}(z)$$

where we have used that the projector $\mathcal{Q}_t$ acting on any relevant variables vanishes.

The irreversible part $\sum_j D_{ij} \lambda_j(t)$ of the general Eq. (12.2) becomes, for the hydroe-

lastic fields

$$
\left.\begin{pmatrix} \partial_t \rho_{\mathbf{r}} \\[6pt] \partial_t \mathbf{g}_{\mathbf{r}} \\[6pt] \partial_t e_{\mathbf{r}} \end{pmatrix}\right|_{\mathrm{irr}} = \int d\mathbf{r}' \begin{pmatrix} M^{\rho\rho}_{\mathbf{rr}'} & M^{\rho\mathbf{g}}_{\mathbf{rr}'} & M^{\rho e}_{\mathbf{rr}'} \\[6pt] M^{\mathbf{g}\rho}_{\mathbf{rr}'} & M^{\mathbf{gg}}_{\mathbf{rr}'} & M^{\mathbf{g}e}_{\mathbf{rr}'} \\[6pt] M^{e\rho}_{\mathbf{rr}'} & M^{e\mathbf{g}}_{\mathbf{rr}'} & M^{ee}_{\mathbf{rr}'} \end{pmatrix} \begin{pmatrix} \beta_{\mathbf{r}'}\nu_{\mathbf{r}'} \\[6pt] -\beta_{\mathbf{r}'}\mathbf{v}_{\mathbf{r}'} \\[6pt] \beta_{\mathbf{r}'} \end{pmatrix}
$$

Because of the first Eq. (18.7), all matrix elements with a ρ superindex vanish. The rest of matrix elements are all of the form $M^{\alpha\beta}_{\mathbf{rr}'} = \boldsymbol{\nabla}_{\mathbf{r}}\boldsymbol{\nabla}_{\mathbf{r}'}\Xi^{ab}_{\mathbf{rr}'}$, where $\Xi^{ab}_{\mathbf{rr}'}$ is a kernel of transport coefficients

$$
\Xi^{ab}_{\mathbf{rr}'} \equiv \int_0^\infty dt' \mathrm{Tr}[\overline{\rho}_t(\mathcal{Q}_t \hat{\mathbf{A}}_{\mathbf{r}})G_{tt'}(\mathcal{Q}_{t'}\hat{\mathbf{B}}_{\mathbf{r}'})]
$$

where $\hat{\mathbf{A}}_{\mathbf{r}}, \hat{\mathbf{B}}_{\mathbf{r}}$ are the corresponding the tensors $\hat{\boldsymbol{\Pi}}_{\mathbf{r}}, \hat{\mathbf{Q}}_{\mathbf{r}}$

The resulting irreversible parts of the hydroelasticity equations are

$$
\partial_t \rho(\mathbf{r},t)|_{\mathrm{irr}} = 0
$$

$$
\partial_t \mathbf{g}(\mathbf{r},t)|_{\mathrm{irr}} = \boldsymbol{\nabla}_{\mathbf{r}}\int d\mathbf{r}'\Xi^{\mathbf{gg}}_{\mathbf{rr}'}\boldsymbol{\nabla}_{\mathbf{r}'}\beta_{\mathbf{r}'}\mathbf{v}_{\mathbf{r}'} - \boldsymbol{\nabla}_{\mathbf{r}'}\int d\mathbf{r}'\Xi^{\mathbf{g}e}_{\mathbf{rr}'}\boldsymbol{\nabla}_{\mathbf{r}'}\beta_{\mathbf{r}'}
$$

$$
\partial_t e(\mathbf{r},t)|_{\mathrm{irr}} = \boldsymbol{\nabla}_{\mathbf{r}}\int d\mathbf{r}'\Xi^{e\mathbf{g}}_{\mathbf{rr}'}\boldsymbol{\nabla}_{\mathbf{r}'}\beta_{\mathbf{r}'}\mathbf{v}_{\mathbf{r}'} - \boldsymbol{\nabla}_{\mathbf{r}'}\int d\mathbf{r}'\Xi^{ee}_{\mathbf{rr}'}\boldsymbol{\nabla}_{\mathbf{r}'}\beta_{\mathbf{r}'}
$$

5.5.1   The reversible part of the dynamics

By using the usual trick [?, ?, ?]

$$
\delta(\mathbf{r} - \mathbf{q}_i) - \delta(\mathbf{r} - \mathbf{q}_j) = -\boldsymbol{\nabla}\int_0^1 d\epsilon \mathbf{q}_{ij}\delta(\mathbf{r} - \mathbf{q}_j - \epsilon\mathbf{q}_{ij})
$$

The time derivatives have the divergence form

$$
i\mathcal{L}\rho(\mathbf{r},t) = -\boldsymbol{\nabla}\cdot\hat{\mathbf{g}}_{\mathbf{r}}(z)
$$

$$
i\mathcal{L}\mathbf{g}(\mathbf{r},t) = -\boldsymbol{\nabla}\cdot\hat{\boldsymbol{\sigma}}_{\mathbf{r}}(z)
$$

$$
i\mathcal{L}e(\mathbf{r},t) = -\boldsymbol{\nabla}\cdot\hat{\mathbf{J}}^e_{\mathbf{r}}(z)
$$

where the microscopic stress tensor and energy flux are given by

$$
\hat{\boldsymbol{\sigma}}_{\mathbf{r}}(z) = \sum_{i=1}^N \frac{\mathbf{p}_i}{m_i}\mathbf{p}_i\delta(\mathbf{r} - \mathbf{q}_i) + \frac{1}{2}\sum_{ij}^N \mathbf{e}_{ij}\hat{\mathbf{F}}_{ij}\int_0^{r_{ij}} dx\delta(\mathbf{r} - \mathbf{q}_i + x\mathbf{e}_{ij})
$$

$$
\hat{\mathbf{J}}^e_{\mathbf{r}}(z) = \sum_i \mathbf{v}_i e_i\delta(\mathbf{r} - \mathbf{r}_i) + \frac{1}{4}\sum_{ij}\mathbf{F}_{ij}\mathbf{e}_{ij}\cdot(\mathbf{v}_i + \mathbf{v}_j)\int_0^1 d\epsilon \mathbf{q}_{ij}\delta(\mathbf{r} - \mathbf{q}_j - \epsilon\mathbf{q}_{ij})
$$

It will be convenient to consider the action of the Galilean operator on the microscopic stress tensor and energy flux.

$$\mathcal{G}_t\hat{\boldsymbol{\sigma}}_{\mathbf{r}}(z) = \sum_{i=1}^{N} m_i(\mathbf{v}_i - \mathbf{v}(\mathbf{q}_i)){\cdot}(\mathbf{v}_i - \mathbf{v}(\mathbf{q}_i))\delta(\mathbf{r} - \mathbf{q}_i) + \frac{1}{2}\sum_{ij}^{N} \mathbf{e}_{ij}\hat{\mathbf{F}}_{ij} \int_0^{r_{ij}} dx\delta(\mathbf{r} - \mathbf{q}_i + x\mathbf{e}_{ij})$$

$$= \hat{\boldsymbol{\sigma}}_{\mathbf{r}}$$

$$\sum_{i=1}^{N} m_i(\mathbf{v}_i - \mathbf{v}(\mathbf{q}_i)){\cdot}(\mathbf{v}_i - \mathbf{v}(\mathbf{q}_i))\delta(\mathbf{r} - \mathbf{q}_i) + \frac{1}{2}\sum_{ij}^{N} \mathbf{e}_{ij}\hat{\mathbf{F}}_{ij} \int_0^{r_{ij}} dx\delta(\mathbf{r} - \mathbf{q}_i + x\mathbf{e}_{ij})$$

The time derivative of the CG variables are

$$i\mathcal{L}\hat{\rho}_{\mathbf{r}}(z) = -\nabla\hat{\mathbf{g}}_{\mathbf{r}}(z)$$

$$i\mathcal{L}\hat{\mathbf{g}}_{\mathbf{r}}(z) = -\nabla\hat{\boldsymbol{\Pi}}_{\mathbf{r}}(z) + \hat{\mathbf{F}}_{\mathbf{r}}(z) + \frac{1}{m}\hat{\rho}_{\mathbf{r}}(z)\mathbf{F}_{\text{ext}}(\mathbf{r})$$

where we have defined the kinetic stress tensor, the force density, and the force due to the external potential as

$$\hat{\boldsymbol{\Pi}}_{\mathbf{r}}(z) \equiv \sum_i \mathbf{v}_i\mathbf{p}_i\delta(\mathbf{r} - \mathbf{q}_i)$$

$$\hat{\mathbf{F}}_{\mathbf{r}}(z) \equiv \sum_i \mathbf{F}_i\delta(\mathbf{r} - \mathbf{q}_i)$$

$$\mathbf{F}_{\text{ext}}(\mathbf{r}) \equiv -\nabla V^{\text{ext}}(\mathbf{r})$$

$\mathbf{F}_i$ is the total force acting on the particle i. For a simple liquid system with pair-wise interactions, the force density $\hat{\mathbf{F}}_{\mathbf{r}}(z)$ can be written as the divergence of a tensor [?],[?]

$$\hat{\mathbf{F}}_{\mathbf{r}}(z) = -\nabla\hat{\boldsymbol{\Sigma}}(z)$$

$$\hat{\boldsymbol{\Sigma}}(z) \equiv \frac{1}{2}\sum_{ij} \mathbf{q}_{ij}\mathbf{F}_{ij} \int_0^1 d\epsilon\delta(\mathbf{r} - \mathbf{q}_i + \epsilon\mathbf{q}_{ij})$$

where use is made of Newton's Third Law $\mathbf{F}_{ij} = -\mathbf{F}_{ji}$. In the simple liquid system, momentum is conserved and this is reflected in the conservation law in divergence form.

For the mass density we have

$$\partial_t\rho(\mathbf{r}, t)|_{\text{rev}} = \text{Tr}[\bar{\rho}_t i\mathcal{L}\hat{\rho}_{\mathbf{r}}] = -\nabla\mathbf{g}(\mathbf{r}, t)$$

where we have used Eq. (18.5) and the fact that the relevant ensemble average of $\hat{\mathbf{g}}_{\mathbf{r}}$ is precisely the momentum density field $\mathbf{g}(\mathbf{r}, t)$. On the other hand, the reversible part of

the momentum density is

$$\partial_t \mathbf{g}(\mathbf{r}, t)|_{\mathrm{rev}} = \mathrm{Tr}[\overline{\rho}_t i\mathcal{L}\hat{\mathbf{g}}_{\mathbf{r}}]$$
$$= -\nabla\mathrm{Tr}[\overline{\rho}_t\hat{\mathbf{\Pi}}_{\mathbf{r}}] + \mathrm{Tr}[\overline{\rho}_t\hat{\mathbf{F}}_{\mathbf{r}}]$$

In the Appendix **??** we show that the relevant ensemble averages appearing in Eq. (11.3) can be computed and lead to the following two equivalent and alternative forms

$$\partial_t \mathbf{g}(\mathbf{r}, t)|_{\mathrm{rev}} = -\nabla\cdot\mathbf{v}(\mathbf{r})\mathbf{g}(\mathbf{r}) - \rho(\mathbf{r})\nabla\mu(\mathbf{r}, t)$$
$$= -\nabla\cdot\mathbf{v}(\mathbf{r})\mathbf{g}(\mathbf{r}) - \nabla P(\mathbf{r}, t)$$

where the chemical potential per unit mass is introduced in Eq. (22.5) and the pressure field is defined as

$$P(\mathbf{r}, t) = k_B T n(\mathbf{r}) - n(\mathbf{r}, t)c(\mathbf{r}, t)$$

where $n(\mathbf{r}, t) = \rho(\mathbf{r}, t)/m$ is the number density field and $c(\mathbf{r})$ is the direct correlation function, which is a functional of the time-dependent density field. We now particularize the general dynamic equation (12.2) to the case that the CG variables are the number and energy density fields, which are assumed to be only slow variables in the system. Microscopically these variables are defined as

$$\hat{n}_{\mathbf{r}}(z) = \sum_i \delta(\mathbf{r} - \mathbf{q}_i)$$

$$\hat{e}_{\mathbf{r}}(z) = \sum_i e_i \delta(\mathbf{r} - \mathbf{r}_i)$$

where $e_i = \frac{\mathbf{p}_i^2}{2m} + \frac{1}{2}\sum_j \phi_{ij} + V_{ext}(\mathbf{r})$ is the energy of particle i. The averages of these phase functions with respect to the solution $\rho_t(z)$ of the Liouville equation are denoted by

$$n(\mathbf{r}, t) = \int dz \rho_t(z)\hat{n}_{\mathbf{r}}(z)$$

$$e(\mathbf{r}, t) = \int dz \rho_t(z)\hat{e}_{\mathbf{r}}(z)$$

The time derivatives of the CG variables, i.e. the terms $i\mathcal{L}A_i$, now become

$$i\mathcal{L}\hat{n}_{\mathbf{r}}(z) = -\sum_i \mathbf{v}_i\nabla\delta(\mathbf{r} - \mathbf{r}_i)$$

$$i\mathcal{L}\hat{e}_{\mathbf{r}}(z) = -\sum_i \mathbf{v}_i e_i\nabla\delta(\mathbf{r} - \mathbf{q}_i) + \frac{1}{4}\sum_{ij} \mathbf{F}_{ij}\mathbf{q}_{ij}\cdot(\mathbf{v}_i + \mathbf{v}_j)\left[\delta(\mathbf{r} - \mathbf{q}_i) - \delta(\mathbf{r} - \mathbf{q}_j)\right]$$

By using the usual trick [?, ?, ?]

$$\delta(\mathbf{r} - \mathbf{q}_i) - \delta(\mathbf{r} - \mathbf{q}_j) = -\nabla \int_0^1 d\epsilon \mathbf{q}_{ij}\delta(\mathbf{r} - \mathbf{q}_j - \epsilon\mathbf{q}_{ij})$$

we may express the time derivatives as divergences of fluxes, this is

$$i\mathcal{L}\hat{n}_{\mathbf{r}}(z) = -\nabla\hat{\mathbf{J}}_{\mathbf{r}}(z)$$
$$i\mathcal{L}\hat{e}_{\mathbf{r}}(z) = -\nabla\hat{\mathbf{Q}}_{\mathbf{r}}(z)$$

where

$$\hat{\mathbf{J}}_{\mathbf{r}}(z) = \sum_i \mathbf{v}_i\delta(\mathbf{r} - \mathbf{q}_i)$$

$$\hat{\mathbf{Q}}_{\mathbf{r}}(z) = \sum_i \mathbf{v}_i e_i\delta(\mathbf{r} - \mathbf{r}_i) + \frac{1}{4}\sum_{ij} \mathbf{F}_{ij}(\mathbf{v}_i + \mathbf{v}_j) \int_0^1 d\epsilon\mathbf{q}_{ij}\delta(\mathbf{r} - \mathbf{q}_j - \epsilon\mathbf{q}_{ij})$$

Now we consider the reversible part $v_i(t)$ in Eq. (12.2) which take the form

$$\text{Tr}[\overline{\rho}_t i\mathcal{L}\hat{n}_{\mathbf{r}}] = 0$$
$$\text{Tr}[\overline{\rho}_t i\mathcal{L}\hat{e}_{\mathbf{r}}] = 0$$

because both terms includes a Gaussian momentum integral of a velocity.

5.6   The dissipative matrix

Note that the time derivative of the density field in Eq. (18.5) is given in terms of the CG variable $\hat{\mathbf{g}}_{\mathbf{r}}$. Therefore, the effect of the projection operator on $i\mathcal{L}\hat{\rho}_{\mathbf{r}}$ is simply

$$i\mathcal{L}\hat{\rho}_{\mathbf{r}} = 0$$

This implies that many terms of the Green-Kubo matrix D_{ij} will vanish. In fact, there will be no irreversible terms in the evolution of the density field, which obeys the well-known continuity equation. This is in contrast to some recent proposals [?, ?], which have to be rejected on the basis of this rigorous approach, as well as from other macroscopic arguments [?].

The irreversible part $\sum_j D_{ij}\lambda_j(t)$ of the general Eq. (12.2) becomes, for the evolution of the momentum density field

$$\partial_t\mathbf{g}(\mathbf{r}, t)|_{\text{irr}} = -\int d\mathbf{r}'\mathbf{M}(\mathbf{r}, \mathbf{r}')\cdot\mathbf{v}(\mathbf{r}', t)$$

where the generalized friction matrix is given by

$$\mathbf{M}(\mathbf{r}, \mathbf{r}') = \frac{1}{k_BT} \int_0^\tau dt'\text{Tr}[\overline{\rho}_t(^ei\mathcal{L}\mathbf{g}_{\mathbf{r}})(\mathcal{Q}i\mathcal{L}\mathbf{g}_{\mathbf{r}'}(t'))]$$

Note that, in general, this friction matrix depends on the time-dependent macroscopic state $\rho(\mathbf{r}, t), \mathbf{g}(\mathbf{r}, t)$ through the relevant ensemble $\overline{\rho}_t$. Near equilibrium, where the conjugate fields vanish, it is possible to approximate the relevant ensemble with the equilibrium ensemble.

For a simple fluid, the friction matrix has the following structure

$$\mathbf{M}^{\mu\nu}(\mathbf{r}, \mathbf{r}') = \frac{1}{k_B T} \nabla_{\mathbf{r}}^{\mu'} \nabla_{\mathbf{r}'}^{\nu'} \int_0^\tau dt' \mathrm{Tr}[\overline{\rho}_t (\mathscr{Q}\boldsymbol{\sigma}_{\mathbf{r}}^{\mu\mu'})(\mathscr{Q}\boldsymbol{\sigma}_{\mathbf{r}'}^{\nu\nu'}(t'))]$$

where $\boldsymbol{\sigma}_{\mathbf{r}} = \boldsymbol{\Pi}_{\mathbf{r}} + \boldsymbol{\Sigma}_{\mathbf{r}}$ is the full microscopic stress tensor, and sum over repeated indices is implied. In Ref. [?] a detailed calculation of the friction matrix is presented. In the irreversible part, for the same reason, the projected current are

$$\mathscr{Q}_t i \mathcal{L} \hat{n}_{\mathbf{r}} = -\nabla \cdot \hat{\mathbf{J}}_{\mathbf{r}}(z)$$

$$\mathscr{Q}_t i \mathcal{L} \hat{e}_{\mathbf{r}} = -\nabla \cdot \hat{\mathbf{Q}}_{\mathbf{r}}(z)$$

the dissipative matrix D_{ij} in Eq. (12.2) becomes now of the form

$$\nabla_{\mathbf{r}} \nabla_{\mathbf{r}'} \int_0^\infty dt' \begin{pmatrix} \mathrm{Tr}[\overline{\rho}_t \hat{\mathbf{J}}_{\mathbf{r}'} \hat{\mathbf{J}}_{\mathbf{r}}(t')] & \mathrm{Tr}[\overline{\rho}_t \hat{\mathbf{Q}}_{\mathbf{r}'} \hat{\mathbf{J}}_{\mathbf{r}}(t')] \\ \mathrm{Tr}[\overline{\rho}_t \hat{\mathbf{J}}_{\mathbf{r}'} \hat{\mathbf{Q}}_{\mathbf{r}}(t')] & \mathrm{Tr}[\overline{\rho}_t \hat{\mathbf{Q}}_{\mathbf{r}'} \hat{\mathbf{Q}}_{\mathbf{r}}(t')] \end{pmatrix}$$

5.7   The transport equation

The final hydrodynamic equations are obtained by collecting Eqs. (11.3), (10.5.1), and (5.6), this is

$$\partial_t \rho(\mathbf{r}, t) = -\nabla \cdot \mathbf{g}(\mathbf{r})$$

$$\partial_t \mathbf{g}(\mathbf{r}, t) = -\nabla \cdot \mathbf{v}(\mathbf{r}) \mathbf{g}(\mathbf{r}) - \rho(\mathbf{r}) \nabla \mu(\mathbf{r}) - \int d\mathbf{r}' \mathbf{M}(\mathbf{r}, \mathbf{r}') \cdot \mathbf{v}(\mathbf{r}', t)$$

In general, the friction matrix will be a non-local function of space, describing correlations of the stress that exist in molecular length scales [?]. If the velocity field does not change appreciably on these length scales, one may use a local approximation of the form

$$\mathbf{M}^{\mu\nu}(\mathbf{r}, \mathbf{r}') = \nabla^{\mu'} \nabla'^{\nu'} \delta(\mathbf{r} - \mathbf{r}') \boldsymbol{\Xi}^{\mu\mu'\nu\nu'}(\mathbf{r})$$

where we have introduced the fourth order viscosity tensor $\boldsymbol{\Xi}(\mathbf{r})$. This tensor, near equilibrium and away from walls, has an isotropic form, with the appropriate symmetries

$$\boldsymbol{\Xi}^{\mu\mu'\nu\nu'} = \eta \left[\delta^{\mu\nu} \delta^{\mu'\nu'} + \delta^{\mu\nu'} \delta^{\mu'\nu} \right] + \left(\zeta - \frac{2\eta}{3} \right) \delta^{\mu\mu'} \delta^{\nu\nu'}$$

The shear η and bulk ζ viscosities may depend, in general, on the position. Substitution of Eq. (5.7) into (5.6) then leads to the usual viscosity terms of the Navier-Stokes

equations.

The present hydrodynamic theory expressed in Eq. (18.8) differs, however, from the "usual" Navier-Stokes equations in that now the full structure of the fluid is retained. These equations (18.8) have been previously obtained in Ref. [?] as a local equilibrium approximation of a more general kinetic Boltzmann density functional approach. It is reassuring that the same hydrodynamic equations are obtained. The present theory reduces to the (isothermal) Navier-Stokes theory, when we approximate the density functional $\Phi[n]$ with a local functional of the form

$$\Phi[n] = \int d\mathbf{r} f(n(\mathbf{r}, t))$$

where $f(n)$ is the equilibrium free energy density, and uses the isotropic local version (5.7) for the friction matrix. As discussed in Ref. [?], the use of a local functional like (10.11) is justified when the scale of variation of the density field is large compared to molecular scales. The hydrodynamic equations (18.8) generalize Navier-Stokes equations to situations when the hydrodynamic fields vary on molecular scales, due to the presence of, for example, confinement or liquid-vapor phase transitions.

The final dynamic equations are

$$\partial_t n(\mathbf{r}, t) = -\nabla_\mathbf{r} \int d\mathbf{r}' \mathbf{M}_{\mathbf{rr}'}^{JJ} \nabla_{\mathbf{r}'} \lambda(\mathbf{r}', t) - \nabla_\mathbf{r} \int d\mathbf{r}' \mathbf{M}_{\mathbf{rr}'}^{JQ} \nabla_{\mathbf{r}'} \beta(\mathbf{r}', t)$$

$$\partial_t e(\mathbf{r}, t) = -\nabla_\mathbf{r} \int d\mathbf{r}' \mathbf{M}_{\mathbf{rr}'}^{QJ} \nabla_{\mathbf{r}'} \lambda(\mathbf{r}', t) - \nabla_\mathbf{r} \int d\mathbf{r}' \mathbf{M}_{\mathbf{rr}'}^{QQ} \nabla_{\mathbf{r}'} \beta(\mathbf{r}', t)$$

where partial integrations have been performed. In these equations, the dissipative matrix of non-local transport coefficients is

$$\mathbf{M}_{\mathbf{rr}'}^{ab} = \int_0^\infty dt' \text{Tr}[\overline{\rho}_t \hat{\mathbf{b}}_{\mathbf{r}'} \hat{\mathbf{a}}_\mathbf{r}(t')]$$

where $\hat{\mathbf{a}}_\mathbf{r}, \hat{\mathbf{b}}_\mathbf{r}$ are $\hat{\mathbf{J}}_\mathbf{r}$ or $\hat{\mathbf{Q}}_\mathbf{r}$ and a, b are J or Q.

5.8 Models and Approximations

5.8.1 Local approximation

In situations where the gradients of the conjugate fields vary in length scales much larger than the molecular correlation lengths, we may expect a local approximation for the evolution equations. For example, near equilibrium the conjugate fields are close to constant and, therefore, a local approximation holds. This local approximation is of the form

$$\partial_t n(\mathbf{r}, t) = -\nabla_\mathbf{r} D(\mathbf{r}) \nabla_\mathbf{r} \lambda(\mathbf{r}, t) - \nabla_\mathbf{r} S(\mathbf{r}) \nabla_\mathbf{r} \beta(\mathbf{r}, t)$$
$$\partial_t e(\mathbf{r}, t) = -\nabla_\mathbf{r} S(\mathbf{r}) \nabla_\mathbf{r} \lambda(\mathbf{r}, t) - \nabla_\mathbf{r} K(\mathbf{r}) \nabla_\mathbf{r} \beta(\mathbf{r}, t)$$

where the usual (local) transport coefficients are defined as

$$D(\mathbf{r}) = \int d\mathbf{r}' \mathbf{M}_{\mathbf{rr}'}^{JJ}$$

$$S(\mathbf{r}) = \int d\mathbf{r}' \mathbf{M}_{\mathbf{rr}'}^{JQ}$$

$$K(\mathbf{r}) = \int d\mathbf{r}' \mathbf{M}_{\mathbf{rr}'}^{QQ}$$

These coefficients depend in a *functional* form on the fields $n(\mathbf{r}), e(\mathbf{r})$ because of the functional dependence of the relevant ensemble with which we compute the correlations in the Green-Kubo expressions (5.7). The relevant ensemble, in situation where the space variation of the gradients is negligible, can be approximated with an ordinary equilibrium ensemble with global parameters λ, β *matched* at the local values. In this way, the above coefficients become *functions* of the local values of the fields $n(\mathbf{r}), e(\mathbf{r})$. At the same time, the kernels, being computed with the equilibrium ensemble, become translationally invariant, this is $\mathbf{M}_{\mathbf{rr}'}^{ab} = \mathbf{M}^{ab}(\mathbf{r} - \mathbf{r}')$. We may, therefore, average over the volume of the system and Green-Kubo expressions for the transport coefficients result

$$D = \frac{1}{V} \int d\mathbf{r} \int d\mathbf{r}' \mathbf{M}_{\mathbf{rr}'}^{JJ} = \frac{1}{V} \int_0^\infty dt \operatorname{Tr} \left[\rho^{\mathrm{eq}} \hat{\mathbf{J}} \hat{\mathbf{J}}(t) \right]$$

$$S = \frac{1}{V} \int d\mathbf{r} \int d\mathbf{r}' \mathbf{M}_{\mathbf{rr}'}^{JQ} = \frac{1}{V} \int_0^\infty dt \operatorname{Tr} \left[\rho^{\mathrm{eq}} \hat{\mathbf{J}} \hat{\mathbf{Q}}(t) \right]$$

$$K = \frac{1}{V} \int d\mathbf{r} \int d\mathbf{r}' \mathbf{M}_{\mathbf{rr}'}^{QQ} = \frac{1}{V} \int_0^\infty dt \operatorname{Tr} \left[\rho^{\mathrm{eq}} \hat{\mathbf{Q}} \hat{\mathbf{Q}}(t) \right]$$

where the total mass and heat fluxes are

$$\hat{\mathbf{J}} = \int d\mathbf{r} \hat{\mathbf{J}}_{\mathbf{r}} = \sum_i \mathbf{v}_i$$

$$\hat{\mathbf{Q}} = \int d\mathbf{r} \hat{\mathbf{Q}}_{\mathbf{r}} = \sum_i \mathbf{v}_i e_i + \frac{1}{4} \sum_{ij} \mathbf{F}_{ij} (\mathbf{v}_i + \mathbf{v}_j) \mathbf{q}_{ij}$$

The transport coefficients D, S, K are functions of the local thermodynamic state $\lambda(\mathbf{r}), \beta(\mathbf{r})$ of the system, through the equilibrium ensemble ρ^{eq} that has its intensive parameters matched to the local values.

The dissipative matrix is positive definite, because for any vector (a, b) we have

$$(a, b) \begin{pmatrix} D & S \\ S & K \end{pmatrix} \begin{pmatrix} a \\ b \end{pmatrix} = \frac{1}{V} \int_0^\infty dt \operatorname{Tr} \left[\rho^{\mathrm{eq}} \hat{\mathbf{R}} \hat{\mathbf{R}}(t) \right] > 0$$

where $\hat{\mathbf{R}} = a\hat{\mathbf{J}} + b\hat{\mathbf{Q}}$. The last inequality follows from Wiener-Kinchine theorem that ensures that the time integral of an *auto*-correlation is always positive. The eigenvalues being positive, translate into the conditions $D > 0, K > 0, DK > S^2$ for the transport coefficients.

Eqs. (5.8.1) are one of the main results of the present paper. They constitute the gen-

eralization of time-dependent DFT to non-isothermal situations. It may look that these equations have the deceptively simple appearance of the equations of thermo-diffusion obtained in standard irreversible thermodynamics [?]. The coefficient $D(\mathbf{r})$ looks like a diffusion coefficient, the coefficient $S(\mathbf{r})$ that couples thermal gradients with density variations in time resembles a Soret coefficient, while $K(\mathbf{r})$ should be related to the thermal conduction coefficient.

However, it should be stressed that the above equations are for a single component fluid, not a mixture, and that the diffusion of the density due to the $D(\mathbf{r})$ is the "diffusion" of the particles within the same fluid.

The dynamic equations (5.8.1) conserve the total number of particles and total energy defined as

$$N = \int d\mathbf{r}\, n(\mathbf{r})$$

$$E = \int d\mathbf{r}\, e(\mathbf{r})$$

At the same time, they have as a Lyapunov functional the entropy functional. This is, we may compute the time derivative of the entropy functional and obtain

$$\frac{d}{dt} S_{FTD}[n(t), e(t)] = \int d\mathbf{r} \frac{\delta S}{\delta n(\mathbf{r})} \partial_t n(\mathbf{r}, t)$$

$$+ \int d\mathbf{r} \frac{\delta S}{\delta e(\mathbf{r})} \partial_t e(\mathbf{r}, t)$$

$$= \int d\mathbf{r} (\nabla \lambda_{\mathbf{r}}, \nabla \beta_{\mathbf{r}}) \begin{pmatrix} D(\mathbf{r}) & S(\mathbf{r}) \\ S(\mathbf{r}) & K(\mathbf{r}) \end{pmatrix} \begin{pmatrix} \nabla \lambda_{\mathbf{r}} \\ \nabla \beta_{\mathbf{r}} \end{pmatrix} \geq 0$$

because the dissipative matrix is definite positive. This implies that the evolution equations describe the tendency of the fields $n(\mathbf{r}), e(\mathbf{r})$ towards the equilibrium state that maximizes the entropy functional subject to the conservation restrictions (5.8.1). The entropy functional contains all the information about profiles and correlations and, therefore, the succession of states towards equilibrium display the non-equilibrium local structure of the system.

Equilibrium ensemble

Translational invariance

Under a translation of the origin of coordinates, the fields change according to

$$\rho(\mathbf{r}) \to \rho(\mathbf{r} + \mathbf{a})$$
$$\mathbf{g}(\mathbf{r}) \to \mathbf{g}(\mathbf{r} + \mathbf{a})$$
$$e(\mathbf{r}) \to e(\mathbf{r} + \mathbf{a})$$

However, if there are no external fields present, the entropy functional should be the same evaluated at any translated field. This implies that

$$\frac{\partial}{\partial \mathbf{a}} S\left[\rho(\mathbf{r} + \mathbf{a}), \mathbf{g}(\mathbf{r} + \mathbf{a}), e(\mathbf{r} + \mathbf{a})\right] = 0$$

$$\int d\mathbf{r} \frac{\delta S}{\delta \rho(\mathbf{r})} \nabla \rho(\mathbf{r} + \mathbf{a}) + \cdots = 0$$

Evaluated at $\mathbf{a} = 0$ this equation gives

$$\int d\mathbf{r}\left[\beta \nu \nabla \rho - \beta \mathbf{v} \nabla \mathbf{g} + \beta \nabla e\right] = \int d\mathbf{r}\left[-\beta \mu \nabla \rho + \beta \nabla u\right] = 0$$

The non-local transport kernels $\mathbf{\Xi}^{ab}_{\mathbf{rr'}}$ depend on the time-dependent macroscopic state $\rho(\mathbf{r},t), \mathbf{d}(\mathbf{r},t), \mathbf{g}(\mathbf{r},t), e(\mathbf{r},t)$ through the relevant ensemble $\overline{\rho}_t$. As such it is a formal object and until approximations to make this object explicit are made, the theory has null predictive power. The first approximation restricts to slowly varying in space fields. In this case, we he near equilibrium assumption. At equilibrium the conjugate fields vanish and it is possible to approximate the relevant ensemble with the equilibrium ensemble. For near equilibrium situations, we have

$$\mathbf{\Xi}^{ab}_{\mathbf{rr'}} \approx \int_0^\infty dt' \mathrm{Tr}[\rho^{\mathrm{eq}}(\delta\hat{\mathbf{A}}_{\mathbf{r}}) G_{tt'}(\delta\hat{\mathbf{B}}_{\mathbf{r'}})]$$

where the effect of the projector $\mathcal{Q}$ turns out to be to simply subtract the equilibrium average, this is $\delta\hat{\mathbf{A}}_{\mathbf{r}} = \hat{\mathbf{A}}_{\mathbf{r}} - \langle\hat{\mathbf{A}}_{\mathbf{r}}\rangle^{\mathrm{eq}}$. The result of this approximation is that the transport kernels do not depend on the relevant variables anymore and they become state independent.

Note that the explicit form of the correlation function cannot be known because it involves the formal time propagator $G_{tt'}$ referred as the projected dynamics. A usual approximation is to take the real dynamics instead of the projected dynamics, leading to the usual Green-Kubo expressions for transport coefficients. An evaluation through molecular simulations of the non-local transport kernel is then possible. However, note that such an evaluation requires to perform one MD simulation for every $\mathbf{r}, \mathbf{r'}$ combination. Even by assuming isotropy and homogeneity, this is, that the kernels depend on the distance between these two points, it is necessary to perform an MD simulation for every relative distance. An alternative to this procedure is to assume that the correlations may be approximated with an exponential decay,

$$\mathrm{Tr}[\rho^{\mathrm{eq}}(\delta\hat{\mathbf{A}}_{\mathbf{r}}) G_{tt'}(\delta\hat{\mathbf{B}}_{\mathbf{r'}}(t'))] \approx \exp\{-t/\tau_{ab}\} \mathrm{Tr}[\rho^{\mathrm{eq}}\delta\hat{\mathbf{A}}_{\mathbf{r}}\delta\hat{\mathbf{B}}_{\mathbf{r'}}]$$

where τ_{ab} are characteristic times that play the role of adjustable parameters in the theory. Note that at $t = 0$ the approximation (18.7) is exact. The static averages $\mathrm{Tr}[\rho^{\mathrm{eq}}\delta\hat{\mathbf{A}}_{\mathbf{r}}\delta\hat{\mathbf{B}}_{\mathbf{r'}}]$ are more accessible than the correlations, and one can express in general these static averages in terms of correlation functions for which density functional approaches may provide explicit expressions.

However, in the present work we restrict to situations in which the relevant fields vary slowly in space. By this we mean that they vary in length scales much larger than the correlation length of the transport kernel correlations. In those situations, the space dependence of transport kernels may be approximated with a Dirac delta function, this is

$$\mathbf{\Xi}^{ab}_{\mathbf{rr'}} \approx \mathbf{\Xi}^{ab}\delta(\mathbf{r} - \mathbf{r'})$$

$$\mathbf{\Xi}^{ab} \equiv \frac{1}{V_T} \int d\mathbf{r} \int d\mathbf{r'} \int_0^\infty dt' \mathrm{Tr}[\rho^{\mathrm{eq}}(\delta\hat{\mathbf{A}}_{\mathbf{r}}) \exp\{i\mathcal{L}t\}(\delta\hat{\mathbf{B}}_{\mathbf{r'}})]$$

$$= \frac{1}{V_T} \int_0^\infty dt' \mathrm{Tr}[\rho^{\mathrm{eq}}(\delta\hat{\mathbf{A}}) \exp\{i\mathcal{L}t\}(\delta\hat{\mathbf{B}})]$$

where $\hat{\mathbf{A}} = \int d\mathbf{r}\hat{\mathbf{A}}_{\mathbf{r}}$, $\hat{\mathbf{B}} = \int d\mathbf{r}\hat{\mathbf{B}}_{\mathbf{r}}$ are the corresponding space integrals of the local fluxes

(18.5, this is

$$\hat{\mathbf{D}}(z) \equiv \sum_i \mathbf{p}_i \mathbf{u}_i$$

$$\hat{\mathbf{\Sigma}}(z) \equiv \frac{1}{2} \sum_{ij} \mathbf{F}_{ij} \mathbf{r}_{ij} + \sum_i \mathbf{v}_i \mathbf{p}_i$$

$$\hat{\mathbf{Q}}(z) \equiv \sum_i \epsilon_i \mathbf{v}_i + \frac{1}{4} \sum_{ij} (\mathbf{v}_i + \mathbf{v}_j) \mathbf{F}_{ij} \mathbf{r}_{ij}$$

5.9   The transport equation

The final hydrodynamic equations are obtained by collecting Eqs. (18.5), (18.5), (5.4) and (**??**),(**??**) and (**??**) this is

$$\partial_t \rho(\mathbf{r}, t) = -\nabla \cdot \mathbf{g}(\mathbf{r}, t)$$
$$\partial_t \mathbf{g}(\mathbf{r}, t) = -\nabla \mathbf{v}(\mathbf{r}, t) \mathbf{v}(\mathbf{r}, t) \rho(\mathbf{r}, t) - \nabla \mathbf{\Pi}(\mathbf{r}, t) + \nabla \mathbf{\Xi}^{\mathbf{gg}} \nabla \beta \mathbf{v}(\mathbf{r}, t) - \nabla \mathbf{\Xi}^{\mathbf{ge}} \nabla \beta(\mathbf{r}, t)$$
$$\partial_t \epsilon(\mathbf{r}, t) = -\nabla \mathbf{Q}(\mathbf{r}, t) + \nabla \mathbf{\Xi}^{eg} \nabla \beta \mathbf{v}(\mathbf{r}, t) - \nabla \mathbf{\Xi}^{ee} \nabla \beta(\mathbf{r}, t)$$

There will be no irreversible terms in the evolution of the density field, which obeys the well-known continuity equation. This is in contrast to some recent proposals [**?**, **?**], which have to be rejected on the basis of this rigorous approach, as well as from other macroscopic arguments [**?**].

The above equations show that mass, momentum and energy are exactly conserved in the absence of external forces, because then, the equations are in divergence form.

The above equations also show that the entropy is a non-decaying function of time. This implies that the equilibrium state will be one in which the entropy (**??**) takes its maximum value, subject to the conditions that the total mass, displacement, momentum, and energy are conserved. Therefore, the equilibrium state is obtained from the maximization of

$$S[\rho, \mathbf{g}, e] + \mu_0 \int d\mathbf{r} \rho(\mathbf{r}) + \mathbf{v}_0 \int d\mathbf{r} \mathbf{g}(\mathbf{r}) + \beta_0 \int d\mathbf{r} e(\mathbf{r})$$

where $\mu_0, \mathbf{v}_0, \beta_0$ are the Lagrange multipliers enforcing the conservation constraints. The solution gives

5.10   Models and Approximations

DDFT

We may now consider the conditions under which the hydrodynamic theory presented above leads to the DDFT of the previous section. A first requirement is that the mass density should decay in a time scale much slower than the momentum density. We may, therefore, assume that in very short times the velocity decays towards its equilibrium

value, which is zero. Eqs. (18.8) can be written as

$$\partial_t \rho(\mathbf{r}, t) = -\nabla \cdot \mathbf{g}(\mathbf{r})$$

$$\partial_t \mathbf{g}(\mathbf{r}, t) = -\rho(\mathbf{r}, t) \nabla \mu(\mathbf{r}, t) - \int d\mathbf{r}' \frac{\mathbf{M}(\mathbf{r}, \mathbf{r}')}{\rho(\mathbf{r}', t)} \cdot \mathbf{g}(\mathbf{r}', t)$$

We may regard these equations as a stiff set of equations in which the friction matrix $\mathbf{M}$ can be understood as being "very large", forcing the momentum density to decay "very fast". In fact, we can solve formally the linear equation for $\mathbf{g}$ in which the density dependent term $-\rho(\mathbf{r}) \nabla \mu(\mathbf{r})$ is regarded as an external forcing (which is time-independent on the supposedly short time scale of momentum decay), and insert this solution into the continuity equation. In this way a closed equation for the density emerges. To show this explicitly, it is convenient to introduce the following exponential operator through the Taylor series

$$\exp\{-\overline{\mathbf{M}}t\}(\mathbf{r}, \mathbf{r}') = \delta(\mathbf{r} - \mathbf{r}')\mathbf{1} - t\frac{\mathbf{M}(\mathbf{r}, \mathbf{r}')}{\rho(\mathbf{r}')} + \frac{t^2}{2!} \int d\mathbf{r}'' \frac{\mathbf{M}(\mathbf{r}, \mathbf{r}'')}{\rho(\mathbf{r}'')} \frac{\mathbf{M}(\mathbf{r}'', \mathbf{r}')}{\rho(\mathbf{r}')} - \cdots$$

This operator satisfies

$$\lim_{t \to 0} \exp\{-\overline{\mathbf{M}}t\}(\mathbf{r}, \mathbf{r}') = \delta(\mathbf{r} - \mathbf{r}')\mathbf{1}$$

We will assume that for a positive definite kernel $\mathbf{M}$, the following limit exists

$$\lim_{t \to \infty} \exp\{-\overline{\mathbf{M}}t\}(\mathbf{r}, \mathbf{r}') = 0$$

By assuming that the density field does not depend on time, the exponential operator satisfies

$$\frac{d}{dt} \exp\{\overline{\mathbf{M}}t\}(\mathbf{r}, \mathbf{r}') = \int d\mathbf{r}'' \exp\{\overline{\mathbf{M}}t\}(\mathbf{r}, \mathbf{r}'') \frac{\mathbf{M}(\mathbf{r}'', \mathbf{r}')}{\rho(\mathbf{r}')} = \int d\mathbf{r}'' \frac{\mathbf{M}(\mathbf{r}, \mathbf{r}'')}{\rho(\mathbf{r}'')} \exp\{\overline{\mathbf{M}}t\}(\mathbf{r}'', \mathbf{r}')$$

In addition, the time integral of the exponential operator satisfies

$$\int d\mathbf{r}' \left[\int_0^\infty dt \exp\{-\overline{\mathbf{M}}t\}(\mathbf{r}, \mathbf{r}') \right] \frac{\mathbf{M}(\mathbf{r}', \mathbf{r}'')}{\rho(\mathbf{r}'')} = \int_0^\infty dt \frac{d}{dt} \exp\{-\overline{\mathbf{M}}t\}(\mathbf{r}, \mathbf{r}'') = \delta(\mathbf{r} - \mathbf{r}'')\mathbf{1}$$

where we have used Eqs. (5.10), (5.10). Eq. (5.10) shows that the time integral operator of the exponential is just the inverse, in functional sense, of the operator $\frac{\mathbf{M}(\mathbf{r}', \mathbf{r}'')}{\rho(\mathbf{r}'')}$

The formal solution of (5.10) is given by

$$\mathbf{g}(\mathbf{r}, t) = -\int_0^t dt' \int d\mathbf{r}' \exp\{-\overline{\mathbf{M}}(t - t')\}(\mathbf{r}, \mathbf{r}')\rho(\mathbf{r}', t')\nabla \mu(\mathbf{r}', t')$$

where we have neglected an initial condition term that decays to zero very fast. Under the

assumption that the density hardly changes in the time scale of decay of the momentum density, we may approximate

$$\mathbf{g}(\mathbf{r}, t) \approx - \int d\mathbf{r}' \rho(\mathbf{r}', t) \nabla \mu(\mathbf{r}', t) \left[\int_0^\infty dt' \exp\{-\overline{\mathbf{M}} t'\}(\mathbf{r}, \mathbf{r}') \right]$$

By substituting Eq. (5.10) into the continuity equation, we obtain a closed equation for the density field in the form

$$\partial_t \rho(\mathbf{r}, t) = \nabla \int d\mathbf{r}' \left[\int_0^\infty dt' \exp\{-\overline{\mathbf{M}} t'\}(\mathbf{r}, \mathbf{r}') \right] \rho(\mathbf{r}', t) \nabla \mu(\mathbf{r}', t)$$

This equation can be written in the form of Eq. (**??**), this is

$$\partial_t \rho(\mathbf{r}, t) = \nabla \int d\mathbf{r}' \mathbf{D}(\mathbf{r}, \mathbf{r}') \nabla \frac{\delta \overline{\Phi}[\rho]}{\delta \rho(\mathbf{r}', t)}$$

with the following explicit expression for the diffusion tensor

$$\mathbf{D}(\mathbf{r}, \mathbf{r}') = \left[\int_0^\infty dt' \exp\{-\overline{\mathbf{M}} t'\}(\mathbf{r}, \mathbf{r}') \right] \rho(\mathbf{r}')$$

This identity should be regarded as a kind of Stokes-Einstein relationship. The Stokes-Einstein relationship for a Brownian particle states that the diffusion coefficient is proportional to the inverse of the friction coefficient. In the present case, Eqs. (5.10) and (5.10) show that the diffusion tensor and the friction matrix are inverse of each other, in a functional sense

$$\int d\mathbf{r}' \mathbf{D}^{\sigma\mu}(\mathbf{r}, \mathbf{r}') \frac{\mathbf{M}^{\mu\nu}(\mathbf{r}', \mathbf{r}'')}{\rho(\mathbf{r}')\rho(\mathbf{r}'')} = \delta(\mathbf{r} - \mathbf{r}') \delta^{\sigma\nu}$$

In principle, given a model for the friction matrix $\mathbf{M}$ this equation can be solved to obtain the diffusion matrix. It is obvious that in a general case one should resort to numerical methods for such a solution. A particular case where it is possible to obtain explicitly the diffusion tensor is when the friction matrix $\mathbf{M}$ is local in space, with position independent viscosities. From Eqs. (5.7), (5.7) we have

$$\mathbf{M}^{\mu\nu}(\mathbf{r}, \mathbf{r}') = -\delta(\mathbf{r} - \mathbf{r}') \left[\eta \delta^{\mu\nu} \nabla^2 + \left(\zeta + \frac{\eta}{3} \right) \nabla^\mu \nabla^\nu \right]$$

$$\mathbf{D}^{\sigma\mu}(\mathbf{r}, \mathbf{r}') = \rho(\mathbf{r})\rho(\mathbf{r}') \mathbf{O}^{\sigma\mu}(\mathbf{r}, \mathbf{r}')$$

where the second equation defines the tensor $\mathbf{O}^{\sigma\mu}(\mathbf{r}, \mathbf{r}')$. Substitution of Eq. (5.10) into Eq. (5.10) gives the following equation to be satisfied by $\mathbf{O}^{\sigma\mu}(\mathbf{r}, \mathbf{r}')$

$$\eta \nabla^2 \mathbf{O}^{\sigma\nu}(\mathbf{r}, \mathbf{r}') + \left(\zeta + \frac{\eta}{3} \right) \nabla^\nu \nabla^\mu \mathbf{O}^{\sigma\mu}(\mathbf{r}, \mathbf{r}') = -\delta(\mathbf{r} - \mathbf{r}') \delta^{\sigma\nu}$$

Therefore, the tensor $\mathbf{O}^{\sigma\mu}(\mathbf{r}, \mathbf{r}')$ is a tensorial Green's function. We should have transla-

tional invariance and, therefore, we may introduce the Fourier transform

$$\mathbf{O}^{\sigma\nu}(\mathbf{r} - \mathbf{r}') = \int \frac{d\mathbf{k}^3}{(2\pi)^3} \exp\{-i\mathbf{k}\cdot(\mathbf{r} - \mathbf{r}')\}\mathbf{O}^{\sigma\nu}(\mathbf{k})$$

and Eq. (5.10) becomes in Fourier space

$$\eta k^2 \mathbf{O}^{\sigma\nu}(\mathbf{k}) + \left(\zeta + \frac{\eta}{3}\right)\mathbf{k}^\nu\mathbf{k}^\mu\mathbf{O}^{\sigma\mu}(\mathbf{k}) = \delta^{\sigma\nu}$$

which suggests the following form

$$\mathbf{O}^{\sigma\nu}(\mathbf{k}) = a(k)\delta^{\sigma\nu} + b(k)\frac{1}{k^2}\mathbf{k}^\sigma\mathbf{k}^\nu$$

By substituting Eq. (5.10) into Eq. (5.10) we obtain

$$\eta k^2\left(a(k)\delta^{\sigma\nu} + b(k)\frac{1}{k^2}\mathbf{k}^\sigma\mathbf{k}^\nu\right) + \left(\zeta + \frac{\eta}{3}\right)\mathbf{k}^\nu\mathbf{k}^\mu\left(a(k)\delta^{\sigma\mu} + b(k)\frac{1}{k^2}\mathbf{k}^\sigma\mathbf{k}^\mu\right) = \delta^{\sigma\nu}$$

This implies

$$\eta k^2 a(k) = 1$$

$$\eta b(k) + \left(\zeta + \frac{\eta}{3}\right)(a(k) + b(k)) = 0$$

this is,

$$a(k) = \frac{1}{\eta k^2}$$

$$b(k) = -\alpha a(k)$$

$$\alpha \equiv \frac{\left(\zeta + \frac{\eta}{3}\right)}{\left(\zeta + \frac{\eta}{3}\right) + \eta}$$

where α is a dimensionless constant.

We can transform the tensor in Eq. (5.10) back to real space by using the well-known results

$$\int \frac{d\mathbf{k}^3}{(2\pi)^3} \exp\{-i\mathbf{k}\cdot\mathbf{r}\}\frac{1}{k^2} = \frac{1}{4\pi r}$$

$$\int \frac{d\mathbf{k}^3}{(2\pi)^3} \exp\{-i\mathbf{k}\cdot\mathbf{r}\}\frac{1}{k^2}\frac{\mathbf{k}}{k}\frac{\mathbf{k}}{k} = \frac{1}{8\pi r}\left(\mathbf{1} - \frac{\mathbf{r}}{r}\frac{\mathbf{r}}{r}\right)$$

In this way,

$$\mathbf{O}(\mathbf{r}) = \frac{1}{4\pi\eta r}\mathbf{1} - \alpha\frac{1}{8\pi\eta r}\left(\mathbf{1} - \frac{\mathbf{r}}{r}\frac{\mathbf{r}}{r}\right)$$

When $\alpha = 1$, this is just the Oseen tensor.

The diffusion equation (5.10) now is

$$\partial_t\rho(\mathbf{r}, t) = \nabla_\mathbf{r}\rho(\mathbf{r})\int d\mathbf{r}'\mathbf{O}(\mathbf{r} - \mathbf{r}')\rho(\mathbf{r}')\nabla_{\mathbf{r}'}\frac{\delta\overline{\Phi}[\rho]}{\delta\rho(\mathbf{r}', t)} \qquad (5.10.\text{-}8)$$

This equation is non-local in space and the non-locality is very strong because of the slow r^{-1} hydrodynamic decay of the tensor $\mathbf{O}(\mathbf{r})$. We do not expect that such a long-range feature will be modified by other models for the friction matrix that may include non-locality in the stress-stress correlation function entering the friction matrix. However, these more refined models for the friction matrix may tame the singularity of r^{-1} at the origin.

The non-local long-ranged equation (5.10) seems to be rather cumbersome to deal with. For this reason, we conclude that for the case of simple fluids, it may be more reasonable to stay at the level of hydrodynamics, where the non-locality of the friction matrix is, at most, of molecular scale. The price we pay in this case is just the need of two partial differential equations (continuity and momentum equation) instead of a non-local long-ranged integro-differential equation. One additional advantage of the hydrodynamic theory is that it is not necessary to assume the strong requirement that the momentum decays much faster than the density. The hydrodynamic functional theory can, therefore, tackle more general situations and in a simpler way.

5.11   Hydrodynamic functional theory for colloidal suspensions

We have seen that for a simple liquid, by extending the set of variables from the mass density to the momentum density, one obtains a Stokes-Einstein type of connection between the transport coefficients of the detailed level of description (the viscosity tensor) with those of the less detailed level (the diffusion tensor). In the same way, we may try to find a similar relationship for a colloidal suspension, and then try to justify an equation like (3.7.6). Note that Eq. (3.7.6) involves the solvent viscosity within the hydrodynamic tensor $\omega_{12}(\mathbf{r} - \mathbf{r}')$, which is a transport coefficient pertaining to the more detailed level of description of hydrodynamics. In this section, we present the Hydrodynamic functional theory for colloidal suspensions.

The CG variables that we will select are the concentration field $c(\mathbf{r}, t)$ of colloidal particles plus the mass $\rho(\mathbf{r}, t)$ and momentum $\mathbf{g}(\mathbf{r}, t)$ density fields of the solvent. These are assumed to be slow variables in the time-scale of molecular processes. In addition, the concentration field is expected to evolve in a much longer time scale from the mass and momentum densities of the solvent. Therefore, in a second step we will be entitled

to take an adiabatic approximation to the coupled hydrodynamic equations and obtain a closed equation for the concentration field of colloidal particles.

5.12   Conclusions

In this Chapter we consider a fluid system that can move macroscopically. In this case, case that not only the (mass) density field but also the momentum density field is a slow variable in the system. This will lead to a functional theory for hydrodynamics [?]. We do not consider the energy density field as a relevant variable. In this doing, we are assuming that this variable is comparatively fast and, therefore, the theory is isothermal. The interest of this chapter is that it shows the explicit connection of the hydrodynamic theory with the dynamic density functional theory of Chapter 22.3. In the overdamped limit, in which the momentum density evolves much faster than the mass density, one recovers the DDFT in the previous section. Also we obtain with this procedure an equivalent of the Stokes-Einstein relationship.

In conclusion, we have derived a dynamical density functional (DDFT) theory using the projection operator technique. Assuming that the one-particle is the only slow dynamical variable, a general dynamical deterministic equation was obtained which still involves a generalized diffusion tensor. The standard form of DDFT can be recovered as a special approximation for the diffusion tensor. Situations with different diffusion tensors were discussed including atomic systems and colloids with hydrodynamic interactions. Our derivation underlines the underlying adiabaticity assumption. The standard result agrees with alternate derivations starting from the Langevin or Smoluchowski picture of Brownian particles.

The standard DDFT equations was applied to a wealth of various situations including: i) time-dependent traps [?, ?, ?], ii) dynamical correlations [?], iii) tagged particle dynamics in confinement [?], iv) sedimentation dynamics [?], v) flow around particles [?, ?], vi) dynamics of fluid phase separation [?], vii) crystal nucleation and growth [?] viii) nonequilibrium phase transitions [?]. It would be interesting to extend the dynamical equations towards more complicated diffusion tensors and treat all these interesting applications i)-viii) again to check for corrections.

We finally mention that DDFT is the starting point for more coarse-grained dynamical descriptions like phase-field [?] or phase-field crystal models [?] which are an important tool to simulate various situations in material science. Recently it was shown how the phenomenological static [?] and dynamical [?] parameters of the phase-field crystal model can be microscopically determined by using DFT resp. DDFT. An improvement of the DDFT equations leads directly to a more realistic parameter choice for phase-field simulations which will finally allow to match phase-field simulations [?] better to material properties.

In a simple liquid, $\mathbf{q}_i, \mathbf{p}_i$ in Eq. (22.4) are the positions and momenta of each atom in the system. In a colloidal system, these variables are the positions and momenta of each colloidal particle. In this case, it may be more appealing to think of the averages $\rho(\mathbf{r}, t), \mathbf{g}(\mathbf{r}, t)$ of $\hat{\rho}_{\mathbf{r}}(z), \hat{\mathbf{g}}_{\mathbf{r}}(z)$ as (proportional to) the probability and probability current of finding the colloidal particles at a given position. The resulting dynamic equations for $\rho(\mathbf{r}, t), \mathbf{g}(\mathbf{r}, t)$ will be an equation for the evolution of these probabilities. Of course,

we can interpret the resulting hydrodynamic equations for a simple liquid also as kinetic equations for the probability and probability current to find a certain atom in a particular location. In this sense, we could name the obtained hydrodynamic equations as *fine grained* Navier-Stokes equations, although we prefer the terminology HydroDynamic Functional theory HDFT, to be compared to Dynamic Density Functional Theory, DDFT.

In the present formulation, that has been derived for an isolated Hamiltonian system, only the tendency towards equilibrium can be described. Examples of systems for which this may be useful are the dynamics of liquid/solid systems with sudden increase or decrease of temperature in some region of the system for which the decay towards the new equilibrium state compatible with the new total energy is described. Of course, most systems of experimental interest are not isolated but rather interacting with the surroundings, either with some global forcing or through boundary conditions. In particular, if stationary temperature gradients are to be established, contact with thermal reservoirs need to be accounted for in the description. The same framework of projection operators used in the present work can be used in order to include the description of the interaction with the "uninteresting surrounding" that corresponds to a thermal bath. In this case, additional terms accounting for the interaction with the thermal bath appear in the dynamic equations. These terms play the role of "microscopically derived" boundary conditions. We will present this finding in a future publication [].

The scope of the present theory is limited by the very selection of $n(\mathbf{r}), e(\mathbf{r})$ as CG variables. In a Markovian description, this selection implicitly assumes that any other variable in the system is sufficiently fast as compared to the time scale of evolution of $n(\mathbf{r}), e(\mathbf{r})$. Otherwise, the memory kernels would contain long lived contributions and the Markovian assumption leading to ordinary differential equations would not apply. In particular, no convective motion should be present in the system, in the sense that any motion is rapidly relaxed towards zero velocity, in a time scale much shorter than the evolution of the density and energy densities. If this is not the case, then it is necessary to include an additional conserved variable, the momentum density field. The resulting description leads to the equations of non-isothermal functional hydrodynamics and will be discussed elsewhere.

If one is interested in profiles or correlations of the density or energy density fields in equilibrium situations, there is no need to consider the FTD level of description. For equilibrium situations the temperature field is constant and all the information about profiles and correlations is already captured by the DFT level of description. However, any non-isothermal situation requires, necessarily, the introduction of the FTD level of description. In the remaining part of this paper we consider the dynamic equations for the density and energy density in non-isothermal situations.

6

Non-isothermal hydrodynamics: $n_{\mathbf{r}}, \mathbf{g_r}, e_{\mathbf{r}}$. Liquid-vapour

6.1   van der Waals fluid

6.2   Introduction

Boiling of water in a pot, the formation of a cloud, or the rise of bubbles in a pint of beer are fascinating everyday experiences that involve liquid-vapor coexistence in non-trivial flow situations. Knowledge of the dynamics of this phenomena is crucial in less pleasant situations like the prediction and control of nuclear accidents in refrigerated nuclear reactors. The complexity of the problem requires the aid of computer simulations in order to extract practical information. Engineering conventional computational fluid mechanics approaches have relied on effective hydrodynamic equations in which the presence of bubbles or drops is taken into account through the introduction of void or vapor fraction which require empirical constitutive equations not always available [?]. In these much coarse grained approaches the detailed interface dynamics of bubbles and droplets is not available.

There is a great recent interest in the computer simulations of interfacial dynamics for liquid-vapor coexistence. Prove of that is the large variety of techniques used to tackle the problem: Lattice-Boltzmann method [?, ?], Direct Montecarlo method [?], Smoothed Particle Hydrodynamics (SPH)[?], Finite Difference discretization of Navier-Stokes equations [?],[?], and the Volume Of Fluid method [?]. Some of these techniques suffer from ad-hoc assumptions, more prominently isothermal behavior. Others require quite specific model technicalities in order to get sensible results or the specification of boundary conditions in complex topologies. It seems, therefore, appropriate to review here the theoretical foundation of the hydrodynamic equations for the van der Waals fluid.

Although hydrodynamics equations for the van der Waals fluid were posed as early as 1901 by Korteveg [?],[?], a clarification of the structure and thermodynamic consistency of the equations is convenient in order to avoid potential problems. In the late

60's, for example, a variant of the theory was introduced by Kawasaki [?], following the ideas of van Kampen [?]. It can be shown that Kawasaki theory is thermodynamically inconsistent. In Kawasaki theory, the long range attractive mean field potential between molecules acts as an external force in the momentum equation. A gradient approximation of this mean field potential leads to purely local equations involving third order spatial derivatives of the density field. Such a theory was proposed by Felderhof who constructed a thermodynamically consistent set of hydrodynamic equations for a van der Waals fluid [?]. However, Felderhof theory deals with the inviscid fluid and no dissipation nor fluctuations where included in his theory so a generalization of his theory seems appropriate. For an excellent review of diffuse interface models described by third order derivative terms see Ref. [?]. On the other hand, the discretization of third order derivatives is subject to high numerical errors. From a computational point of view, a treatment of the diffuse interfaces though a non-local integral term as in Kawasaki theory might represent an advantage worth exploring.

The essential theoretical tool for describing *equilibrium* properties of liquid-vapor interfaces is the Density Functional Theory (DFT) [?]. A well-known *local* realization of the DFT known as the Density Gradient Theory successfully describes the equilibrium properties of liquid-vapor interfaces like surface tension and density profiles, and the correct relation between different scaling exponents near the critical point [?]. This is due to the relatively smooth behavior of these interfaces as compared with fluid-solid interfaces for which a non-local expression for the free energy functional is needed [?]. The work presented in this paper can be understood as a generalization of the local DFT to *non-equilibrium* situations in which an entropy functional instead of a free energy functional is used to describe both flow and thermal transport [?].

The strategy we follow is to derive the *entropy* functional from microscopic principles following ideas of van Kampen, who derived a coarse grained *free energy* functional for the van der Waals gas [?]. This entropy functional is one of the building blocks of a recently developed framework for non-equilibrium thermodynamics known as GENERIC [?]. This two generator formalism ensures thermodynamic consistency of its dynamic equations. Under a set of well-defined assumptions, the GENERIC formalism can be *derived* from first principles by means of a projection operator technique [?]. It is therefore not surprising that all well-established dynamic equations for non-equilibrium systems fit into the GENERIC formalism: Relativistic and non-relativistic hydrodynamics, kinetic theory of gases (the Boltzmann equation) and of polymer systems in non-isothermal situations, chemical reactions, just to mention a few, have the GENERIC structure [?]. Significant new dynamical models for a number of complex systems, such as polymer/surface interactions[?], liquid crystals[?], or polymer blends[?] have already been obtained, and even new cosmological models have been developed[?]. In particular, the recognition of the role of the reversible dynamics in the system evolution equations has led to interesting new conclusions regarding closure approximations[?] and polymer reptation models[?, ?]. It seems, therefore, sensible to formulate a thermohydrodynamic theory for liquid-vapor coexistence according to the GENERIC framework. The basic bonus for this procedure is that strict respect for the first and second law of thermodynamics is guarded.

The paper is distributed as follows. In Section 6.3 we present a brief summary of the GENERIC formalism and of the entropy functional for a van der Waals fluid. The

entropy functional is computed explicitly in the Appendix 7.3.4. This appendix can be regarded as providing solid microscopic ground to the plausible assumptions made by Felderhof when postulating the entropy functional. In Section 6.4 we propose the hydrodynamic equations of a van der Waals fluid according to the GENERIC formalism and compare it with the theory of Kawasaki. In Section 6.5 the local gradient theory is presented and compared with Felderhof's theory. Some concluding remarks are given in Section 6.6, while some further information is given in Appendix 6.8, and 6.9.

6.3 The GENERIC framework and the entropy

A brief summary of the GENERIC structure is presented and we refer to the original references for further details [**?**]. The first essential step in the description of a system is the selection of the proper relevant variables x used to describe the system at a given level of description. The GENERIC dynamical equation for x is

$$\dot{x} = L(x){\cdot}\nabla E(x) + M(x){\cdot}\nabla S(x).$$

The first term in the right hand side produces the reversible part of the dynamics whereas the second term is responsible for the irreversible dissipative dynamics. Here, $E(x), S(x)$ are the energy and entropy of the system expressed in terms of the variables x, ∇ is the gradient operator in x-space, and $L(x), M(x)$ are matrices that satisfy the following degeneracy requirements,

$$L{\cdot}\nabla S = 0, \qquad M{\cdot}\nabla E = 0.$$

In addition, L is antisymmetric (this guarantees that energy is conserved, i.e. the First Law) and satisfies the stringent Jacobi property [**?**]. M is a positive definite symmetric matrix (this guarantees that the entropy is a nondecreasing function of time, i.e. the Second Law). If the system presents dynamical invariants $I(x)$ different from the total energy, then further restrictions on the form of L and M are required

$$\nabla I{\cdot}L{\cdot}\nabla E = 0, \qquad \nabla I{\cdot}M{\cdot}\nabla S = 0.$$

These conditions ensure that $dI/dt = 0$. The deterministic equations (6.3) are, actually, an approximation in which thermal fluctuations are neglected. If thermal fluctuations are not neglected, the dynamics is described by a Fokker-Planck equation (FPE) that governs the probability distribution function $\rho = \rho(x, t)$ [**?**]. This FPE has as equilibrium solution the Einstein's distribution function generalized to take into account the presence of dynamical invariants E_0, I_0 [**?**], this is

$$\rho^{\mathrm{eq}}(x) = \delta(E(x) - E_0)\delta(I(x) - I_0) \exp\{S(x)/k_B\},$$

where k_B is Boltzmann's constant.

Our approach for constructing the entropy function for a liquid-vapor system is to compute microscopically $\rho^{\mathrm{eq}}(x)$ and, through Eqn. (6.3), identify the entropy functional.

That is, we compute the joint probability that an extended simple fluid in equilibrium has a particular realization of the mass, momentum and internal energy density fields. We follow a cell-method first used by van Kampen in order to derive the equilibrium probability that a simple fluid has a particular realization of the mass density field [?]. The explicit details of the calculation are given in Appendix 7.3.4. Physical space is divided in $\mathscr{M}$ cells of volume $\mathscr{V}_\mu$ and the mass M_μ, momentum $\mathbf{P}_\mu$ and internal energy ϵ_μ of cell μ in terms of microscopic coordinates of the molecules is considered. The internal energy contains the potential energy of interaction between particles within the same cell *and* the energy of interaction with particles of other cells. Provided that the microscopic coordinates are distributed according to the microcanonical ensemble we compute in Appendix 7.3.4 the joint probability $P[M, \mathbf{P}, \epsilon]$ following similar steps as in Ref. [?]. An essential step in the derivation is the assumption that the molecular potential has a repulsive hard core $\phi^{\mathrm{hc}}(r)$ and a long range attractive tail $\phi^l(r)$. The interaction of particles between *different* cells is taken in mean field approximation and it involves only $\phi^l(r)$. The final outcome is

$$
P[M, \mathbf{P}, \epsilon] = \frac{1}{\Omega_0} \delta \left(\sum_\mu^{\mathscr{M}} M_\mu - M_0 \right) \delta \left(\sum_\mu^{\mathscr{M}} \mathbf{P}_\mu \right)
$$

$$
\times \qquad\qquad\qquad \delta \left(\sum_\mu^{\mathscr{M}} \left(\frac{\mathbf{P}_\mu^2}{2 M_\mu} + \epsilon_\mu \right) - E_0 \right) \exp \left\{ \frac{S[M, \epsilon]}{k_B} \right\}.
$$

We recognize the dynamical invariants (total mass M_0, momentum $\mathbf{P}_0 = \mathbf{0}$ and energy E_0) in the conserving delta functions. The entropy functional is given by

$$
S[M, \epsilon] = \sum_\mu S^{\mathrm{hc}}(\epsilon_\mu - \overline{\phi}_\mu, M_\mu, \mathscr{V}_\mu).
$$

Here, $S^{\mathrm{hc}}(\epsilon, M, V)$ is the entropy function of an isolated system of $N = M/m$ molecules (m is the mass of a molecule) interacting with *only* the hard core potential $\phi^{\mathrm{hc}}(r)$ in a volume V. Note the non-trivial appearance of the mean field interaction energy $\overline{\phi}_\mu$, which is defined by

$$
\overline{\phi}_\mu = \frac{1}{2m^2} \sum_\nu{}' \phi^l(R_{\mu\nu}) M_\mu M_\nu,
$$

where $R_{\mu\nu}$ is the distance between cell centers and the prime denotes $\mu \neq \nu$. This mean field potential involves only the long ranged part of the molecular potential. Integration of (6.3) with respect to N, ϵ and using a steepest descent approximation (see Appendix 6.8) leads to van Kampen's expression,

$$
P[M] = \frac{1}{Z_0} \exp\left\{ -\beta F[M] \right\} \delta \left(\sum_\mu^{\mathscr{M}} M_\mu - M_0 \right),
$$

where the coarse-grained free energy functional is given by

$$F[M] = \sum_{\mu}^{\mathcal{M}} F^{\mathrm{hc}}(\beta, M_\mu, \mathscr{V}_\mu) + \beta\overline{\phi}_\mu.$$

Here, $F^{\mathrm{hc}}(\beta, M_\mu, \mathscr{V}_\mu)$ is the free energy of a system of hard core particles at temperature $\beta^{-1}/k_B = 2K^*/DM$ (K^* is the most probable value of the kinetic energy in the system). Both Eqns. (6.3) and (6.3) admit a continuum notation provided that the cells are large enough in order that the entropy and free energy are first order functions of their arguments

$$S[\rho_{\mathbf{r}}, \epsilon_{\mathbf{r}}] = \int d\mathbf{r} s^{\mathrm{hc}}(\epsilon_{\mathbf{r}} - \overline{\phi}_{\mathbf{r}}, \rho_{\mathbf{r}}),$$

$$F[\rho_{\mathbf{r}}] = \int d\mathbf{r} \left(f^{\mathrm{hc}}(\rho_{\mathbf{r}}, \beta) + \overline{\phi}_{\mathbf{r}} \right),$$

where $\epsilon_{\mathbf{r}} = \epsilon_\mu/\mathscr{V}_\mu$, $\overline{\phi}_{\mathbf{r}} = \overline{\phi}_\mu/\mathscr{V}_\mu$, $\rho_{\mathbf{r}} = M_\mu/\mathscr{V}_\mu$, and $s^{\mathrm{hc}}(\epsilon_{\mathbf{r}} - \overline{\phi}_{\mathbf{r}}, \rho_{\mathbf{r}})$ is the entropy *density* of a hard core system, while $f^{\mathrm{hc}}(\rho_{\mathbf{r}}, \beta)$ is the corresponding free energy density. The continuum form for the mean field potential energy (6.3) is

$$\overline{\phi}_{\mathbf{r}} = \rho_{\mathbf{r}} \int d\mathbf{r}' \frac{\phi^l(|\mathbf{r} - \mathbf{r}'|)}{2m^2} \rho_{\mathbf{r}'}$$

The main benefit of the microscopic derivation presented in Appendix 6.8 is the clear separation at the macroscopic level of the effects of the short and long ranged part of the microscopic potential, in particular the realization that the entropy of the full system is given directly in terms of the entropy of the hard core system, suitably evaluated at the corrected internal energy, Eqns. (6.3) or (6.3).

We now consider the particular situation in which the density field varies slowly in the scale of the range of $\phi^l(r)$. In this case, we can Taylor expand $\rho_{\mathbf{r}'}$ around $\mathbf{r}$ and retain up to second order in gradients in order to get

$$\overline{\phi}_{\mathbf{r}} \approx -a\rho_{\mathbf{r}}^2 - \frac{c}{2}\rho_{\mathbf{r}}\nabla^2\rho_{\mathbf{r}},$$

where we introduced $a, c > 0$ through

$$a = -\int d\mathbf{r} \frac{\phi^l(r)}{2m^2}, \qquad c = -\int d\mathbf{r} r^2 \frac{\phi^l(r)}{3m^2}.$$

Substitution of (6.3) into (6.3) leads to

$$F[\rho_{\mathbf{r}}] = \int d\mathbf{r} \left(f^{\mathrm{hc}}(\rho_{\mathbf{r}}, \beta) - a\rho^2 + \frac{c}{2}(\nabla\rho_{\mathbf{r}})^2 \right),$$

which is the usual local gradient density expression for the free energy functional, also

known as the Cahn-Hilliard or Ginzburg-Landau free energy functional for liquid surfaces [?]. The corresponding entropy functional (6.3), thus, has been computed at the same level of approximation. The coefficient c provides the overall magnitude of the surface tension coefficient [?].

The energy function given by

$$E(M, \mathbf{P}, \epsilon) = \sum_{\mu}^{\mathscr{M}} \left(\frac{\mathbf{P}_{\mu}^2}{2M_{\mu}} + \epsilon_{\mu} \right),$$

can also be written in continuum form as an energy functional

$$E[\rho_{\mathbf{r}}, \mathbf{g}_{\mathbf{r}}, \epsilon_{\mathbf{r}}] = \int \left[\frac{1}{2} \frac{\mathbf{g}_{\mathbf{r}}^2}{\rho_{\mathbf{r}}} + \epsilon_{\mathbf{r}} \right] d\mathbf{r}.$$

where $\mathbf{g}_{\mathbf{r}} = \mathbf{P}_{\mu}/\mathscr{V}_{\mu}$ is the momentum density field.

6.4   Hydrodynamic equations for a van der Waals fluid

In this section, we construct the hydrodynamic equations for a van der Waals fluid following the GENERIC formalism.

Due to the form in which the internal energy appears in the entropy, it proves convenient to use as the proper hydrodynamic variable the "intrinsic" internal energy $\epsilon_{\mathbf{r}}^i = \epsilon_{\mathbf{r}} - \overline{\phi}_{\mathbf{r}}$ which involves the interaction of molecules through the hard core part only. The energy (6.3) and the entropy (6.3) expressed in terms of these hydrodynamic variables are then

$$E[\rho, \mathbf{g}, \epsilon^i] = \int \left[\frac{1}{2} \frac{\mathbf{g}_{\mathbf{r}}^2}{\rho_{\mathbf{r}}} + \epsilon_{\mathbf{r}}^i + \overline{\phi}_{\mathbf{r}} \right] d\mathbf{r},$$

$$S[\rho, \mathbf{g}, \epsilon^i] = \int s^{hc}(\rho_{\mathbf{r}}, \epsilon_{\mathbf{r}}^i) d\mathbf{r}.$$

We have now the two basic building blocks for the GENERIC formulation of the dynamic equations (6.3). The derivatives of the energy and entropy with respect to the relevant variables become functional derivatives with respect to the hydrodynamic variables, this is,

$$\frac{\partial E}{\partial x} = \begin{pmatrix} \frac{\delta E}{\delta \rho_{\mathbf{r}}} \\[2mm] \frac{\delta E}{\delta \mathbf{g}_{\mathbf{r}}} \\[2mm] \frac{\delta E}{\delta \epsilon_{\mathbf{r}}^i} \end{pmatrix} = \begin{pmatrix} -\frac{1}{2}\mathbf{v}_{\mathbf{r}}^2 - \frac{2\overline{\phi}_{\mathbf{r}}}{\rho_{\mathbf{r}}} \\[2mm] \mathbf{v}_{\mathbf{r}} \\[2mm] 1 \end{pmatrix},$$

and

$$\frac{\partial S}{\partial x} = \begin{pmatrix} \frac{\delta S}{\delta \rho_{\mathbf{r}}} \\ \frac{\delta S}{\delta \mathbf{g}_{\mathbf{r}}} \\ \frac{\delta S}{\delta \epsilon_{\mathbf{r}}^i} \end{pmatrix} = \begin{pmatrix} -\frac{\mu^{\mathrm{hc}}(\rho_{\mathbf{r}}, \epsilon_{\mathbf{r}}^i)}{T^{\mathrm{hc}}(\rho_{\mathbf{r}}, \epsilon_{\mathbf{r}}^i)} \\ 0 \\ \frac{1}{T^{\mathrm{hc}}(\rho_{\mathbf{r}}, \epsilon_{\mathbf{r}}^i)} \end{pmatrix}.$$

The velocity field is $\mathbf{v}_{\mathbf{r}} = \mathbf{g}_{\mathbf{r}}/\rho_{\mathbf{r}}$, and the local temperature T^{hc} and chemical potential μ^{hc} per unit mass are

$$T_{\mathbf{r}}^{\mathrm{hc}} = \left(\frac{\partial s^{\mathrm{hc}}}{\partial \epsilon_{\mathbf{r}}^i}\right)^{-1}, \qquad \frac{\mu_{\mathbf{r}}^{\mathrm{hc}}}{T_{\mathbf{r}}^{\mathrm{hc}}} = -\frac{\partial s^{\mathrm{hc}}}{\partial \rho_{\mathbf{r}}}.$$

Note that these equations of state are those of the hard core system. By focusing on the reversible part of the dynamics, we must construct now the matrix L. A reasonable proposal is to use the same expression for L as in the case of hydrodynamics of a simple fluid. Note that if we neglect the interfacial potential energy $\overline{\phi}_{\mathbf{r}}$ we should recover the hydrodynamics of a simple hard core fluid. We propose, therefore, for the matrix $L \to L_{\mathbf{rr}'}$ the following one [?]

$$\begin{pmatrix} 0 & \rho_{\mathbf{r}'} \nabla' \delta_{\mathbf{rr}'} & 0 \\ \rho_{\mathbf{r}} \nabla' \delta_{\mathbf{rr}'} & \mathbf{g}_{\mathbf{r}'} \nabla' \delta_{\mathbf{rr}'} + \nabla' \delta_{\mathbf{rr}'} \mathbf{g}_{\mathbf{r}} & \epsilon_{\mathbf{r}}^i \nabla' \delta_{\mathbf{rr}'} + P_{\mathbf{r}'}^{\mathrm{hc}} \nabla' \delta_{\mathbf{rr}'} \\ 0 & \epsilon_{\mathbf{r}'}^i \nabla' \delta_{\mathbf{rr}'} + P_{\mathbf{r}}^{\mathrm{hc}} \nabla' \delta_{\mathbf{rr}'} & 0 \end{pmatrix}.$$

Here, $\nabla' = \partial/\partial \mathbf{r}'$ and $\delta_{\mathbf{rr}'} = \delta(\mathbf{r} - \mathbf{r}')$ is Dirac's delta function, $P_{\mathbf{r}}^{\mathrm{hc}} = P^{\mathrm{hc}}(\rho_{\mathbf{r}}, \epsilon_{\mathbf{r}}^i)$ is the pressure field as a function of the mass and intrinsic internal energy densities.

As has been shown in Ref. [?], the matrix L satisfies the condition $L\nabla S = 0$ because of the Gibbs-Duhem relationship (for the hard core system). The fulfillment of $L\nabla S = 0$ is the basic reason for using $P_{\mathbf{r}}^{\mathrm{hc}}$ in Eqn. (6.4) instead of any other possible expression for the pressure. The matrix L also satisfies the stringent Jacobi identity [?]. With the explicit form (6.4) for the L matrix and the gradient of the energy in Eqn. (6.4) the reversible part $L\nabla E$ of the equations of motion for the hydrodynamic variables are readily constructed

$$\partial_t \rho_{\mathbf{r}} = -\nabla \rho_{\mathbf{r}} \mathbf{v}_{\mathbf{r}},$$

$$\partial_t \mathbf{g}_{\mathbf{r}} = -\nabla \mathbf{v}_{\mathbf{r}} \mathbf{g}_{\mathbf{r}} - \nabla P^{\mathrm{hc}}(\epsilon_{\mathbf{r}}^i, \rho_{\mathbf{r}}) - \rho_{\mathbf{r}} \nabla \frac{2\overline{\phi}_{\mathbf{r}}}{\rho_{\mathbf{r}}},$$

$$\partial_t \epsilon_{\mathbf{r}}^i = -\nabla \epsilon_{\mathbf{r}}^i \mathbf{v}_{\mathbf{r}} - P^{\mathrm{hc}}(\epsilon_{\mathbf{r}}^i, \rho_{\mathbf{r}}) \nabla \mathbf{v}_{\mathbf{r}}.$$

Eqns. (6.4) are identical to the Euler equations of an inviscid (hard cored) fluid except for the additional term in the momentum equation that involves the long range part of

the molecular potential.

Concerning the irreversible part of the dynamics $M\nabla S$, we observe that the same matrix $M \to M_{\mathbf{rr'}}$ that corresponds to the usual hydrodynamic equations is perfectly adequate. For simplicity, we assume that there is no extra dissipation due to the presence of interfaces. The matrix M is thus given by [**?**]

$$
\begin{pmatrix}
0 & 0 & 0 \\[2mm]
0 & (\nabla\nabla' + \mathbf{1}\nabla\cdot\nabla')\eta_\mathbf{r} T_\mathbf{r}^{\mathrm{hc}}\delta_{\mathbf{rr'}} + 2\nabla\nabla'\hat\kappa_\mathbf{r} T_\mathbf{r}^{\mathrm{hc}}\delta_{\mathbf{rr'}} & \nabla\eta_\mathbf{r} T_\mathbf{r}^{\mathrm{hc}}\dot\gamma\delta_{\mathbf{rr'}} + \nabla\hat\kappa_\mathbf{r} T_\mathbf{r}^{\mathrm{hc}}\mathrm{tr}\dot\gamma\delta_{\mathbf{rr'}} \\[2mm]
0 & \nabla'\eta_\mathbf{r} T_\mathbf{r}^{\mathrm{hc}}\dot\gamma\delta_{\mathbf{rr'}} + \nabla'\hat\kappa_\mathbf{r} T_\mathbf{r}^{\mathrm{hc}}\mathrm{tr}\dot\gamma\delta_{\mathbf{rr'}} & \frac12\eta_\mathbf{r} T_\mathbf{r}^{\mathrm{hc}}\dot\gamma : \dot\gamma\delta_{\mathbf{rr'}} + \nabla\nabla'\lambda_\mathbf{r} T_\mathbf{r}^{\mathrm{hc2}}\delta_{\mathbf{rr'}} + \frac12\hat\kappa_\mathbf{r} T_\mathbf{r}^{\mathrm{hc}}(\mathrm{tr}\dot\gamma)^2\delta_{\mathbf{rr'}}
\end{pmatrix},
$$

where $\dot\gamma = \nabla\mathbf{v_r} + (\nabla\mathbf{v_r})^T$ is the symmetrized velocity gradient tensor. This matrix M satisfies the degeneracy $M\nabla E = 0$ as in the usual hydrodynamic case [**?**], as the only modification of ∇E is in the term in the density component. We remark, however, that the transport coefficients (shear viscosity $\eta_\mathbf{r}$, bulk viscosity $\kappa_\mathbf{r} = \hat\kappa_\mathbf{r} + 2\eta_\mathbf{r}/3$ and thermal conductivity $\lambda_\mathbf{r}$) that appear in M should be taken as state dependent and are expected to be strongly varying functions of the density field, in order to encompass the fact that vapor and liquid have very different transport properties. This is the reason for its space dependence displayed as a subindex $\mathbf{r}$. The presence of $T_\mathbf{r}^{\mathrm{hc}}$ in Eqn. (7.3.5) instead of other possible choices for the temperature, is dictated by the fact that $M\nabla S$ should produce the usual dissipative terms in the Navier-Stokes equation (note that ∇S in Eqn. (7.3.2) involves $T_\mathbf{r}^{\mathrm{hc}}$).

The final set of hydrodynamic equations for the thermohydrodynamics of the van der Waals fluid are

$$
\begin{aligned}
\partial_t \rho_\mathbf{r} &= -\nabla\rho_\mathbf{r}\mathbf{v_r}, \\
\partial_t \mathbf{g_r} &= -\nabla\cdot\mathbf{v_r}\mathbf{g_r} - \nabla P^{\mathrm{hc}}(\epsilon_\mathbf{r}^i, \rho_\mathbf{r}) - \nabla\cdot\tau + \rho_\mathbf{r}\overline{\mathbf{F}}_\mathbf{r}, \\
\partial_t \epsilon_\mathbf{r}^i &= -\nabla\epsilon_\mathbf{r}^i\mathbf{v_r} - P^{\mathrm{hc}}(\epsilon_\mathbf{r}^i, \rho_\mathbf{r})\nabla\cdot\mathbf{v_r} - \nabla\cdot\mathbf{q} - \tau : \nabla\mathbf{v_r},
\end{aligned}
$$

where the constitutive equations for the viscous stress τ and heat flux are given by

$$
\begin{aligned}
\tau_\mathbf{r} &= -\eta_\mathbf{r}\left[\nabla\mathbf{v_r} + \nabla\mathbf{v_r}^T\right] - (\kappa_\mathbf{r} - 2\eta_\mathbf{r}/3)(\nabla\cdot\mathbf{v_r})\mathbf{1}, \\
\mathbf{q_r} &= -\lambda_\mathbf{r}\nabla T_\mathbf{r}^{\mathrm{hc}}.
\end{aligned}
$$

and the mean field force is given by

$$
\overline{\mathbf{F}}_\mathbf{r} = -\nabla_\mathbf{r}\frac{1}{m^2}\int d\mathbf{r}'\overline{\phi}^l(|\mathbf{r} - \mathbf{r}'|)\rho_{\mathbf{r}'}
$$

Equations (6.4) are deterministic equations in which thermodynamic fluctuations are neglected. Thermodynamic fluctuations are very easily included in the GENERIC formalism. One simply needs to take the square root in matrix sense of the M matrix,

and this provides the amplitude of the noises [**?**], in accordance with the Fluctuation-Dissipation theorem. Because the matrix M in Eqn. (7.3.5) has the same structure of that of a one phase fluid, we can advance that the final fluctuating equations are obtained by simply adding to the stress tensor $\tau_{\mathbf{r}}$ and heat flux $\mathbf{q_r}$ a random counterparts given by [**?**]

$$\tilde{\tau}_{\mathbf{r}} = \sqrt{2T_{\mathbf{r}}^{\mathrm{hc}}\eta_{\mathbf{r}}}(\tilde{\sigma}_{\mathbf{r}}(t) - \mathrm{tr}[\tilde{\sigma}_{\mathbf{r}}(t)]\mathbf{1}) + \sqrt{3T_{\mathbf{r}}^{\mathrm{hc}}\kappa_{\mathbf{r}}}\,\mathrm{tr}[\tilde{\sigma}_{\mathbf{r}}(t)]\mathbf{1}$$
$$\tilde{\mathbf{q}}_{\mathbf{r}} = T_{\mathbf{r}}^{\mathrm{hc}}\sqrt{2\lambda_{\mathbf{r}}}\tilde{\zeta}_{\mathbf{r}}(t),$$

where $\tilde{\sigma}_{\mathbf{r}}(t)$ is a matrix of delta correlated white noises and $\tilde{\zeta}_{\mathbf{r}}(t)$ is a vector of delta correlated white noises (in space and time). Note that the form in which thermal fluctuations appear is similar to the approach proposed by Landau and Lifshitz [**?**]. However, one should note that in counterdistintion to their approach, here the random stress tensor and heat flux are *multiplicative* noises which *are not* Gaussian. What is Gaussian are the white noises $\tilde{\sigma}_{\mathbf{r}}(t), \tilde{\zeta}_{\mathbf{r}}(t)$. The strong dependence of the transport coefficients on the density due to the phase change has a direct effect on the amplitude of the thermal fluctuations.

Associated to the stochastic differential equations describing hydrodynamic fluctuating variables there is a mathematical equivalent functional Fokker-Planck equation [**?**]. The GENERIC structure ensures that the equilibrium solution of this Fokker-Planck equation is given by the continuum version of Eqn. (6.3), as it should.

Kawasaki proposed a set of hydrodynamic equations for a van der Waals fluid on intuitive grounds [**?**]. Both the continuity equation and the momentum balance equation in (6.4) coincide with Kawasaki's postulated equations. On the other hand, he uses the entropy per unit mass $\hat{s}_{\mathbf{r}}^{\mathrm{hc}} = s_{\mathbf{r}}^{\mathrm{hc}}/\rho_{\mathbf{r}}$ instead of the intrinsic internal energy $\epsilon_{\mathbf{r}}^i$. A standard calculation which uses the definitions (6.4) and the Euler equation $T^{\mathrm{hc}}s^{\mathrm{hc}} + \mu^{\mathrm{hc}}\rho - P^{\mathrm{hc}} - \epsilon^i = 0$ shows that our equations (6.4) imply $\partial_t\hat{s}^{\mathrm{hc}} + \mathbf{v_r}\cdot\nabla\hat{s}^{\mathrm{hc}} = 0$. This is consistent with the fact that the reversible part of the dynamics should not produce an increase of the entropy in the system. In contrast, in Kawasaki treatment the reversible part of the substantial derivative of the entropy per unit mass is equated to $\rho_{\mathbf{r}}\mathbf{v_r}\cdot\nabla(\overline{\phi}_{\mathbf{r}}/\rho_{\mathbf{r}})$ (in our notation). It is apparent that the addition of this term violates the conservation of the energy (**??**) and should not be present for thermodynamic consistency.

6.5   Gradient approximation

In this section we consider the gradient approximation (6.3) as applied to the obtained equations (6.4). The last two terms of the momentum equation can be re-arranged in the form

$$-\nabla P_{\mathbf{r}}^{\mathrm{hc}} - \rho_{\mathbf{r}}\nabla\frac{\overline{\phi_{\mathbf{r}}}}{\rho_{\mathbf{r}}} = -\nabla\overline{P}_{\mathbf{r}} + c\rho_{\mathbf{r}}\nabla\nabla^2\rho_{\mathbf{r}},$$

where we have introduced

$$\overline{P}_{\mathbf{r}} = P^{\mathrm{hc}}(\rho_{\mathbf{r}}, \epsilon_{\mathbf{r}}^i) - a\rho_{\mathbf{r}}^2.$$

The momentum equation thus becomes

$$\partial_t \mathbf{g_r} = -\nabla \mathbf{v_r g_r} - \nabla \overline{P}(\epsilon_{\mathbf{r}}^i, \rho_{\mathbf{r}}) + c\rho_{\mathbf{r}} \nabla \nabla^2 \rho_{\mathbf{r}}.$$

It is illuminating to use as the set of hydrodynamic variables $\rho_{\mathbf{r}}, \mathbf{g_r}, u_{\mathbf{r}}$ instead of $\rho_{\mathbf{r}}, \mathbf{g_r}, \epsilon_{\mathbf{r}}^i$. Here, the local internal energy is defined by

$$u_{\mathbf{r}} = \epsilon_{\mathbf{r}}^i - a\rho_{\mathbf{r}}^2,$$

which, from a microscopic point of view, represents the potential energy due to local interactions, that is, hard core interactions plus the mean field attraction "within" the small volume at $\mathbf{r}$. By taking the time derivative of (6.5) and using the hydrodynamic equations (6.4), a standard calculation leads to

$$\partial_t \rho_{\mathbf{r}} = -\nabla \rho_{\mathbf{r}} \mathbf{v_r},$$
$$\partial_t \mathbf{g_r} = -\nabla \mathbf{v_r g_r} - \nabla P^{\mathrm{vdW}}(u_{\mathbf{r}}, \rho_{\mathbf{r}}) + c\rho_{\mathbf{r}} \nabla \nabla^2 \rho_{\mathbf{r}} - \nabla \cdot \tau,$$
$$\partial_t u_{\mathbf{r}} = -\nabla u_{\mathbf{r}} \mathbf{v_r} - P^{\mathrm{vdW}}(u_{\mathbf{r}}, \rho_{\mathbf{r}}) \nabla \cdot \mathbf{v_r} - \nabla \cdot \mathbf{q} - \tau : \nabla \mathbf{v_r},$$

where the heat flux is given by

$$\mathbf{q_r} = -\lambda_{\mathbf{r}} \nabla T^{\mathrm{vdW}}(u_{\mathbf{r}}, \rho_{\mathbf{r}}).$$

Here, $P^{\mathrm{vdW}}, T^{\mathrm{vdW}}$ are the two equations of state for the van der Waals fluid (see Appendix 6.9). In obtaining (6.5) and (6.5), use has been made of the identities (6.9) in the Appendix 6.9.

The hydrodynamic equations (6.5) are equivalent to those proposed by Felderhof [?]. However, in Felderhof's theory, dissipation was neglected and, consistently, thermal fluctuations where not considered. Thus, equations (6.5) with (??) and (6.5) can be taken as the natural generalization of Felderhof theory.

It is not obvious at a first glance that the total momentum of the system is conserved by the term $c\rho_{\mathbf{r}} \nabla \nabla^2 \rho_{\mathbf{r}}$ in (6.5). That this is the case can be seen by noting that this term can be cast into the form $-\nabla \cdot \mathbf{P_r}$, and the momentum equation has the form of a balance equation. The "surface tension" contribution to the stress tensor $\mathbf{P_r}$ has the form [?]

$$\mathbf{P_r} = 2c \left[\frac{1}{6} \nabla \rho_{\mathbf{r}} \nabla \rho_{\mathbf{r}} + \frac{1}{12} (\nabla \rho_{\mathbf{r}})^2 \mathbf{1} - \frac{1}{3} \rho_{\mathbf{r}} \nabla \nabla \rho_{\mathbf{r}} - \frac{1}{6} \rho_{\mathbf{r}} \nabla^2 \rho_{\mathbf{r}} \mathbf{1} \right].$$

This contribution to the stress tensor is identical to the one derived from molecular considerations for the *equilibrium* stress tensor [?] under the gradient approximation[?].

We observe, therefore, that the theory that is being presented relies also on the hypothesis of *local equilibrium*, in much the same way as in the usual continuum hydrodynamics approach.

6.6   Summary and discussion

We have computed the entropy functional for a simple fluid starting from microscopic principles under the classic van der Waals assumption that the molecular potential has two well-separated ranges, a hard core repulsive part plus a very long ranged attractive tail. Under the further assumption that the hydrodynamic fields vary slowly on the total range of the potential it is possible to write a local entropy functional that depends on the density gradients. We have also presented the connection between this entropy functional and the local gradient free energy functional which is used in the context of the study of equilibrium of liquid-vapor interfaces. Even though the assumption of the unrealistic molecular potential seems to be too restrictive, the equilibrium gradient theory is highly successful in describing the equilibrium properties of these interfaces [?], and gives confidence on the dynamical approach taken in this paper.

The entropy functional describes the equilibrium properties of the system but it is also one of the basic inputs for constructing the non-equilibrium evolution equations for the hydrodynamic fields through the GENERIC formalism. By making use of all the well-known information about the L and M matrices for the hydrodynamics of a single phase fluid flow, we can construct the hydrodynamic equations for a van der Waals fluid in a rather simple way.

The hydrodynamic equations proposed predict unstable forces if the thermodynamic state is in the positive slope part of the van der Waals pressure diagram. When this happens, the fluid spontaneously adopts one of the two possible densities corresponding to liquid and vapor. Density variations appear in the short length scales associated to the interfaces of bubbles or drops. It is precisely in these interfacial regions where the last term in Eqn. (6.5) is important. This term generates forces in the fluid associated to the surface tension of the interface. Actually, the interfaces try to adopt a spherical shape. The interface is a diffuse object with a finite width. Note that no boundary conditions are required on the interface of a bubble or a drop. Actually, there is no need to known a priori the location of the "interface" in order to have a well-posed hydrodynamic problem.

The set of equations (6.4) with the gradient approximation (6.3) and the set of equations (6.5) are mathematically equivalent. We regard as the main benefit of the microscopic derivation presented in this paper the clear physical interpretation of the variables (either $\epsilon_{\mathbf{r}}^i$ or $u_{\mathbf{r}}$) and the correct equations of state (either P^{hc} or P^{vdW}) to be used in the equations. This issue is not always clear in the usual presentations of this subject based on phenomenological arguments that simply add gradient terms either in the energy or the entropy [?].

From the computational point of view of numerically solving the hydrodynamic equations obtained, we observe that a theory like Kawasaki's in which the mean field long range forces appear in integral form, Eqns. (6.4), might represent an advantage in front of a theory like Felderhof's in which these forces appear in differential form through third derivatives of the density field, Eqns. (6.5). In those regions where the interfaces

are located, the density field changes strongly which means that the third derivatives present a rather complex structure in very short length scales. In order to get stable and convergent results, very fine grids are required. These problems do not arise in the discretization of the integral form of the long range forces.

The theory derived here connects with the well-known phase field theories that deal with systems that present complex boundary conditions like those occurring in melting and dendritic growth [**?**] or immiscible fluids [**?**]. In these systems, the partial differential equations governing the evolution of the relevant variables require the formulation of boundary conditions on moving surfaces. The motion of the surface is, in turn, coupled in a complex way with the dynamics of the relevant variables. The approach taken by the phase field method is to include the boundary conditions into the equations of motion through the introduction of an auxiliary phase field that locates in a somewhat diffuse way the position of the interface. A further dynamics is generated for the phase field which is coupled with the dynamics of the rest of fields in the system. This dynamics is obtained from a phenomenological formulation of a "free energy". The theory we have derived is then in the class of a phase field theory for bubbles and drops. In our case, the phase field has a definite physical meaning in terms of the density field, and no phenomenological free-energy needs to be introduced ad hoc.

6.7   Appendix: Microscopic derivation of the entropy functional

In this section, we compute from first principles the joint probability that an extended simple fluid in equilibrium has a particular realization of the mass, momentum and internal energy density fields. This generalizes van Kampen derivation which only considered the mass density field [**?**].

The isolated fluid is assumed to be described microscopically by z, the set of positions $\mathbf{q}_i$ and momenta $\mathbf{p}_i$ of the center of mass of its N_0 constituent molecules (no rotational or vibrational degrees of freedom are considered, for simplicity). The Hamiltonian of the system is given by

$$H(z) = \sum_i^{N_0} \frac{\mathbf{p}_i^2}{2m} + \frac{1}{2} \sum_{ij} \phi_{ij},$$

where m is the mass of a molecule and ϕ_{ij} is the pair-wise potential function between molecules i and j, assumed to depend only on its separation r_{ij}. The total momentum of the system is given by

$$\mathbf{P}(z) = \sum_i^{N_0} \mathbf{p}_i.$$

The microscopic dynamics is such that $H(z)$ and $\mathbf{P}(z)$ are dynamical invariants. Obvi-

ously, the total number N_0 of particles (or the total mass) is also a dynamical invariant.

On a mesoscopic scale, the space containing the fluid is partitioned in M cells. The state of the system at that scale is described with the mesoscopic variables $N_\mu, \mathbf{P}_\mu, \epsilon_\mu$, $\mu = 1, \ldots, M$, where N_μ is the number of particles in cell μ, $\mathbf{P}_\mu$ is the momentum of the center of mass of the particles of cell μ and ϵ_μ is the energy with respect to the center of mass of the particles in cell μ. In order to relate the mesoscopic variables with the microscopic ones, we introduce the characteristic function $\chi_\mu(\mathbf{r})$ of cell μ which takes the value 1 if $\mathbf{r}$ is within cell μ and 0 otherwise. For example, the space can be partitioned into Voronoi cells whose characteristic function is $\chi_\mu(\mathbf{r}) \equiv \prod_{\nu \neq \mu}^{M} \theta(|\mathbf{r} - \mathbf{R}_\nu| - |\mathbf{r} - \mathbf{R}_\mu|)$ where $\theta(x)$ is the Heaviside step function and $\mathbf{R}_\mu$ is the center of the Voronoi cell μ. Obviously,

$$\sum_{\mu}^{M} \chi_\mu(\mathbf{r}) = 1,$$

because the cells cover all space without overlapping. The volume of the cell is given by

$$\mathscr{V}_\mu = \int_{V_0} d^3\mathbf{r}\chi_\mu(\mathbf{r}),$$

where V_0 is the total volume of the system. The mesoscopic variables N_μ, $\mathbf{P}_\mu$ and ϵ_μ can now be written as functions of the microstate z, this is

$$N_\mu(z) = \sum_i \chi_\mu(\mathbf{q}_i),$$

$$\mathbf{P}_\mu(z) = \sum_i \mathbf{p}_i \chi_\mu(\mathbf{q}_i),$$

$$\epsilon_\mu(z) = \sum_i \left(\frac{1}{2m} \left(\mathbf{p}_i - \frac{\mathbf{P}_\mu}{N_\mu} \right)^2 + \phi_i \right) \chi_\mu(\mathbf{q}_i),$$

where we have introduced the potential energy of particle i through

$$\phi_i = \frac{1}{2} \sum_j \phi_{ij}.$$

Note that we use Latin indices to refer to variables at the microscopic level and Greek indices to refer to mesoscopic variables.

The dynamical invariants can be written in terms of the mesoscopic variables by using

Eqn. (6.7), this is

$$H(z) = \sum_\mu \frac{\mathbf{P}_\mu^2(z)}{2M_\mu(z)} + \epsilon_\mu(z),$$

$$\mathbf{P}(z) = \sum_\mu \mathbf{P}_\mu(z),$$

where $M_\mu = mN_\mu$ is the mass of cell μ.

We will assume that the system is at equilibrium, which means that the effective probability density $\rho^{\mathrm{eq}}(z)$ of finding a particular value of z is a function of the dynamical invariants of the system only. If we assume that these invariants are known with precision, the equilibrium distribution function is given by the molecular ensemble

$$\rho^{\mathrm{eq}}(z) = \frac{1}{N_0!\Omega_0}\delta(\mathbf{P}(z) - \mathbf{P}_0)\delta(H(z) - E_0),$$

where $\mathbf{P}_0$ is the total momentum of the system and E_0 the total energy. The factor $N_0!$ is quantum mechanically in origin (it comes from the undistinguishability of the particles) and solves the Gibbs paradox (and makes the macroscopic entropy a first order function of energy and number of particles). The normalization factor Ω_0 is given by

$$\Omega_0 = \Omega(U_0, N_0, V_0) = \int \frac{dz}{N_0!}\delta(\mathbf{P}(z) - \mathbf{P}_0)\delta(H(z) - E_0).$$

Here, $U_0 = E_0 - P_0^2/2M_0$ is the internal energy of the total system and the total volume V_0 appears parametrically as the region of integration of positions. The *macroscopic* entropy for this system is defined as

$$S^{\mathrm{mac}}(U, N, V) = k_B \ln \Omega_0(U, N, V).$$

The intensive parameters are defined as the derivatives of the macroscopic entropy, this is,

$$\frac{1}{T} = \frac{\partial S^{\mathrm{mac}}}{\partial U},$$

$$\frac{\mu}{T} = \frac{\partial S^{\mathrm{mac}}}{\partial N},$$

$$-\frac{P}{T} = \frac{\partial S^{\mathrm{mac}}}{\partial V},$$

where T is the temperature, μ the chemical potential, and P the pressure.

6.7.1   Calculation of $P[N, P, \epsilon]$

The probability that a set of functions $X(z)$ take particular values x when the system is at equilibrium is given by

$$P(x) = \int dz \delta(X(z) - x)\rho^{\text{eq}}(z),$$

where $\rho^{\text{eq}}(z)$ is the equilibrium ensemble. We now consider the functions $X(z)$ that appear in Eqn. (7.2.4) to be the set of mesoscopic variables (6.7). In this way, the probability that the system adopts a particular set of values $N_\mu, \mathbf{P}_\mu, \epsilon_\mu$ for each cell is given by

$$P[N, \mathbf{P}, \epsilon] = \int dz \rho^{\text{eq}}(z) \prod_\mu^M \chi(N_\mu(z) - N_\mu)$$

$$\times \qquad\qquad\qquad\qquad \delta(\mathbf{P}_\mu(z) - \mathbf{P}_\mu)\,\delta(\epsilon_\mu(z) - \epsilon_\mu).$$

In this expression, we have introduced the characteristic function $\chi(N_\mu(z) - N_\mu)$ that takes the value 1 (not infinity) for the region of phase space in which the microstate z produces exactly the value N_μ for the number of particles in cell μ. The probability (6.7.1) is normalized according to

$$\int d\mathbf{P}_1 \ldots d\mathbf{P}_M \int d\epsilon_1 \ldots d\epsilon_M \sum_{N_1,\ldots,N_M}^{N_0} P[N, \mathbf{P}, \epsilon] = 1,$$

where the numbers N_μ are subject to $\sum_\mu N_\mu = N_0$. By using the equilibrium ensemble (6.7) and Eqns. (6.7) we obtain

$$P[N, \mathbf{P}, \epsilon] = \frac{1}{\Omega_0} \delta\left(\sum_\mu^M \mathbf{P}_\mu - \mathbf{P}_0\right)$$

$$\times \qquad\qquad\qquad\qquad \delta\left(\sum_\mu^M \left(\frac{\mathbf{P}_\mu^2}{2M_\mu} + \epsilon_\mu\right) - E_0\right)$$

$$\times \qquad\qquad \int \frac{dz}{N_0!} \prod_\mu^M \chi(N_\mu(z) - N_\mu)\delta(\mathbf{P}_\mu(z) - \mathbf{P}_\mu)$$

$$\times \qquad\qquad\qquad\qquad \delta(\epsilon_\mu(z) - \epsilon_\mu).$$

The term $\prod_\mu^M \chi(N_\mu(z) - N_\mu)$ within the integral is zero unless the microstate z is such that there are exactly N_1 particles in the first cell, N_2 in the second, etc. There are $N_0!/N_1! \cdots N_M!$ ways of having the N_0 particles distributed among the M cells with the

prescribed numbers in each cell. Therefore, we can write

$$\int \frac{dz}{N_0!} \prod_\mu^M \chi(N_\mu(z) - N_\mu)\delta(\mathbf{P}_\mu(z) - \mathbf{P}_\mu)\delta(\epsilon_\mu(z) - \epsilon_\mu)$$

$$= \frac{1}{N_1! \cdots N_M!} \int_{\mathscr{V}_1} \underbrace{d\mathbf{q} \ldots d\mathbf{q}}_{N_1} \cdots \int_{\mathscr{V}_M} \underbrace{d\mathbf{q} \ldots d\mathbf{q}}_{N_M}$$

$$\times \int d\mathbf{p}_1 \ldots d\mathbf{p}_M \prod_\mu^M \delta \left(\sum_{i_\mu}^{N_\mu} \mathbf{p}_{i_\mu} - \mathbf{P}_\mu \right)$$

$$\times \delta \left(\sum_{i_\mu}^{N_\mu} \left(\frac{1}{2m} \left(\mathbf{p}_{i_\mu} - \frac{\mathbf{P}_\mu}{N_\mu} \right)^2 + \phi_{i_\mu} \right) - \epsilon_\mu \right)$$

$$= \frac{1}{N_1! \cdots N_M!} \int_{\mathscr{V}_1} \underbrace{d\mathbf{q}_1 \ldots d\mathbf{q}_{N_1}}_{N_1} \cdots \int_{\mathscr{V}_M} \underbrace{d\mathbf{q} \ldots d\mathbf{q}_M}_{N_M}$$

$$\times \prod_\mu^M \Phi(\mathbf{0}, \epsilon_\mu - \sum_{i_\mu}^{N_\mu} \phi_{i_\mu}, N_\mu),$$

where the function $\Phi(\mathbf{P}, E, N)$ is introduced and computed in the Appendix 6.8. The numbers $N_1, \ldots, N_M$ are subject to $\sum_\mu N_\mu = N_0$ and, therefore, we can extend the above result to arbitrary $N_1, \ldots, N_M$ provided that we multiply Eqn. (6.7.1) with the factor $\chi(\sum_\mu N_\mu - N_0)$, which takes the value 1 if its argument is zero.

Let us write now the potential energy of cell μ as follows,

$$\sum_{i_\mu}^{N_\mu} \phi_{i_\mu} = \frac{1}{2} \sum_{i_\mu}^{N_\mu} \sum_{j_\mu}^{N_\mu} \phi_{i_\mu j_\mu} + \frac{1}{2} \sum_\nu' \sum_{i_\mu}^{N_\mu} \sum_{j_\nu}^{N_\nu} \phi_{i_\mu j_\nu}.$$

The first term is the potential energy due to the particles of cell μ and it is a function solely of the coordinates of the particles that are in cell μ. The second term, the potential energy due to the interaction of particles in different cells, involve coordinates of particles in cells ν different from μ. It is this last term which hinders the decoupling of the integrals in positions in Eqn. (6.7.1). For this reason, it is necessary to make approximations to this last term. In what follows, we will approximate the potential energy due to different cells by a mean field constant (independent of coordinates of particles), this is,

$$\frac{1}{2} \sum_\nu' \sum_{i_\mu}^{N_\mu} \sum_{j_\nu}^{N_\nu} \phi_{i_\mu j_\nu} \approx \sum_\nu' \frac{1}{2} N_\mu N_\nu C_{\mu\nu}.$$

This approximation is fully justified when the potential $\phi(r)$ has two typical ranges, a short length scale r_s much smaller than the typical size of Voronoi cells and a long

length scale r_l much larger than the size of the cells. In this case, we can separate $\phi(r) = \phi^s(r) + \phi^l(r)$ and write

$$\frac{1}{2}\sum_{i_\mu}^{N_\mu}\sum_{j_\nu}^{N_\nu}\phi_{i_\mu j_\nu} \approx \frac{1}{2}\sum_{i_\mu}^{N_\mu}\sum_{j_\nu}^{N_\nu}\phi^l_{i_\mu j_\nu},$$

because the short range part is negligible for different cells $\mu \neq \nu$. Also, because the range r_l is much larger than the size of a cell, we can further approximate Eqn. (6.7.1) as if all particles in each cell where located at the center of the cell and, therefore, we can write

$$\frac{1}{2}\sum_{i_\mu}^{N_\mu}\sum_{j_\nu}^{N_\nu}\phi^l_{i_\mu j_\nu} \approx \frac{1}{2}\phi^l(R_{\mu\nu})N_\mu N_\nu,$$

and the potential energy due to different cells has the structure of Eqn. (6.7.1).

Under the mean field approximation (6.7.1), the different position integrals in (6.7.1) decouple, so that Eqn. (6.7.1) can be written as

$$\prod_\mu^M \left[\frac{1}{N_\mu!} \int_{\mathscr{V}_\mu} d\mathbf{q}_{1_\mu} \dots d\mathbf{q}_{N_\mu} \Phi(\mathbf{0}, \epsilon_\mu - \phi_\mu, N_\mu) \right],$$

where

$$\phi_\mu = \phi_\mu(\mathbf{q}_{1_\mu}, \dots, \mathbf{q}_{N_\mu}) = \frac{1}{2}\sum_{i_\mu}^{N_\mu}\sum_{j_\mu}^{N_\mu}\phi_{i_\mu j_\mu} + \overline{\phi}_\mu$$

$$\overline{\phi}_\mu = \frac{1}{2}\sum_\nu{}' \phi^l(R_{\mu\nu})N_\mu N_\nu,$$

where $\overline{\phi}_\mu$ is the mean field inter-cell potential energy of cell μ.

We can write Eqn. (6.7.1) as

$$\prod_\mu^M \Omega^{\mathrm{hc}}(\epsilon_\mu - \overline{\phi}_\mu, N_\mu, \mathscr{V}_\mu),$$

where $\Omega^{\mathrm{hc}}(U, N, V)$ is defined in Eqn. (6.7). Note that the Hamiltonian that should appear in Eqn. (6.7) is that of a system of particles interacting through the short range part of the potential $\phi^s(r)$. Finally, Eqn. (6.7.1) can be written as

$$P[N, \mathbf{P}, \epsilon] = \frac{1}{\Omega_0} \chi \left(\sum_{\mu}^{M} N_{\mu} - N_0 \right) \delta \left(\sum_{\mu}^{M} \mathbf{P}_{\mu} - \mathbf{P}_0 \right)$$

$$\times \qquad\qquad\qquad\qquad \delta \left(\sum_{\mu}^{M} \left(\frac{\mathbf{P}_{\mu}^2}{2M_{\mu}} + \epsilon_{\mu} \right) - E_0 \right)$$

$$\times \qquad\qquad\qquad\qquad\qquad\qquad \exp \left\{ S[N, \epsilon]/k_B \right\},$$

where the entropy functional at the mesoscopic level is defined by

$$S[N, \epsilon] = \sum_{\mu} S^{\mathrm{hc}}(\epsilon_{\mu} - \overline{\phi}_{\mu}, N_{\mu}, \mathscr{V}_{\mu}),$$

where we have used Eqn. (6.7). The mesoscopic entropy is given in terms of the sum of the *macroscopic* entropies of each cell, as if they were isolated systems in a volume $\mathscr{V}_{\mu}$, with number of particles N_{μ} and with an energy $\epsilon_{\mu} - \overline{\phi}_{\mu}$. The internal energy ϵ_{μ} in (6.7) includes in its microscopic definition the potential energy of particles that interact with particles of neighboring cells, that is, ϵ_{μ} includes the inter-cell energy. In this way, $\epsilon_{\mu} - \overline{\phi}_{\mu}$ represents the purely internal energy due to the particles within the cell (in mean field). Even though we have made progress in writing the probability for the mesoscopic variables, Eqn. (6.7.1), the entropy of each cell $S^{\mathrm{hc}}(\epsilon_{\mu}, \mathscr{V}_{\mu}, N_{\mu})$ is still an unknown quantity. We remark that this entropy is the macroscopic entropy of a system of molecules interacting with the short range part of the potential. In applications of the model, this entropy will be given by simple models (see Appendix 6.9) or by very accurate expressions like the Carnahan-Starling equation of state [?].

Apparently, Eqn. (6.7.1) simply says that "the entropy is additive". However, this sentence is imprecise: The entropy $S[N, \epsilon]$ in the lhs of Eqn. (6.7.1) is a different object from the entropy $S^{\mathrm{hc}}(\epsilon_{\mu}, N_{\mu}, \mathscr{V}_{\mu})$ appearing in the rhs. They depend on a different number of variables. Therefore, one should rather say that "the mesoscopic entropy at the level of hydrodynamic variables is the sum of the entropy at the level of dynamical invariants (the macroscopic entropy) of each cell as if they were isolated".

The macroscopic entropy is a first order function of its variables and therefore,

$$S[N, \epsilon] = \sum_{\mu} \mathscr{V}_{\mu} S^{\mathrm{hc}} \left(\frac{\epsilon_{\mu}}{\mathscr{V}_{\mu}} - \frac{\overline{\phi}_{\mu}}{\mathscr{V}_{\mu}}, \frac{N_{\mu}}{\mathscr{V}_{\mu}}, 1 \right)$$

which admits the continuum *notation*

$$S[n_{\mathbf{r}}, \epsilon_{\mathbf{r}}] = \int d\mathbf{r} \, s^{\mathrm{hc}}(\epsilon_{\mathbf{r}} - \overline{\phi}_{\mathbf{r}}, n_{\mathbf{r}}),$$

where we have introduced the continuum version of the effective interaction energy between molecules in different points of space (cells),

$$
\begin{aligned}
\mathbf{R}_\mu &\to & \mathbf{r}, \\
\sum_\mu \mathscr{V}_\mu &\to & \int d\mathbf{r}, \\
\frac{\epsilon_\mu}{\mathscr{V}_\mu} &\to & \epsilon_\mathbf{r}, \\
\frac{N_\mu}{\mathscr{V}_\mu} &\to & n_\mathbf{r}, \\
\frac{\overline{\phi}_\mu}{\mathscr{V}_\mu} &\to & \overline{\phi}_\mathbf{r}.
\end{aligned}
$$

Note that in this continuum notation we can write the dynamical invariants (6.7) of the system as

$$
E = \int d\mathbf{r} \left(\frac{1}{2} \frac{\mathbf{g_r}}{m n_\mathbf{r}} + \epsilon_\mathbf{r} \right),
$$

$$
P = \int d\mathbf{r} \mathbf{g_r},
$$

where $\mathbf{P}_\mu / \mathscr{V}_\mu \to \mathbf{g_r}$ is the momentum density field. We stress that we regard Eqn. (6.7.1) not as an strict mathematical limit in which the volume of the cells tend to zero, but rather as a convenient notational tool.

In spite of its apparent form, the mesoscopic entropy (6.7.1) is *not local* in space. This is, it is not given by a sum of a function of the variables at a given point. This is due to the presence of the term $\overline{\phi}_\mathbf{r}$ which can be written in continuous notation as

$$
\overline{\phi}_\mathbf{r} = \int d\mathbf{r}' \phi^l(|\mathbf{r} - \mathbf{r}'|) n_\mathbf{r} n_{\mathbf{r}'}.
$$

We have implicitly associated the potential energy of interaction with other cells $\overline{\phi}_\mathbf{r}$ with the phenomena of surface tension. In order to make this connection more explicit, in the following subsections we consider the marginal probability distribution functions and will make contact with the Density Functional Theory.

6.7.2 The marginal distribution $P[N, \epsilon]$

By integrating the distribution function $P[N, \mathbf{P}, \epsilon]$ over momenta we will have the probability of a realization of the "fields" N, ϵ irrespective of the values of the momenta in each cell, this is

$$P[N, \epsilon] = \exp\left\{S[N, \epsilon]/k_B\right\} \frac{1}{\Omega_0} \chi\left(\sum_\mu^M N_\mu - N_0\right)$$

$$\times \qquad\qquad\qquad\qquad \int d\mathbf{P}_1 \ldots d\mathbf{P}_M \delta\left(\sum_\mu^M \mathbf{P}_\mu - \mathbf{P}_0\right)$$

$$\times \qquad\qquad\qquad\qquad \delta\left(\sum_\mu^M\left(\frac{\mathbf{P}_\mu^2}{2M_\mu} + \epsilon_\mu\right) - E_0\right)$$

$$= \exp\left\{S[N, \epsilon]/k_B\right\} \frac{1}{\Omega_0} \chi\left(\sum_\mu^M N_\mu - N_0\right)$$

$$\times \qquad\qquad\qquad \prod_\mu^M (2mN_\mu)^{D/2} \frac{\omega_{D(M-1)}}{2}\left[U_0 - \sum_\mu \epsilon_\mu\right]^{\frac{D(M-1)}{2} - 1},$$

where we have used once more Eqn. (6.8) in the appendix.

The most probable realization $N_1^*, \ldots, N_M^*, \epsilon_1^*, \ldots, \epsilon_M^*$ of the fields is the one which maximizes the functional

$$k_B^{-1} S[N, \epsilon] + \left(\frac{D(M-1)}{2} - 1\right)\log\left(U_0 - \sum_\mu \epsilon_\mu\right)$$

$$+ \frac{D}{2}\sum_\mu \log(2mN_\mu) + \beta\lambda\sum_\mu N_\mu,$$

where we have introduce the Lagrange multiplier $\beta\lambda$ that takes into account the restriction $\sum_\mu N_\mu = N_0$ The maximum N^*, ϵ^* of the functional (6.7.2) is the solution of the following set of equations

$$\frac{\partial S}{\partial N_\mu}[N^*, \epsilon^*] = k_B\beta\lambda,$$

$$\frac{\partial S}{\partial \epsilon_\mu}[N^*, \epsilon^*] = \frac{(\frac{D(M-1)}{2} - 1)k_B}{U_0 - \sum_\nu \epsilon_\nu^*},$$

$$\sum_\mu N_\nu^* = N_0.$$

We have neglected a term of order N_μ^{-1} in the first equation, which is reasonable if typically there are many particles in each cell. Eqns. (6.7.2) is a set of $2M + 1$ equations for the unknowns $N_\mu^*, \epsilon_\mu^*, \lambda$. Note that the solution $N_\mu^*, \epsilon_\mu^*, \beta\lambda$ depends parametrically on N_0, U_0.

We find now a convenient approximation to Eqn. (6.7.2) by noting that this prob-

ability is expected to be highly peaked around the most probable state. Therefore, for those values of the field ϵ for which $P[N, \epsilon]$ is appreciably different from zero (that is, around ϵ^*), we can approximate

$$\left[U_0 - \sum_\mu \epsilon_\mu \right]^P = \left[U_0 - \sum_\mu \epsilon_\mu^* \right]^P$$

$$\times \qquad \left[1 + \frac{\beta}{P} \sum_\mu (\epsilon_\mu^* - \epsilon_\mu) \right]^P$$

$$\approx \qquad \left[U_0 - \sum_\mu \epsilon_\mu^* \right]^P \exp\{\beta \sum_\mu (\epsilon_\mu^* - \epsilon_\mu)\}$$

$$= \text{ctn.} \exp\{-\beta \sum_\mu \epsilon_\mu\},$$

where $P = D(M-1)/2 - 1$ is a very large number and we have introduced

$$\beta = \frac{D(M-1)/2 - 1}{U_0 - \sum_\nu \epsilon_\nu^*}.$$

Note that β is proportional to the inverse of the most probable value of the kinetic energy per cell.

Finally, we can write Eqn. (6.7.2) as

$$P[N, \epsilon] = \frac{1}{\Omega_0'} \exp\left\{ S[N, \epsilon]/k_B - \beta \sum_\mu \epsilon_\mu \right\}$$

$$\times \qquad \chi \left(\sum_\mu N_\mu - N_0 \right),$$

where Ω_0' is the corresponding normalization function. We see, therefore, that by integrating the momenta the "microcanonical" form Eqn. (6.7.1) becomes the "canonical" form (6.7.2).

6.7.3   The marginal distribution $P[N]$

There are two different routes to compute the probability of a certain distribution $N_1, \ldots, N_M$ of the particles in the cells. We could simply start the calculation from Eqn. (6.7.1) without the momentum and energy conserving delta functions. This route is essentially the one taken by van Kampen [?]. The alternative is to integrate out the energy field in Eqn. (6.7.2). The same results are obtained in both approaches and we illustrate here this second one, this is,

$$P[N] = \int d\epsilon_1 \ldots d\epsilon_M P[N, \epsilon]$$

$$= \frac{1}{Z_0} \exp\left\{ -\beta \sum_\mu F^{\mathrm{hc}}(\beta, N_\mu, \mathscr{V}_\mu) - \beta \overline{\phi}_\mu \right\}$$

$$\times \qquad\qquad\qquad \chi\left(\sum_\mu^M N_\mu - N_0 \right),$$

where we have used the form (6.7.1) for the entropy function, we have changed variables to $\epsilon'_\mu = \epsilon_\mu - \overline{\phi}_\mu$ and have introduced the macroscopic free energy $F^{\mathrm{hc}}(\beta, N, V)$ of a system of N particles at inverse temperature β in a volume V, and interacting with a short range potential. In deriving Eqn. (6.7.3) we have made use of the following identity

$$\int_0^\infty \exp\{S(U)/k_B - \beta U\}dU = \exp\{-\beta F(\beta)\}.$$

This expression is the statistical mechanics link between the macroscopic entropy and the free energy and can be proved by computing the Laplace transform of Ω_0 in Eqn. (6.7). One has

$$\int_0^\infty \Omega_0(U, N, V) \exp -\{\beta U\}dU$$

$$= \int dz \delta(\sum_i \mathbf{p}_i) \exp -\{\beta H(z)\} = Z(\beta, N - 1, V),$$

where the partition function $Z(\beta)$ is defined through this equation. The presence or absence of the momentum conservation delta function is irrelevant when the number of particles is large so we may very well drop it. The free energy $F(\beta)$ is defined as

$$\beta F(\beta) = -\ln Z(\beta),$$

The usual thermodynamic link between entropy and free energy,

$$F(T, N, V) = U - TS(U, N, V),$$

can be obtained under the assumption that the integrand in (6.7.3) is highly peaked.

6.8   Appendix: Molecular ensemble

In this appendix we compute explicitly the following integral

$$\Phi(\mathbf{P}_0, E_0, M) = \int d^{DM}\mathbf{p}\; \delta\left(\sum_i^M \frac{\mathbf{p}_i^2}{2m_i} - E_0\right)$$

$$\times \qquad\qquad\qquad \delta^D\left(\sum_i^M \mathbf{p}_i - \mathbf{P}_0\right),$$

which appears repeatedly when computing molecular averages. By a simple change of variables we obtain

$$\Phi(\mathbf{P}_0, E_0, M) = \prod_i^M (2m_i)^{D/2} \int d^{DM}\mathbf{p}\; \delta\left(\sum_i^M \mathbf{p}_i^2 - E_0\right)$$

$$\times \qquad\qquad\qquad \delta^D\left(\sum_i^M (2m_i)^{1/2}\mathbf{p}_i - \mathbf{P}_0\right),$$

The equation $\sum_i^M (2m_i)^{1/2}\mathbf{p}_i = \mathbf{P}_0$ are actually D equations (one for each component of the momentum) which define D planes in R^{DM}. The integral in (24.6.1) is actually over a submanifold which is the intersection of the D planes with the surface of a DM dimensional sphere of radius $E_0^{1/2}$. This intersection will be also a sphere, which will be now of smaller radius and also of smaller dimension, $D(M-1)$.

In order to compute (24.6.1), we change to the following notation

$$\mathcal{P} = (p_1^x, \ldots, p_M^x, p_1^y, \ldots, p_M^y, p_1^z, \ldots, p_M^z)$$
$$\mathcal{C}_x = ((2m_1)^{1/2}, \ldots, (2m_M)^{1/2}, 0, \ldots, 0, 0, \ldots, 0)$$
$$\mathcal{C}_y = (0, \ldots, 0, (2m_1)^{1/2}, \ldots, (2m_M)^{1/2}, 0, \ldots, 0)$$
$$\mathcal{C}_z = (0, \ldots, 0, 0, \ldots, 0, (2m_1)^{1/2}, \ldots, (2m_M)^{1/2}).$$

Note that these vectors satisfy $\mathcal{C}_x\cdot\mathcal{C}_y = 0\; \mathcal{C}_y\cdot\mathcal{C}_z = 0\; \mathcal{C}_z\cdot\mathcal{C}_x = 0$. With these vectors so defined, Eqn. (24.6.1) becomes

$$\Phi(\mathbf{P}_0, E_0, M) = \int d^{DM}\mathcal{P}\delta\left(\mathcal{P}^2 - E_0\right)\; \delta(\mathcal{C}_x\cdot\mathcal{P} - P_0^x)$$

$$\times \qquad\qquad\qquad \delta(\mathcal{C}_y\cdot\mathcal{P} - P_0^y)\; \delta(\mathcal{C}_z\cdot\mathcal{P} - P_0^z)$$

$$\times \qquad\qquad\qquad \prod_i^M (2m_i)^{D/2}.$$

Now we consider the following change of variables

$$\mathscr{P}' = \mathscr{P} - \left(\frac{\mathscr{C}_x}{|\mathscr{C}_x|^2} P_0^x + \frac{\mathscr{C}_y}{|\mathscr{C}_y|^2} P_0^y + \frac{\mathscr{C}_z}{|\mathscr{C}_z|^2} P_0^z \right),$$

which is simply a translation and has unit Jacobian. Simple algebra leads to

$$\Phi(\mathbf{P}_0, E_0, M) = \prod_i^M (2m_i)^{D/2} \int d^{DM} \mathscr{P}' \, \delta\big(\mathscr{P}'^2 - U_0\big)$$

$$\times \qquad\qquad\qquad\qquad \delta\big(\mathscr{C}_x \cdot \mathscr{P}'\big) \, \delta\big(\mathscr{C}_y \cdot \mathscr{P}'\big) \, \delta\big(\mathscr{C}_z \cdot \mathscr{P}'\big),$$

where we have introduced the total internal energy

$$U_0 = \left(E_0 - \frac{\mathbf{P}_0^2}{2\mathscr{M}_0} \right),$$

where $\mathscr{M}_0 = \sum_i m_i$ is the total mass.

We now consider a second change of variables $\mathscr{P}'' = \mathbf{\Lambda} \cdot \mathscr{P}'$ through a rotation $\mathbf{\Lambda}$ such that

$$\mathbf{\Lambda}\mathscr{C}_x = (1, \ldots, 0, 0, \ldots, 0, 0, \ldots, 0)$$
$$\mathbf{\Lambda}\mathscr{C}_y = (0, \ldots, 0, 1, \ldots, 0, 0, \ldots, 0)$$
$$\mathbf{\Lambda}\mathscr{C}_z = (0, \ldots, 0, 0, \ldots, 0, 1, \ldots, 0).$$

It is always possible to find a matrix $\mathbf{\Lambda}$ that satisfies Eqns. (6.8). For example, consider a block diagonal matrix made of three identical blocks of size $M \times M$. Then assume that each block is the same orthogonal matrix which transforms the vector $((2m_1)^{1/2}, (2m_2)^{1/2}, \ldots, (2m_M)^{1/2})$ into $(2\mathscr{M}_0)^{1/2}(1, 0, \ldots, 0)$. After the rotation (which has unit Jacobian and leaves the modulus of a vector invariant) the integral (24.6.1) becomes

$$\Phi = \prod_i^M (2m_i)^{D/2} \int d^{DM} \mathscr{P}'' \delta\big(\mathscr{P}''^2 - U_0\big)$$

$$\times \qquad\qquad\qquad\qquad \delta(p_1''^x) \, \delta(p_1''^y) \, \delta(p_1''^z)$$

$$= \prod_i^M (2m_i)^{D/2} \int d^{D(M-1)} \mathscr{P}'' \delta\big(\mathscr{P}''^2 - U_0\big) .$$

We compute now the integral over the sphere in Eqn. (24.6.10) by using that the integral of an arbitrary function $F(\mathbf{x}) = f(|\mathbf{x}|)$ that depends on $\mathbf{x}$ only through its

modulus $|\mathbf{x}|$ can be computed by changing to polar coordinates

$$\int F(\mathbf{x})d^M\mathbf{x} = \omega_M \int_0^\infty f(r)r^{M-1}dr.$$

The numerical factor ω_M, which comes from the integration of the angles, can be computed by considering the special case when $f(r)$ is a Gaussian. The result is

$$\omega_M = 2\frac{\pi^{M/2}}{\Gamma(M/2)}$$

By using Eqn. (24.5.1), Eqn. (24.6.10) becomes

$$\Phi(\mathbf{P}_0, E_0, M) = \prod_i^M (2m_i)^{D/2}\omega_{D(M-1)}$$

$$\times \qquad \int dp\, p^{D(M-1)-1}\, \delta\!\left(p^2 - U\right).$$

We need now the property

$$\delta(f(x)) = \sum_i \frac{\delta(x - x_i)}{|f'(x_i)|}$$

where x_i are the zeros of $f(x_i) = 0$. For the case of Eqn. (6.8) we have $f(x) = x^2 - U$, $x_i = \pm(U)^{1/2}$ and $f'(x) = 2x$. Therefore,

$$\Phi(\mathbf{P}_0, E_0, M) = \frac{1}{2}\omega_{D(M-1)}U_0^{\frac{D(M-1)-2}{2}} \prod_i^M (2m_i)^{D/2}.$$

6.9 Appendix: van der Waals and hard core models

The particular functional form of $s^{\mathrm{hc}}(\epsilon, \rho)$ cannot be computed from the microscopic analysis presented in the previous appendix. The approach taken in this paper is that this fundamental thermodynamic equation (in the sense of Callen [?]) is known either from empirical sources or by suitable modelling. In this appendix we summarize the results for the fundamental equation of van der Waals model and for its corresponding hard core model.

The van der Waals model can be defined through the following fundamental equation, which relates the entropy density with the internal energy density ϵ and number density n,

$$s^{\mathrm{vdW}}(\epsilon, n) = \frac{D+2}{2}k_B n - k_B n \ln\left(\frac{\left[\Lambda^{\mathrm{vdW}}(\epsilon, n)\right]^D n}{1 - nb}\right).$$

The number density is $n = \rho/m_0$ where ρ is the mass density and m_0 is the mass of a molecule. The thermal wavelength is defined by

$$\Lambda^{\mathrm{vdW}}(\epsilon, n) = \frac{h}{(2\pi m_0 k_B \mathscr{T}^{\mathrm{vdW}}(\epsilon, n))^{1/2}},$$

and we have introduced the function

$$\mathscr{T}^{\mathrm{vdW}}(\epsilon, n) = \frac{2}{D} \frac{\epsilon + an^2}{k_B n}.$$

The two equations of state are the derivatives of the entropy with respect to each variable

$$\frac{\partial s^{\mathrm{vdW}}}{\partial \epsilon} = \frac{1}{T^{\mathrm{vdW}}(\epsilon, n)},$$

$$\frac{\partial s^{\mathrm{vdW}}}{\partial n} = -\frac{\mu^{\mathrm{vdW}}(\epsilon, n)}{T^{\mathrm{vdW}}(\epsilon, n)},$$

where T^{vdW} is the temperature and μ^{vdW} is the chemical potential. Straightforward calculations lead to

$$T^{\mathrm{vdW}}(\epsilon, n) = \mathscr{T}^{\mathrm{vdW}}(\epsilon, n),$$

$$\mu^{\mathrm{vdW}}(\epsilon, n) = k_B T^{\mathrm{vdW}} \left(\ln \left(\frac{n[\Lambda^{\mathrm{vdW}}]^D}{1 - nb} \right) + \frac{nb}{1 - nb} \right) - 2an.$$

The third equation of state can be obtained from the Euler equation $P = Ts - \epsilon + \mu n$, which leads to

$$P^{\mathrm{vdW}}(\epsilon, n) = n\frac{k_B T^{\mathrm{vdW}}(\epsilon, n)}{1 - nb} - an^2.$$

The hard core model that corresponds to the van der Waals model can be defined as the model that results from taking the attractive parameter $a = 0$ in the van der Waals model. This model is essentially the gas ideal model but with excluded volume effects. In this way, one obtains

$$s^{\mathrm{hc}}(\epsilon, n) = \frac{D + 2}{2} k_B n - k_B n \ln \left(\frac{\Lambda^{\mathrm{hc}D}(\epsilon, n)n}{1 - nb} \right),$$

where now

$$\Lambda^{\mathrm{hc}}(\epsilon, n) = \frac{h}{(2\pi m_0 k_B \mathscr{T}^{\mathrm{hc}}(\epsilon, n))^{1/2}},$$

$$\mathscr{T}^{\mathrm{hc}}(\epsilon, n) = \frac{2}{D} \frac{\epsilon}{k_B n}.$$

The equations of state are now

$$T^{\text{hc}}(\epsilon, n) = \mathscr{T}^{\text{hc}}(\epsilon, n),$$

$$\mu^{\text{hc}}(\epsilon, n) = k_B T^{\text{vdW}} \left(\ln \left(\frac{n[\Lambda^{\text{hc}}]^D}{1 - nb} \right) + \frac{nb}{1 - nb} \right),$$

$$P^{\text{hc}}(\epsilon, n) = n \frac{k_B T^{\text{hc}}(\epsilon, n)}{1 - nb}.$$

Note that the following functional relations hold

$$T^{\text{hc}}(u + an^2, n) = T^{\text{vdW}}(u, n),$$

$$P^{\text{hc}}(u + an^2, n) - an^2 = P^{\text{vdW}}(u, n),$$

$$\mu^{\text{hc}}(u + an^2, n) - 2an = \mu^{\text{vdW}}(u, n).$$

7

Liquid-liquid: Fluid mixtures $\rho_{\mathbf{r}}^1, \rho_{\mathbf{r}}^2, \mathbf{g_r}, e_{\mathbf{r}}$

Mass density of specie k velocity of the fluid and tempertature.

The hydrodynamic equations of a phase-separating fluid mixture are derived from the underlying microscopic dynamics of the system. A projection operator method is used in the GENERIC form [H.C. Öttinger, Phys. Rev E, **57**, 1416 (1998).] In this way, the thermodynamic consistency of the final equations is apparent. The microscopic potential is separated into short and long range parts, in the spirit of the original work of van der Waals. Explicit expressions for surface tension terms in the hydrodynamic equations are obtained. These terms describe diffuse interfaces in the system. Miscible-immiscible and gas-liquid phase transitions are possible, non-isothermal situations can be studied, and explicit account of cross effects is taken.

7.1 Introduction

Fluid mixtures at equilibrium may present a very rich phase diagram which increases in complexity with the number of different species. The equilibrium phase diagram is determined by the free energy of the system for which many models exist, as presented in the excellent textbook by Davis [**?**]. Of outstanding importance is the van der Waals model that allows to understand qualitatively and, sometimes, quantitatively the phase behaviour of these fluid systems [**?**]. According to the van der Waals picture, phase transitions and surface tension effects in mixtures can be explained by assuming that the potential of interaction $\phi_{i_\alpha j_\beta}$ between molecules of species α, β can be expressed as the sum of two contributions,

$$\phi_{i_\alpha j_\beta} = \hat{\phi}^{\alpha\beta}(\mathbf{q}_{i_\alpha} - \mathbf{q}_{j_\beta}) + \overline{\phi}^{\alpha\beta}(\mathbf{q}_{i_\alpha} - \mathbf{q}_{j_\beta})$$

Here, $\mathbf{q}_{i_\alpha}$ is the position of the i-th molecule of species α and $\hat{\phi}^{\alpha\beta}(r) \geq 0$ is a short range repulsive (hard core) part and $\overline{\phi}^{\alpha\beta}(r) \leq 0$ is a long range attractive tail [**?**]. Realistic

potentials can be decomposed usually in the above way. However, one of the assumptions in the van der Waals model is that the range of the long range potential is *much* larger than the range of the hard core potential [?]. Although this is not the case for realistic potentials, the van der Waals picture seems to be more general than what its assumptions suggest [?],[?].

In this paper, we want to contribute to the theoretical understanding of the interplay of equilibrium phase transitions and hydrodynamics, by formulating in a thermodynamically consistent way the hydrodynamic equations of a mixture of fluids that display phase separation. Although the hydrodynamic equations for mixtures of liquids are well-known and different approaches have been considered for their derivation ranging from kinetic theory [?], microscopic derivations [?],[?] or phenomenological approaches [?],[?],[?], what seems to be lacking is the formulation of the general hydrodynamic equations when phase transitions and surface tension effects are present. A promising approach for dealing with the dynamics of phase separating mixtures is based on the phase field method [?]. Within this context several derivations of the hydrodynamic equations for phase separating fluids have been proposed based on *phenomenological* linear irreversible thermodynamics [?],[?],[?]. We are not aware of any *microscopic* derivation of the hydrodynamics of phase separating fluids. It will become apparent that ambiguities in the definition of the hydrodynamic variables in the phenomenological approaches can be dispelled by resorting to a microscopic derivation.

The results presented in this paper can be understood as the answer to the following question: how the equilibrium van der Waals picture for a fluid mixture can be generalized to non-equilibrium situations? To this end, we derive the hydrodynamic equations for a phase separating mixture starting from the microscopic dynamics of the system, which is governed by a separable potential like in Eqn. (7.1). This is achieved by calculating the microscopically defined [?] building blocks of the recently developed framework for non-equilibrium thermodynamics known as GENERIC [?]. A similar approach has been taken for the case of a *simple fluid* without phase transitions in Ref. [?]. The hydrodynamic equations of a simple fluid able to display a gas-liquid phase transition have been presented within the GENERIC framework in Ref. [?].

Due to the large number of equations required in order to obtain the final hydrodynamic equations for a mixture starting from the microscopic dynamics of the system, we present in section 7.2 a summary and a discussion of the main results of the paper. This section should be sufficient for those readers who are not interested in the detailed microscopic calculations presented in latter sections. In section **??**, we present a summary of the GENERIC framework along with the microscopic definitions of its different building blocks. In section 7.3, we present the detailed calculation of these microscopically defined building blocks for the particular case of a mixture of fluids.

7.2   The hydrodynamic equations

In this section, we summarize the main results of this paper. The state x of a fluid mixture of r species, is described by the set of hydrodynamic variables, that is, the number density $n_{\mathbf{r}}^\alpha$ of species α, with $\alpha = 1, \ldots, r$, the momentum density $\mathbf{g_r}$ of the full mixture, and the internal energy density $\hat{\epsilon}_{\mathbf{r}}$, which are defined in terms of molecular

coordinates and momenta in Eqns. (7.3.1) in section 7.3. It is important to note that the molecular definition of the internal energy density field contains only the short range part $\hat{\phi}$ of the potential of Eqn. (7.1). In this way, the total energy of the system written in terms of the hydrodynamic variables is given by

$$E[x] = \int d\mathbf{r} \left(\frac{\mathbf{g_r}^2}{2\rho_\mathbf{r}} + \hat{\epsilon}_\mathbf{r} \right) + \overline{\Phi}$$

where we have introduced the total mass density field as

$$\rho_\mathbf{r} = \sum_\alpha^r m_\alpha n_\mathbf{r}^\alpha$$

and the contribution $\overline{\Phi}$ due to the long range part of the potential defined by

$$\overline{\Phi} = \frac{1}{2} \sum_{\alpha\beta} \int d\mathbf{r}d\mathbf{r}' n_\mathbf{r}^\alpha n_{\mathbf{r}'}^\beta \overline{\phi}^{\alpha\beta}(\mathbf{r} - \mathbf{r}')$$

where $\overline{\phi}^{\alpha\beta}(\mathbf{r} - \mathbf{r}')$ is the long range part of the potential of interaction between two molecules of species α and β located at $\mathbf{r}$ and $\mathbf{r}'$, respectively. This long range potential energy is a quadratic functional of the density fields. We recognize in Eqn. (7.2) the three contributions to the total energy of the fluid due to the kinetic energy of the fluid, the internal energy due to the hard core part of the potential and the final contribution due to the long range part of the potential. In this paper, variables with a hat such as $\hat{A}$ will refer to the hard core potential whereas variables with an overline such as $\overline{A}$ will refer to the long range potential.

The energy functional (7.2) is one of the building blocks of the GENERIC framework, as summarized in section **??**. Another building block is the entropy functional. Even though the equilibrium properties of an inhomogeneous fluid mixture can be fully understood from the *free energy functional* of the system, when considering inhomogeneous non-isothermal situations it is necessary to deal with *entropy functional* of the fluid mixture. By following the pioneering ideas of Green [**?**] and van Kampen [**?**], we compute in subsection 7.3.2 the entropy functional of a fluid mixture under the van der Waals approximation. Green computed the entropy of a simple fluid by assuming that the little cells in which the fluid is divided are essentially non-interacting, thus precluding the description of surface tension [**?**]. On the other hand, van Kampen derived the free energy functional for the van der Waals fluid with the possibility of describing surface tension effects, albeit for isothermal situations only [**?**].

The entropy functional in the van der Waals approximation has the following form for a binary mixture of species A, B

$$S[x] = \int d\mathbf{r} \hat{s}(n_\mathbf{r}^A, n_\mathbf{r}^B, \hat{\epsilon}_\mathbf{r})$$

where $\hat{s}(n^A, n^B, \hat{\epsilon})$ is the entropy density function of a system of A and B molecules *which are interacting with only the short range part of the potential $\hat{\phi}^{\alpha\beta}$,* as a function of the densities n^A and n^B and the internal energy $\hat{\epsilon}$. That the entropy functional contains only the short range part of the potential is a non-trivial result that follows from the van der Waals assumption (see section 7.3.2). We will not need in this paper the actual functional form of $\hat{s}(n^A, n^B, \hat{\epsilon})$. The original ideas of van der Waals suggest to use a simple excluded volume model, but more sophisticated expressions for hard core fluid mixtures can certainly be used.

The main result of this paper is the following set of hydrodynamic equations for a fluid mixture

$$\partial_t n^\alpha = -\nabla \mathbf{v} n^\alpha + \nabla \left(\sum_\beta D^{\alpha\beta} \hat{T} \nabla \left(\frac{\hat{\mu}^\beta}{\hat{T}} \right) \right) - \nabla \left(S^\alpha \hat{T}^2 \nabla \left(\frac{1}{\hat{T}} \right) \right) - \nabla \left(\sum_\beta D^{\alpha\beta} \overline{\mathbf{F}}^\beta \right)$$

$$\partial_t \mathbf{g} = -\nabla \cdot (\mathbf{g} \mathbf{v}) - \nabla \hat{P} - \nabla \hat{\mathbf{\Pi}} + \sum_\alpha n^\alpha \overline{\mathbf{F}}^\alpha$$

$$\partial_t \hat{\epsilon} = -\nabla \cdot (\mathbf{v} \hat{\epsilon}) - \hat{P} \nabla \cdot \mathbf{v} - \hat{\mathbf{\Pi}} : \nabla \mathbf{v} + \nabla \left(\sum_\alpha S^\alpha \hat{T}^2 \nabla \left(\frac{\hat{\mu}^\alpha}{\hat{T}} \right) \right) - \nabla \left(\hat{\kappa} \hat{T}^2 \nabla \left(\frac{1}{\hat{T}} \right) \right)$$

$$- \sum_{\alpha\beta} \left[\hat{T} \nabla \left(\frac{\hat{\mu}^\alpha}{\hat{T}} \right) - \overline{\mathbf{F}}^\alpha \right] D^{\alpha\beta} \overline{\mathbf{F}}^\beta - \nabla \left(\sum_\alpha S^\alpha \overline{\mathbf{F}}^\alpha \hat{T} \right) - \sum_\alpha S^\alpha \overline{\mathbf{F}}^\alpha \nabla \hat{T}$$

These equations have been derived from the microscopic dynamics in section 7.3. The quantities appearing in these equations are enumerated and defined in what follows. The temperature $\hat{T}$, chemical potential $\hat{\mu}^\alpha$ of species α, and pressure $\hat{P}$ are defined in the usual way [?] from the entropy density $\hat{s}$ introduced after Eqn. (7.2), this is

$$\frac{1}{\hat{T}} = \frac{\partial}{\partial \hat{\epsilon}} \hat{s}(n^A, n^B, \hat{\epsilon})$$

$$\frac{\hat{\mu}^A}{\hat{T}} = -\frac{\partial}{\partial n^A} \hat{s}(n^A, n^B, \hat{\epsilon})$$

$$\frac{\hat{\mu}^B}{\hat{T}} = -\frac{\partial}{\partial n^B} \hat{s}(n^A, n^B, \hat{\epsilon})$$

$$\hat{P} = \hat{T} \hat{s} - \hat{\epsilon} + \sum_\alpha n^\alpha \mu^\alpha$$

These intensive quantities become field quantities in Eqn. (7.2) when evaluated at the local values of $n_\mathbf{r}^\alpha, \hat{\epsilon}_\mathbf{r}$. It is quite remarkable that the equations of state appearing in the hydrodynamic equations (7.2) are those of the hard core system. This is a direct consequence of the functional form of the entropy functional in Eqn. (7.2).

The viscous stress tensor in Eqn. (7.2) has a usual form [?]

$$\hat{\mathbf{\Pi}} = -\hat{\eta} \left[\nabla \mathbf{v} + \nabla \mathbf{v}^T - \frac{2}{3} \nabla \cdot \mathbf{v} \mathbf{1} \right] - \hat{\zeta} \nabla \cdot \mathbf{v} \mathbf{1}$$

The shear and bulk viscosities $\hat{\eta}$ and $\hat{\zeta}$ are defined through the usual Green-Kubo expressions in Eqns. (7.3.5) in section 7.3. The rest of transport coefficients $D^{\alpha\beta}, S^{\alpha}, \hat{\kappa}$ in Eqns. (7.2) are related to mass diffusion, cross effects, and heat conductivity, respectively. Again, we have in Eqns. (7.3.5), (7.3.5), and (7.3.5) in section 7.3 their expression in terms of Green-Kubo formulae [?],[?],[?]. Not all the transport coefficients are independent, because momentum conservation implies the following conditions (see Eqns. (7.3.5) and (7.3.5) in section 7.3),

$$\sum_{\alpha} m_{\alpha} D_{\mathbf{r}}^{\alpha\beta} = \qquad\qquad 0$$

$$\sum_{\alpha} m_{\alpha} S_{\mathbf{r}}^{\alpha} = 0$$

The remaining quantity appearing in Eqns. (7.2) is the long range force $\overline{\mathbf{F}}_{\mathbf{r}}^{\alpha}$, which is defined by

$$\overline{\mathbf{F}}_{\mathbf{r}}^{\alpha} = \sum_{\beta} \int d\mathbf{r}' \overline{\mathbf{F}}_{\mathbf{r}\mathbf{r}'}^{\alpha\beta} n_{\mathbf{r}'}^{\beta}$$

and $\overline{\mathbf{F}}_{\mathbf{r}\mathbf{r}'}^{\alpha\beta}$ is the long range attractive force that a molecule of specie β at $\mathbf{r}'$ exerts on a molecule of specie α at $\mathbf{r}$. We can write this force in terms of the functional derivatives with respect to the density field of the total long range potential energy $\overline{\Phi}$ defined in Eqn. (7.2) as

$$\overline{\mathbf{F}}_{\mathbf{r}}^{\alpha} = -\nabla \frac{\delta \overline{\Phi}}{\delta n_{\mathbf{r}}^{\alpha}}$$

By neglecting in Eqn. (7.2) the terms containing the long range force $\overline{\mathbf{F}}_{\mathbf{r}}^{\alpha}$, we recover the equations for the diffusion of heat and mass of a mixture of hard core fluids [?],[?],[?]. We have made plausible in section 7.3 that, under the van der Waals assumptions, *all the transport coefficients correspond to those of a purely hard core system*. Therefore, Eqns. (7.2) are a generalization of the above mentioned equations whenever the potential of interaction can be decomposed, according to van der Waals, in terms of a hard core and a long range attractive tail. It is quite remarkable that the van der Waals approximation (7.1) for the intermolecular potential has a direct but non-trivial reflection in the hydrodynamic equations, where all the effects of the long range part of the potential are "superimposed" on the usual hydrodynamics of the hard core fluid. Note that when only one species is present, Eqns. (7.2) imply that the diffusion and cross-effect coefficients vanish. In this particular case, Eqns. (7.2) reduce to the hydrodynamic equations presented in Ref. [?] for a van der Waals simple fluid.

The simplest possible model for a hard core fluid mixture is the excluded volume model of van der Waals, that does not display phase separation [?]. The presence of the long range attractive tail of the potential is the responsible for the phase separation, either at equilibrium or in dynamic situations governed by Eqs. (7.2). As will be apparent in section 7.2.2, the long range force can be decomposed in two parts. One of them is

purely local and gives rise to typical van der Waals attractive terms in the thermodynamic pressure and chemical potentials. The other is non-local and is the responsible for the surface tension appearing at the interfaces that form when the mixture phase separate.

7.2.1   General properties

The set of equations (7.2) have the GENERIC structure, as shown in section 7.3. For this reason, they automatically satisfy that the total energy (7.2) is exactly conserved, and that the time derivative of the total entropy (7.2) is positive (positive entropy production). It can also be shown that the reversible part of equations (7.2), which is obtained by setting the transport coefficients to zero, produces no entropy. All these properties can be explicitly checked by direct calculation of the time derivatives of (7.2) and (7.2). In order to pursue this check, we should recall that the transport coefficients satisfy the conditions $D^{\alpha\alpha} > 0$, $\hat{\kappa} > 0$, and $D^{\alpha\alpha}\hat{\kappa} > \hat{T}S^{\alpha 2}$, as shown in section 7.4. Eqns. (7.2) also conserve the total momentum defined as

$$\mathbf{P} = \int d\mathbf{r}\mathbf{g_r}$$

By taking the time derivative of $\mathbf{P}$ and using the momentum equation in (7.2), we easily arrive at

$$\dot{\mathbf{P}} = \sum_{\alpha\beta} \int d\mathbf{r}d\mathbf{r}' n_{\mathbf{r}}^{\alpha} n_{\mathbf{r}'}^{\beta} \overline{\mathbf{F}}_{\mathbf{rr}'}^{\alpha\beta}$$

where we have neglected those terms that are the integral of a divergence, which can be converted to surface integrals. However, the remaining term is also zero because the long range force satisfies Newton's Third Law $\overline{\mathbf{F}}_{\mathbf{rr}'}^{\alpha\beta} = -\overline{\mathbf{F}}_{\mathbf{r}'\mathbf{r}}^{\beta\alpha}$ and, therefore, $\dot{\mathbf{P}} = 0$. Finally, the total mass of each species

$$M^{\alpha} = \int d\mathbf{r}m_{\alpha}n_{\mathbf{r}}^{\alpha}$$

is also a conserved quantity, as can be easily seen by computing its time derivative, using the density equations in Eqns. (7.2) together with properties (7.2).

Because $\dot{S}[x] \geq 0$, the state x of the fluid mixture will evolve according to Eqns. (7.2) towards higher values of the entropy functional but conserving the values of the energy, mass and momentum. The final equilibrium state of Eqns. (7.2) can be obtained then by maximizing the entropy functional in Eqn. (7.2) subjected to the restrictions of conservation of mass, momentum, and energy. This is, we maximize the functional

$$S[x] + \beta E[x] + \sum_{\alpha} \beta \lambda^{\alpha} N_{\alpha}[x] - \beta \mathbf{V}\cdot\mathbf{P}[x]$$

where β, λ^{α} and $\mathbf{V}$ are Lagrange multipliers. The result of the unrestricted maximization of (7.2.1) is simply

$$-\frac{\hat{\mu}^\alpha}{\hat{T}_\mathbf{r}} + \beta m_\alpha \frac{\mathbf{v}_\mathbf{r}^2}{2} + \beta \frac{\delta \Phi}{\delta n_\mathbf{r}^\alpha} + \beta \lambda^\alpha = 0$$

$$\frac{\mathbf{g}_\mathbf{r}}{\rho_\mathbf{r}} - \mathbf{V} = 0$$

$$\frac{1}{\hat{T}_\mathbf{r}} - \beta = 0$$

In words, the temperature field is constant at equilibrium, the velocity field is also constant (and we can choose without loosing generality $\mathbf{V} = 0$) and the chemical potential satisfies the following equation

$$\hat{\mu}_\mathbf{r}^\alpha - \frac{\delta \Phi}{\delta n_\mathbf{r}^\alpha} = \lambda^\alpha$$

7.2.2 Local approximation

Our claim is that Eqns. (7.2) describe the dynamics of a fluid mixture that can phase separate according to the van der Waals equation of state. This might not be obvious despite of the fact that the fundamental assumption (7.1) implicit in the van der Waals picture has been taken. In order to prove this statement and to make contact with gradient theories for phase separating fluids [?], we study a local approximation for the long range forces $\overline{\mathbf{F}}_\mathbf{r}^\alpha$ that appear in the hydrodynamic equations (7.2). If the space variations of the density field are small in the range of the attractive mean field potential, then we are allowed to perform the following local approximation [?]. From (7.2) it is easily shown that

$$\overline{\Phi} = -\frac{1}{2} \sum_{\alpha\beta} \int d\mathbf{r} n_\mathbf{r}^\alpha n_\mathbf{r}^\beta a_{\alpha\beta} - \frac{1}{4} \sum_{\alpha\beta} \int d\mathbf{r} \int d\mathbf{r}' \left[n_\mathbf{r}^\alpha - n_{\mathbf{r}'}^\alpha \right] \left[n_\mathbf{r}^\beta - n_{\mathbf{r}'}^\beta \right] \overline{\phi}_{\mathbf{r}\mathbf{r}'}^{\alpha\beta}$$

where

$$a_{\alpha\beta} = -\int d\mathbf{s} \overline{\phi}^{\alpha\beta}(\mathbf{s}) \geq 0$$

Under the assumption of slowly varying density fields, the last term in (7.2.2) can be Taylor expanded with the result

$$\overline{\Phi} = -\frac{1}{2} \sum_{\alpha\beta} a_{\alpha\beta} \int d\mathbf{r} n_\mathbf{r}^\alpha n_\mathbf{r}^\beta + \frac{1}{2} \sum_{\alpha\beta} c_{\alpha\beta} \int d\mathbf{r} \nabla n_\mathbf{r}^\alpha \cdot \nabla n_\mathbf{r}^\beta$$

where

$$c_{\alpha\beta} = -\frac{1}{6} \int d\mathbf{s} s^2 \overline{\phi}^{\alpha\beta}(\mathbf{s}) \geq 0$$

The first interesting consequence of this local approximation is obtained after substi-

tuting Eqn. (7.2.2) into the equilibrium condition (7.2.1)

$$\hat{\mu}_\mathbf{r}^\alpha + \sum_\beta a_{\alpha\beta} n_\mathbf{r}^\alpha + \sum_\beta c_{\alpha\beta} \nabla^2 n_\mathbf{r}^\alpha = \lambda^\alpha$$

We recognize in the term $\hat{\mu}_\mathbf{r}^\alpha + \sum_\beta a_{\alpha\beta} n_\mathbf{r}^\alpha$ the van der Waals expression for the chemical potential [?] and, therefore, the above equilibrium condition predicts the usual phase separation of a van der Waals mixture.

It is also illustrative to consider the momentum equation in (7.2) within this local approximation. The force $\overline{\mathbf{F}}_\mathbf{r}^\alpha$ can be computed from (7.2) and (7.2.2) and one obtains

$$\overline{\mathbf{F}}_\mathbf{r}^\alpha = \nabla \left(\sum_\beta a_{\alpha\beta} n_\mathbf{r}^\beta \right) + \sum_\beta c_{\alpha\beta} \nabla \nabla^2 n_\mathbf{r}^\beta$$

The effect of the long range force in the momentum equation in Eqns. (7.2) can be obtained by computing the term $\sum_\alpha n_\mathbf{r}^\alpha \overline{\mathbf{F}}_\mathbf{r}^\alpha$ as

$$\sum_\alpha n_\mathbf{r}^\alpha \overline{\mathbf{F}}_\mathbf{r}^\alpha = \nabla \left(\frac{1}{2} \sum_{\alpha\beta} a_{\alpha\beta} n_\mathbf{r}^\alpha n_\mathbf{r}^\beta \right) + \sum_{\alpha\beta} c_{\alpha\beta} n_\mathbf{r}^\alpha \nabla \nabla^2 n_\mathbf{r}^\beta$$

$$= -\nabla \left(-\frac{1}{2} \sum_{\alpha\beta} a_{\alpha\beta} n_\mathbf{r}^\alpha n_\mathbf{r}^\beta + \mathbf{P_r} \right)$$

where the surface stress tensor $\mathbf{P_r}$ is given by [?]

$$\mathbf{P}_\mathbf{r}^{\mu\nu} = \sum_{\alpha\beta} 2c_{\alpha\beta} \left[\frac{1}{6} \nabla^\mu n_\mathbf{r}^\alpha \nabla^\nu n_\mathbf{r}^\beta + \frac{1}{12} (\nabla n_\mathbf{r}^\alpha \cdot \nabla n_\mathbf{r}^\beta) \delta^{\mu\nu} - \frac{1}{3} n_\mathbf{r}^\alpha \nabla^\mu \nabla^\nu n_\mathbf{r}^\beta - \frac{1}{6} n_\mathbf{r}^\alpha \nabla^2 n_\mathbf{r}^\beta \delta^{\mu\nu} \right]$$

In this way, the momentum equation becomes

$$\partial_t \mathbf{g_r} = -\nabla \cdot (\mathbf{g_r} \mathbf{v_r}) - \nabla \left(\hat{P}_\mathbf{r} - \frac{1}{2} \sum_{\alpha\beta} a_{\alpha\beta} n_\mathbf{r}^\alpha n_\mathbf{r}^\beta \right) - \nabla \mathbf{P_r} - \nabla \hat{\Pi}_\mathbf{r}$$

We recognize in the combination $(\hat{P}_\mathbf{r} - \frac{1}{2} \sum_{\alpha\beta} a_{\alpha\beta} n_\mathbf{r}^\alpha n_\mathbf{r}^\beta)$ the van der Waals pressure of a fluid mixture [?], whereas the capillary stress tensor $\mathbf{P_r}$ in (7.2.2) is used thoroughly in the study of equilibrium interfacial phenomena and it is directly related to surface tension [?]. The dynamic equation (7.2.2) is, therefore, the non-equilibrium generalization of the condition of mechanical equilibrium in the usual gradient theory for equilibrium interfaces. Note that one of the implicit assumptions in the hydrodynamic equations

(7.2) is that of local equilibrium. The local equilibrium assumption valid not only for the bulk but also for the interfacial regions of a phase separated fluid has been validated from molecular dynamics simulations for a one component fluid [?] and it is expected that a similar situation occurs for multicomponent fluids.

7.2.3 Binary mixture case

It proves convenient to restrict to a binary fluid and to perform a change of variables from $\{n^A, n^B, \mathbf{g}, \hat{\epsilon}\}$ to $\{\rho, c, \mathbf{g}, u\}$, with the latter variables defined as

$$\rho = m_A n^A + m_B n^B$$

$$c = \frac{m_A n^A}{m_A n^A + m_B n^B}$$

$$u = \hat{\epsilon} - \frac{1}{2} \sum_{\alpha\beta} a_{\alpha\beta} n^\alpha n^\beta$$

These variables are the total mass density ρ, the mass fraction c of component A and the full local internal energy u. This last quantity has a clear microscopic interpretation as the internal energy density of those molecules in a small region of space that are interacting with the *full* potential $\phi = \hat{\phi} + \overline{\phi}$, where the long range contribution is treated in mean field, given that the range of $\overline{\phi}$ is much larger than the size of the region being considered.

The relationships inverse to those in Eqn. (7.2.3) are

$$n^A = \frac{\rho c}{m_A}$$

$$n^B = \frac{\rho(1-c)}{m_B}$$

$$\hat{\epsilon} = u + \overline{u}(\rho, c)$$

$$\overline{u}(\rho, c) = \frac{\rho^2}{2} \left[\frac{a_{AA}}{m_A^2} c^2 + 2 \frac{a_{AB}}{m_A m_B} c(1-c) + \frac{a_{BB}}{m_B^2} (1-c)^2 \right]$$

We introduce the specific entropy s^{vdw} (entropy per unit mass) as a function of the new variables

$$s^{\mathrm{vdW}}(\rho, c, u) = \frac{1}{\rho} \hat{s}(n^A, n^B, \hat{\epsilon})$$

$$= \frac{1}{\rho} \hat{s} \left(\frac{\rho c}{m_A}, \frac{\rho(1-c)}{m_B}, u + \overline{u} \right)$$

We emphasize that the above entropy is actually the specific entropy of the van der Waals model of a binary mixture, expressed in the variables ρ, c, u.

In what follows, we will need the derivatives of the specific entropy. We introduce the temperature of the van der Waals model as

$$\frac{1}{T^{\mathrm{vdW}}} = \frac{\partial \rho s^{\mathrm{vdW}}}{\partial u}$$

and easily obtain from Eqn. (7.2.3) the functional form of T^{vdW}

$$T^{\mathrm{vdW}}(\rho, c, u) = \hat{T}\left(\frac{\rho c}{m_A}, \frac{\rho(1-c)}{m_B}, u + \bar{u}\right)$$

that is, the temperature of the van der Waals fluid mixture is given by the temperature of the hard core fluid mixture, evaluated at the variables ρ, c, u. In a similar way, we introduce the chemical potential per unit mass μ_c^{vdW} as

$$\frac{\partial s^{\mathrm{vdW}}}{\partial c} = -\frac{\mu_c^{\mathrm{vdW}}}{T^{\mathrm{vdW}}}$$

By using Eqn. (7.2.3) we easily arrive at

$$\mu_c^{\mathrm{vdW}} = \frac{\hat{\mu}^A}{m_A} - \frac{\hat{\mu}^B}{m_B} - \rho[\alpha_1 c + \alpha_2]$$

where we have introduced the following interaction parameters

$$\alpha_1 = \frac{a_{AA}}{m_A m_A} + \frac{a_{BB}}{m_B m_B} - 2\frac{a_{AB}}{m_A m_B}$$
$$\alpha_2 = \frac{a_{AB}}{m_A m_B} - \frac{a_{BB}}{m_B m_B}$$

By using the dynamic equations for n^A, n^B we can easily obtain the corresponding dynamic equations for ρ, c, which are

$$\partial_t \rho = -\nabla \rho \mathbf{v}$$

$$\partial_t c = -\mathbf{v} \cdot \nabla c + \frac{1}{\rho} \nabla \left(D\hat{T}\nabla \frac{1}{\hat{T}}\left(\frac{\hat{\mu}^A}{m_A} - \frac{\hat{\mu}^B}{m_B}\right)\right) + \frac{1}{\rho}\nabla D\left(\frac{\overline{\mathbf{F}}^B}{m_B} - \frac{\overline{\mathbf{F}}^A}{m_A}\right) + \frac{1}{\rho}\nabla(S\nabla\hat{T})$$

where we have introduced the coefficient $S = S^A m_A = -S^B m_B$ and $D = m_A^2 D^{AA} = -m_B m_A D^{AB} = m_B^2 D^{BB}$. These equalities derive from Eqns. (7.3.5) and (7.3.5) [?].

By using the local approximation (7.2.2) for the long range forces, and after some

algebra one arrives at

$$\rho \frac{d}{dt} c = \nabla \left(D \nabla \left(\mu_c^{\mathrm{vdW}} + \nabla^2 ((\gamma_1 c + \gamma_2)\rho) \right) \right)$$
$$+ \nabla \left(\left(S - \frac{D}{T^{\mathrm{vdW}}} \left(\mu_c^{\mathrm{vdW}} + (\alpha_1 c + \alpha_2)\rho \right) \right) \nabla T^{\mathrm{vdW}} \right)$$

where we have introduced the usual substantial derivative $\frac{d}{dt} = \partial_t + \mathbf{v} \cdot \nabla$ and the following interaction parameters

$$\gamma_1 = \frac{c_{AA}}{m_A m_A} + \frac{c_{BB}}{m_B m_B} - 2 \frac{c_{AB}}{m_A m_B}$$
$$\gamma_2 = \frac{c_{AB}}{m_A m_B} - \frac{c_{BB}}{m_B m_B}$$

We observe that the dynamic equations for the new variables ρ, c are the continuity equation for the total mass density ρ, and an advection-diffusion equation, Eqn. (7.2.3), for the mass fraction c. For a quiescent isothermal incompressible ($\dot{\rho} = 0$) fluid, it becomes the well-known Cahn-Hilliard equation [?],[?]. Therefore, the above equation is the appropriate generalization for a non-equilibrium van der Waals mixture, and the previous derivation can be understood as a microscopic basis for the non-equilibrium Cahn-Hilliard equation. The non-trivial form in which thermal gradients affect the evolution of the mass fraction is quite remarkable. Even if the Soret-like coefficient S can be neglected, it is not correct to neglect cross-effects (gradients of temperature inducing flux of mass), as important contributions due to the diffusion-like coefficient D still exist. Finally, we could write the hydrodynamic equation for the internal energy u, in order to have a closed set of equations for ρ, c, u, but nothing essential is gained in doing so.

In the local approximation, the energy functional in Eqn. (7.2) becomes a local functional of the density fields, hard core internal energy, and also of the gradients of the density fields. It is apparent that such gradient terms do not occur in the entropy functional in Eqn. (7.2) within the van der Waals picture. Of course, if instead of using the hard core internal energy variable $\hat{\epsilon}$ we make a change of variable and use a total internal energy variable defined as

$$e_{\mathbf{r}} = \hat{\epsilon}_{\mathbf{r}} - \frac{1}{2} \sum_{\alpha\beta} a_{\alpha\beta} n_{\mathbf{r}}^{\alpha} n_{\mathbf{r}}^{\beta} + \frac{1}{2} \sum_{\alpha\beta} c_{\alpha\beta} \nabla n_{\mathbf{r}}^{\alpha} \cdot \nabla n_{\mathbf{r}}^{\beta}$$

then the energy functional does not depend on the gradients of the density field and the entropy does depend on these gradients. We believe that one of the benefits of the microscopic derivation presented in this paper is the fact that a well-defined meaning is ascribed to the energy density variable. For example, in phenomenological theories based on linear irreversible thermodynamics, it is postulated a dependence of the entropy density on the gradients of the density fields [?]. From the presentation in this paper, it is apparent that this is possible only if the energy density field is given by (7.2.3). In a phenomenological approach it is not evident at all which is the physical meaning to be associated to the energy density field, i.e. $\hat{\epsilon}_{\mathbf{r}}, \epsilon_{\mathbf{r}}$ or $u_{\mathbf{r}}$, despite of the fact that very

different forms of the hydrodynamic equations are obtained in each case.

A general remark can be made about the local approximation. The basic assumption behind this local approximation, which is that the density fields do not change much within the range of the long range potential, is expected to be valid near critical points, where the density profiles are usually very broad. In subcritical regions well below the critical points we expect that the density fields vary on the same length scale as the long range potential and renders the local approximation dubious. In this case, it seems more appropriate to use the non-local form (7.2) for the hydrodynamic equations. Actually, it may appear as an advantage from a practical computational point of view to use these non-local equations. In fact, the local equations involve high order spatial derivatives (third order in the momentum equation and fourth order in the density equations) that must be resolved accurately at interfacial regions. Clearly, an integral representation of surface effects may be much more stable than high order derivatives.

The hydrodynamic model presented in this paper belongs to the class of phase fields models for phase separating fluids [?]. The main difference to many of existing phase field models is that the phase fields here are not mathematical devices used to pinpoint interfacial regions, but have actually a definite physical meaning as they are the number density fields of the mixture [?]. The spirit of the model presented, though, is similar to phase field models in which interfaces appear whenever the system is in a region of thermodynamic parameters where phase separation occur. In this case, regions of different concentrations of the components appear and they are separated by transition regions, or diffuse interfaces. It is noteworthy that there is no need in this sort of theories to apply boundary conditions on the interfaces separating two phases. The boundaries appear (or disappear) as a dynamical process. Critical and subcritical states are treated on an equal footing and there is no need to worry about topological changes of the interfaces, a subtle problem in interface tracking algorithms. This makes the model presented in this paper very suitable for numerical simulations of non-equilibrium phase separation in mixtures.

The remaining of the paper deals with the actual derivation of Eqns. (7.2) from the underlying microscopic dynamics at a molecular level.

7.2.4   Equilibrium at the coarse-grained level

The equilibrium probability density at the coarse-grained level is given by

$$P(x) = \int dz \delta(\hat{X}(z) - x)\rho^{\text{eq}}(z)$$

where $\rho^{\text{eq}}(z)$ is the equilibrium ensemble. This is the well-know rule for relating the probability density of a random variable with the probability density of a function of the random variable.

If the dynamical invariants can be written as a function of the CG variables, this is $\hat{\mathscr{I}}(z) = \mathscr{I}(\hat{X}(z))$ and the microscopic ensemble is given by (**??**), then the probability in (7.2.4) takes the form

$$P(x) = \frac{1}{\Omega_0}\delta(\mathscr{I}(x) - I_0)\exp\{S(x)/k_B\}$$

This expression is a generalization of Einstein's formula for equilibrium fluctuations for the case that there exist dynamical invariants in the system which can be written in terms of the relevant variables [?]. In the next section, following the methodology presented in Ref. [?], we will compute the entropy function for a fluid mixture by first computing $P(x)$ through Eqn. (7.2.4) and then identifying $S(x)$ from (7.2.4).

7.3 Microscopic calculation of the GENERIC building blocks

7.3.1 CG variables for a fluid mixture

At the most microscopic level, a fluid mixture is described by $z = \{\mathbf{q}_{i_\alpha}, \mathbf{p}_{i_\alpha}\}$, where $\mathbf{q}_{i_\alpha}$ is the position of particle i_α of specie α and $\mathbf{p}_{i_\alpha}$ is the momentum of particle i_α of specie $\alpha = 1, \ldots, r$. The Hamiltonian of the system is

$$\hat{H}(z) = \sum_\alpha^r \sum_{i_\alpha}^{N^\alpha} \frac{\mathbf{p}_{i_\alpha}^2}{2m_\alpha} + \frac{1}{2}\sum_{\alpha\beta}^r \sum_{i_\alpha j_\beta}^{N^\alpha N^\beta} \phi_{i_\alpha j_\beta}$$

Here, m_α is the mass of the molecules of specie α, and $\phi_{i_\alpha j_\beta}$ is the potential energy of interaction between molecule i_α of species α and molecule j_β of species β. This potential energy depends only on the relative positions of both molecules. Note that the index i_α runs from 1 to N^α, which is the total number of particles of specie α. We will assume that the potential can be decomposed according to Eqn. (7.1).

The hydrodynamic fields for which a reasonable hydrodynamic description is valid can only be defined in terms of spatially discrete variables (or smooth fields that have a finite number of Fourier components). In order to define the set of discrete hydrodynamic CG variables, we first need to perform a partition of physical space into a set of M non-overlapping cells. For every cell labelled μ in which the space is divided one has a characteristic function $\chi_\mu(\mathbf{r})$, which takes the value 1 if the point $\mathbf{r}$ belongs to the cell μ and zero otherwise. The characteristic function satisfies the partition of unity property

$$\sum_\mu \chi_\mu(\mathbf{r}) = 1$$

The state of the system at the mesoscopic level of description will be given by the numerical values $x = \{N_\mu^\alpha, \mathbf{P}_\mu, \hat{\mathscr{e}}_\mu\}$ that take the following discrete hydrodynamic vari-

ables

$$N_\mu^\alpha(z) = \sum_{i_\alpha}^{N^\alpha} \chi_\mu(\mathbf{q}_{i_\alpha})$$

$$\mathbf{P}_\mu(z) = \sum_\alpha^r \sum_{i_\alpha}^{N^\alpha} \mathbf{p}_{i_\alpha} \chi_\mu(\mathbf{q}_{i_\alpha})$$

$$\hat{\mathscr{E}}_\mu(z) = \sum_\alpha^r \sum_{i_\alpha}^{N^\alpha} \hat{\epsilon}_{i_\alpha} \chi_\mu(\mathbf{q}_{i_\alpha})$$

We have introduced

$$\hat{\epsilon}_{i_\alpha} = \frac{m_\alpha}{2} \left(\frac{\mathbf{p}_{i_\alpha}}{m_\alpha} - \mathbf{v}_\mu(z) \right)^2 + \hat{\phi}_{i_\alpha}$$

where the potential energy associated to molecule i_α due to its *hard core* interaction with any other molecule of the system is given by

$$\hat{\phi}_{i_\alpha} = \frac{1}{2} \sum_\beta^r \sum_{j_\beta}^{N^\beta} \hat{\phi}_{i_\alpha j_\beta}$$

The phase function $N_\mu^\alpha(z)$ in Eqns. (7.3.1) is simply the number of molecules of species α that happen to be in cell μ when the microstate is z. It is apparent from Eqn. (7.3.1) that $\sum_\mu N_\mu^\alpha(z) = N^\alpha$, that is, the total number of molecules of specie α is constant, irrespective of the microstate z. In a similar way, $\mathbf{P}_\mu$ is the momentum of all the molecules that are in cell μ. The velocity $\mathbf{v}_\mu$ of the center of mass of the molecules in cell μ is defined by

$$\mathbf{v}_\mu(z) = \frac{\mathbf{P}_\mu(z)}{M_\mu(z)}$$

where $M_\mu = \sum_\alpha m_\alpha N_\mu^\alpha(z)$ is the total mass of cell μ. Finally, $\hat{\mathscr{E}}_\mu$ is the internal energy of the molecules that are in cell μ. Note that the internal energy does not contain the long range part of the potential. We call this internal energy *the hard core internal energy*.

It is straightforward to show by using the definitions (7.3.1) and the property (7.3.1) that the Hamiltonian (7.3.1) can be written as

$$\hat{H}(z) = \sum_\mu \frac{\mathbf{P}_\mu^2(z)}{2M_\mu(z)} + \sum_\mu \hat{\mathscr{E}}_\mu(z) + \frac{1}{2} \sum_{\alpha\beta}^r \sum_{i_\alpha j_\beta}^{N^\alpha N^\beta} \overline{\phi}_{i_\alpha j_\beta}$$

As we have mentioned in section **??**, in order to have the GENERIC structure, it is necessary that the Hamiltonian may be expressed as a function of the CG variables. Therefore, we need to express the last long range potential term as a function of the CG

variables. This is possible only *if the size of the cells in which we have divided space is much smaller than the range of the attractive potential.* In this case we may insert Eqn. (7.3.1) in the form

$$\sum_\nu \sum_\mu \chi_\mu(\mathbf{q}_{i_\alpha})\chi_\nu(\mathbf{q}_{j_\beta}) = 1$$

within the sum in the long range potential energy, this is,

$$\frac{1}{2}\sum_{\alpha\beta}^r \sum_{i_\alpha j_\beta}^{N^\alpha N^\beta} \overline{\phi}_{i_\alpha j_\beta} \sum_\nu \sum_\mu \chi_\mu(\mathbf{q}_{i_\alpha})\chi_\nu(\mathbf{q}_{j_\beta}) \approx \frac{1}{2}\sum_{\mu\nu}^r \sum_{\alpha\beta} \overline{\phi}^{\alpha\beta}(\mathbf{r}_\mu - \mathbf{r}_\nu) \sum_{i_\alpha j_\beta}^{N^\alpha N^\beta} \chi_\mu(\mathbf{q}_{i_\alpha})\chi_\nu(\mathbf{q}_{j_\beta})$$

$$= \frac{1}{2}\sum_{\mu\nu} \sum_{\alpha\beta}^r \overline{\phi}_{\mu\nu}^{\alpha\beta} N_\mu^\alpha(z)N_\nu^\beta(z)$$

where $\overline{\phi}_{\mu\nu}^{\alpha\beta} = \overline{\phi}^{\alpha\beta}(\mathbf{r}_\mu - \mathbf{r}_\nu)$. In Eqn. (7.3.1) we have assumed that the long range part of the potential can be approximated as if all the particles where located at the centers of the cells (note that $\overline{\phi}^{\alpha\beta}(r)$ is non-singular at the origin, as all the singular behaviour of the potential is assumed to be contained in $\hat{\phi}^{\alpha\beta}$). This approximation is a good one given the small variation of $\overline{\phi}^{\alpha\beta}$ in a cell dimension. In this way, the Hamiltonian depends on the microstate z only through the CG variables, this is,

$$\hat{H}(z) = \sum_\mu \frac{\mathbf{P}_\mu^2(z)}{2M_\mu(z)} + \sum_\mu \hat{\mathcal{E}}_\mu(z) + \frac{1}{2}\sum_{\mu\nu}\sum_{\alpha\beta}^r \overline{\phi}_{\mu\nu}^{\alpha\beta} N_\mu^\alpha(z)N_\nu^\beta(z)$$

The total momentum of the system can also be expressed in terms of the hydrodynamic CG variables,

$$\mathbf{P}(z) = \sum_\mu \mathbf{P}_\mu(z)$$

Because the dynamical invariants of the system are expressed in terms of the CG variables, we have that the hydrodynamical description can be written in the GENERIC form.

In a continuum theory, one introduces the hydrodynamic *fields* rather than the discrete set of variables (7.3.1). By dividing the extensive discrete variables (7.3.1) by the volume $\mathcal{V}_\mu$ of cell μ one obtains a set of densities. We also introduce the continuum notation in which each label of the cell is denoted by the cell center position $\mathbf{r}_\mu$, and we introduce the coarse-grained Dirac's delta function

$$\overline{\delta}(\mathbf{r}, \mathbf{r}_\mu) = \frac{\chi_\mu(\mathbf{r})}{\mathcal{V}_\mu}$$

which has a continuum index $\mathbf{r}$ and a discrete one $\mathbf{r}_\mu$. Due to the definition of the volume of cell μ as $\mathscr{V}_\mu = \int d\mathbf{r}\chi_\mu(\mathbf{r})$, this function satisfies

$$\int d\mathbf{r}\overline{\delta}(\mathbf{r}, \mathbf{r}_\mu) = 1$$

At the same time, the partition of unity (7.3.1) implies

$$\sum_\mu \mathscr{V}_\mu \overline{\delta}(\mathbf{r}, \mathbf{r}_\mu) = 1$$

Note that in a continuum notation we understand $\sum_\mu \mathscr{V}_\mu$ as providing the integral $\int d\mathbf{r}$. Actually, for any arbitrary function $\overline{f}(\mathbf{r})$ whose length scale of spatial variation is much larger than the typical size of the cells, we have the approximate expressions

$$\int d\mathbf{r}\overline{\delta}(\mathbf{r}, \mathbf{r}_\mu)\overline{f}(\mathbf{r}) = \overline{f}(\mathbf{r}_\mu)$$
$$\sum_\mu \mathscr{V}_\mu \overline{f}(\mathbf{r}_\mu)\overline{\delta}(\mathbf{r}, \mathbf{r}_\mu) = \overline{f}(\mathbf{r})$$

The exact relationships (7.3.1) and (7.3.1) and the approximate equation (7.3.1) allows to treat $\overline{\delta}(\mathbf{r}, \mathbf{r}_\mu)$ as a truly Dirac delta function $\overline{\delta}(\mathbf{r} - \mathbf{r}_\mu)$, whenever it appears under integral signs accompanying spatially smooth functions $\overline{f}(r)$.

The *density* fields are the number density fields of each specie $n_{\mathbf{r}}^\alpha = N_\mu^\alpha/\mathscr{V}_\mu$, the momentum density field $\mathbf{g_r} = \mathbf{P}_\mu/\mathscr{V}_\mu$, and the internal energy density fields $\hat{\epsilon}_{\mathbf{r}} = \hat{\mathscr{E}}_\mu/\mathscr{V}_\mu$, where

$$n_{\mathbf{r}}^\alpha(z) = \sum_{i_\alpha} \overline{\delta}(\mathbf{r} - \mathbf{q}_{i_\alpha})$$
$$\mathbf{g_r}(z) = \sum_\alpha \sum_{i_\alpha} \mathbf{p}_{i_\alpha} \overline{\delta}(\mathbf{r} - \mathbf{q}_{i_\alpha})$$
$$\hat{\epsilon}_{\mathbf{r}}(z) = \sum_\alpha \sum_{i_\alpha} \hat{\epsilon}_{i_\alpha} \overline{\delta}(\mathbf{r} - \mathbf{q}_{i_\alpha})$$

In order to have a continuum description, we will assume that the typical realizations of the microstates z are such that the hydrodynamic fields are continuous and differentiable functions of space.

The Hamiltonian (7.3.1) can be written in a continuum fashion as

$$\hat{H}(z) = \int d\mathbf{r} \left(\frac{\mathbf{g}_{\mathbf{r}}^2(z)}{2\rho_{\mathbf{r}}(z)} + \hat{\epsilon}_{\mathbf{r}}(z) \right) + \frac{1}{2} \sum_{\alpha\beta}^r \int d\mathbf{r} \int d\mathbf{r}' \overline{\phi}_{\mathbf{r}\mathbf{r}'}^{\alpha\beta} n_{\mathbf{r}}^\alpha(z) n_{\mathbf{r}'}^\beta(z)$$

where we have introduced the total mass density field as

$$\rho_{\mathbf{r}}(z) = \sum_{\alpha}^{r} m_\alpha n_{\mathbf{r}}^\alpha(z)$$

Other dynamical invariants of the microscopic dynamics are the total momentum $\mathbf{P}(z)$ in (7.3.1) of the system, which can also be written in terms of the continuum variables (7.3.1),

$$\mathbf{P}(z) = \int d\mathbf{r}\,\mathbf{g_r}(z)$$

and the total mass of each specie

$$M^\alpha(z) = \int d\mathbf{r}\,m_\alpha n_{\mathbf{r}}^\alpha(z)$$

Clearly, the energy function as defined in Eqn. (**??**) is, for the fluid mixture,

$$E(x) = \int d\mathbf{r}\left(\frac{\mathbf{g_r^2}}{2\rho_{\mathbf{r}}} + \hat{\epsilon}_{\mathbf{r}} + \frac{1}{2}\sum_{\alpha\beta}^{r} n_{\mathbf{r}}^\alpha \int d\mathbf{r}'\overline{\phi}_{\mathbf{rr}'}^{\alpha\beta}n_{\mathbf{r}'}^\beta\right)$$

The functional derivatives of the energy functional with respect to the hydrodynamic fields are the following

$$\frac{\delta E}{\delta x} = \begin{pmatrix} \frac{\delta E}{\delta n_{\mathbf{r}}^A} \\[6pt] \frac{\delta E}{\delta n_{\mathbf{r}}^B} \\[6pt] \frac{\delta E}{\delta \mathbf{g_r}} \\[6pt] \frac{\delta E}{\delta \hat{\epsilon}_{\mathbf{r}}} \end{pmatrix} = \begin{pmatrix} -m_A\frac{1}{2}\mathbf{v_r^2} + \int d\mathbf{r}'\overline{\phi}_{\mathbf{rr}'}^{AB}\,n_{\mathbf{r}}^B \\[6pt] -m_B\frac{1}{2}\mathbf{v_r^2} + \int d\mathbf{r}'\overline{\phi}_{\mathbf{rr}'}^{BA}\,n_{\mathbf{r}}^A \\[6pt] \mathbf{v_r} \\[6pt] 1 \end{pmatrix}$$

where $\mathbf{v_r} = \mathbf{g_r}/\rho_{\mathbf{r}}$ is the velocity field.

7.3.2 The entropy of a fluid mixture in the van der Waals approximation

In Ref. [**?**] we have computed the entropy of a simple fluid by following a cell-method first used by Green [**?**] and van Kampen [**?**]. Our approach in Ref. [**?**] has been to compute the probability distribution that a fluid system has a particular realization of the *full set* of discrete hydrodynamic variables. From this probability and through Eqn. (7.2.4) we have inferred the entropy function. The method is easily generalized to the case of

a fluid mixture. In this case, one computes the equilibrium probability functional that the system adopts a particular realization of the r density fields, the momentum density field and the internal energy density field.

By following identical steps as for the simple fluid case [?] we have that Eqn. (7.2.4) when specialized to the phase functions (7.3.1) becomes

$$P[x] = \int dz \rho^{\mathrm{eq}}(z) \prod_\mu \delta(\mathbf{P}_\mu(z) - \mathbf{P}_\mu) \delta(\hat{\mathscr{E}}_\mu(z) - \mathscr{E}_\mu) \chi(N_\mu^A(z) - N_\mu^A) \chi(N_\mu^B(z) - N_\mu^B)$$

We assume that there are only two species $\alpha = A, B$, but the generalization to r species is straightforward. The equilibrium distribution of the microscopic state z is given by

$$\rho^{\mathrm{eq}}(z) = \frac{1}{N^A! N^B! \Omega_0} \delta(\mathbf{P}(z) - \mathbf{P}_0) \delta(\hat{H}(z) - E_0)$$

The functions $\chi(\cdots)$ in Eqn. (7.3.2) are non-zero only for those microstates z that provide exactly N_μ^A particles of specie A and N_μ^B particles of specie B in each cell μ. There are

$$\frac{N^A!}{N_1^A! \cdots N_M^A!} \frac{N^B!}{N_1^B! \cdots N_M^B!}$$

equivalent ways of having the molecules with the prescribed distribution of particles in each cell and, therefore, we can write Eqn. (7.3.2) as

$$P[x] = \frac{1}{\Omega_0} \delta(\mathbf{P}(x) - \mathbf{P}_0) \delta(E(x) - E_0) \chi\left(\sum_\mu N_\mu^A - N_0^A\right) \chi\left(\sum_\mu N_\mu^B - N_0^B\right)$$

$$\times \frac{1}{N_1^A!} \int_{\mathscr{V}_1} \underbrace{d\mathbf{q}^A \dots d\mathbf{q}^A}_{N_1^A} \cdots \frac{1}{N_M^A!} \int_{\mathscr{V}_M} \underbrace{d\mathbf{q}^A \dots d\mathbf{q}^A}_{N_M^A}$$

$$\times \frac{1}{N_1^B!} \int_{\mathscr{V}_1} \underbrace{d\mathbf{q}^B \dots d\mathbf{q}^B}_{N_1^B} \cdots \frac{1}{N_M^B!} \int_{\mathscr{V}_M} \underbrace{d\mathbf{q}^B \dots d\mathbf{q}^B}_{N_M^B}$$

$$\times \int d\mathbf{p} \prod_\mu^M \delta\left(\sum_\alpha \sum_{i_\mu}^{N_\mu^\alpha} \mathbf{p}_{i_\mu^\alpha} - \mathbf{P}_\mu\right) \delta\left(\sum_\alpha \sum_{i_\mu}^{N_\mu^\alpha} \left(\frac{m_\alpha}{2}\left(\frac{\mathbf{p}_{i_\mu^\alpha}}{m_\alpha} - \mathbf{v}_\mu\right)^2 + \hat{\phi}_{i_\mu^\alpha}\right) - \hat{\mathscr{E}}_\mu\right)$$

Here, N_0^α is the total number of molecules of species α, E_0 is the total energy of the system and $\mathbf{P}_0$ is the total momentum of the system. We have introduced the functions $\chi(\sum_\mu N_\mu^\alpha - N^\alpha)$ that take the value 1 if its argument is zero and zero otherwise in order to encompass the fact that $P[x]$ is zero if the total number of molecules of specie α does not exactly coincide with N_0^α.

Our aim now is to decouple the multiple integral (7.3.2) *by cells*. Note that the momentum integrals trivially decouple. The term that hinders the decoupling of the position integrals is the potential energy. This potential energy can be decomposed in two parts, one that accounts for the interaction of particles within cell μ plus another that accounts for the interaction of particles of cell μ with particles in different cells ν. Mathematically,

$$\sum_\alpha \sum_{i_\mu^\alpha}^{N_\mu^\alpha} \hat{\phi}_{i_\mu^\alpha} = \frac{1}{2} \sum_{\alpha\beta} \sum_{i_\mu^\alpha}^{N_\mu^\alpha} \sum_{j_\mu^\beta}^{N_\mu^\beta} \hat{\phi}_{i_\mu^\alpha j_\mu^\beta} + \frac{1}{2} {\sum_\nu}' \left(\sum_{\alpha\beta} \sum_{i_\mu^\alpha}^{N_\mu^\alpha} \sum_{j_\nu^\beta}^{N_\nu^\beta} \hat{\phi}_{i_\mu^\alpha j_\nu^\beta} \right)$$

In this expression, the prime in the term $\sum_\nu'$ denotes that this sum involves coordinates of particles of cells ν *different* from μ. This last term is the one that hinders the decoupling of the multiple integral in cells. This term is actually a surface energy due to the hard core interaction between neighbouring cells. We will neglect this contribution in front of the "bulk" contribution represented by the first term of the left hand side of (7.3.2). In this way, we can decouple the integrals in Eqn. (7.3.2) by cells with the result

$$P[x] = \frac{1}{\Omega_0} \delta(\mathbf{P}(x) - \mathbf{P}_0) \delta(E(x) - E_0) \prod_\alpha^r \chi \left(\sum_\mu N_\mu^\alpha - N^\alpha \right) \prod_\mu^M \hat{\Omega} \left(N_\mu^A, N_\mu^B, \hat{\mathscr{e}}_\mu, \mathscr{V}_\mu \right)$$

where

$$\hat{\Omega}(N^A, N^B, \hat{\mathscr{e}}, V) = \frac{1}{N^A!} \int_V \underbrace{d\mathbf{q}^A \dots d\mathbf{q}^A}_{N^A} \int \underbrace{d\mathbf{p}^A \dots d\mathbf{p}^A}_{N^A} \frac{1}{N^B!} \int_V \underbrace{d\mathbf{q}^B \dots d\mathbf{q}^B}_{N^B} \int \underbrace{d\mathbf{p}^B \dots d\mathbf{p}^B}_{N^B}$$

$$\times \delta \left(\sum_\alpha \sum_{i_\alpha}^{N_\alpha} \mathbf{p}_{i_\alpha} \right) \delta \left(\sum_\alpha \sum_{i_\alpha}^{N_\alpha} \left(\frac{\mathbf{p}_{i_\alpha}^2}{2m_\alpha} + \hat{\phi}_{i_\alpha} \right) - \hat{\mathscr{e}} \right)$$

where we have made a Galilean change of variables $\mathbf{p}_{i_\alpha} \to \mathbf{p}_{i_\alpha} + m_\alpha \mathbf{v}_\mu$.

We introduce the usual definition of the entropy of a macroscopic system containing N_A, N_B particles interacting with a hard core potential in a volume V and with total energy $\hat{\mathscr{e}}$, this is

$$\hat{S}(N_A, N_B, \hat{\mathscr{e}}, V) = k_B \ln \hat{\Omega}(N_A, N_B, \hat{\mathscr{e}}, V)$$

In this way, the distribution function of the hydrodynamic variables for a fluid mixture at equilibrium is given by

$$P[x] = \frac{1}{\Omega_0} \delta(\mathbf{P}(x) - \mathbf{P}_0) \delta(E(x) - E_0) \prod_\alpha^r \chi\left(\sum_\mu N^\alpha_\mu - N^\alpha\right)$$

$$\times \exp\left\{\sum_\mu^M \frac{1}{k_B} \hat{S}(N^A_\mu, N^B_\mu, \hat{\mathscr{E}}_\mu, \mathscr{V}_\mu)\right\}$$

By comparing (7.3.2) with the general expression (7.2.4), we can extract the explicit form of the entropy of the system at the level of hydrodynamic variables, which for a binary mixture $\alpha = A, B$ is

$$S(x) = \sum_\mu^M \hat{S}(N^A_\mu, N^B_\mu, \hat{\mathscr{E}}_\mu, \mathscr{V}_\mu)$$

This result may appear at first sight as deceptively simple, and one may wonder what is the need to go to the detailed calculation of the probability functional $P[x]$ presented above to derive (7.3.2). At the end of the day, one could say that the entropy is an additive quantity, and therefore, the total entropy of the system cannot be anything but (7.3.2). Yet, this type of reasoning is not without hazard as it strongly depends on the type of hydrodynamic variables one is using. Actually, (7.3.2) says much more than simply "the entropy is additive". It states that the total entropy of the system is the sum of the entropies of a *hard core* system, evaluated at the *hard core* internal energy. That only hard core quantities enter into the definition of the entropy is not a trivial result.

By using the fact that $\hat{S}$ is a first order function of its arguments, we can write

$$\hat{S}(N_A, N_B, \hat{\mathscr{E}}, V) = V\hat{s}(n^A, n^B, \hat{\epsilon})$$

and then (7.3.2) admits the continuum notation

$$S(x) = \int d\mathbf{r} \hat{s}(n^A_{\mathbf{r}}, n^B_{\mathbf{r}}, \hat{\epsilon}_{\mathbf{r}})$$

Note that behind the property (7.3.2) it is implicitly assumed the thermodynamic limit. In this way, we are assuming that the size of the cell μ is much larger than the range of the hard core potential. Note also the remark previous to Eqn. (7.3.1). Taken together, these remarks imply that the size of the cell has to be large in front of the range of the hard core potential, but small in front of the range of the long ranged part of the potential.

The functional derivatives of the entropy functional with respect to the hydrodynamic fields are

$$\frac{\delta S}{\delta x} = \begin{pmatrix} -\frac{\hat{\mu}_{\mathbf{r}}^A}{\hat{T}_{\mathbf{r}}} \\[2ex] -\frac{\hat{\mu}_{\mathbf{r}}^B}{\hat{T}_{\mathbf{r}}} \\[2ex] 0 \\[2ex] \frac{1}{\hat{T}_{\mathbf{r}}} \end{pmatrix}$$

where we have introduced the usual definition of the intensive parameters (chemical potentials $\hat{\mu}^\alpha$ of species α and temperature $\hat{T}$) of the hard core system

$$\frac{1}{\hat{T}} = \frac{\partial}{\partial \hat{\epsilon}} \hat{s}(n^A, n^B, \hat{\epsilon})$$

$$\frac{\hat{\mu}^A}{\hat{T}} = -\frac{\partial}{\partial n^A} \hat{s}(n^A, n^B, \hat{\epsilon})$$

$$\frac{\hat{\mu}^B}{\hat{T}} = -\frac{\partial}{\partial n^B} \hat{s}(n^A, n^B, \hat{\epsilon})$$

The property (7.3.2) and the definitions (7.3.2) have as a consequence the Gibbs-Duhem relation [?]

$$\sum_\alpha n^\alpha d\left(\frac{\hat{\mu}^\alpha}{\hat{T}}\right) - \hat{\epsilon} d\left(\frac{1}{\hat{T}}\right) - d\left(\frac{\hat{P}}{\hat{T}}\right) = 0$$

where $\hat{P}$ is the pressure of the hard core system. The Gibbs-Duhem relation can be written in the continuum form

$$\sum_\alpha n_{\mathbf{r}}^\alpha \nabla \left(\frac{\hat{\mu}_{\mathbf{r}}}{\hat{T}_{\mathbf{r}}}\right) - \hat{\epsilon}_{\mathbf{r}} \nabla \left(\frac{1}{\hat{T}_{\mathbf{r}}}\right) - \nabla \left(\frac{\hat{P}_{\mathbf{r}}}{\hat{T}_{\mathbf{r}}}\right) = 0$$

where all the intensive parameters are regarded as functions of $n_{\mathbf{r}}^\alpha, \hat{\epsilon}_{\mathbf{r}}$.

7.3.3   Constrained averages

In the microscopic definitions of the reversible and irreversible operators in Eqns. (**??**) and (**??**), the constrained averages defined in general in Eqn. (**??**) appear. We present in this section the calculation of the constrained average of an arbitrary *local function* G_μ of the form

$$G_\mu(z) = \sum_\alpha \sum_{i_\alpha} g_{i_\alpha}(z) \overline{\delta}(\mathbf{q}_{i_\alpha} - \mathbf{r}_\mu)$$

where g_{i_α} is an arbitrary function of the coordinates $\mathbf{r}_{i_\alpha}$ and momenta $\mathbf{p}_{i_\alpha}$ of particle i of specie α. We say that G_μ is *local* because it only involves the coordinates of those particles that are in cell μ.

The general definition of the constrained average (**??**) becomes, for the case that the CG variables x are (7.3.1),

$$\langle G_\mu \rangle^x = \exp\{-S(x)/k_B\} \int dz \, G_\mu(z)$$
$$\times \prod_\nu \delta(\mathbf{P}_\nu(z) - \mathbf{P}_\nu)\delta(\hat{\mathscr{E}}_\nu(z) - \mathscr{E}_\nu)\chi\left(N_\nu^A(z) - N_\nu^A\right)\chi\left(N_\nu^B(z) - N_\nu^B\right)$$

Under the assumption of negligible hard core interaction between neighbouring cells, we can write the above average as simply

$$\langle G_\mu \rangle^x = \exp\{-\hat{S}(N_\mu^A, N_\mu^B, \hat{\mathscr{E}}_\mu, V_\mu)/k_B\}$$
$$\times \frac{1}{N_\mu^A!}\frac{1}{N_\mu^B!}\int_{\mathscr{V}_\mu}\underbrace{d\mathbf{q}^A \dots d\mathbf{q}^A}_{N_\mu^A}\int_{\mathscr{V}_\mu}\underbrace{d\mathbf{q}^B \dots d\mathbf{q}^B}_{N_\mu^B}\int\underbrace{d\mathbf{p}^A \dots d\mathbf{p}^A}_{N_\mu^A}\int\underbrace{d\mathbf{p}^B \dots d\mathbf{p}^B}_{N_\mu^B}$$
$$\times \frac{1}{\mathscr{V}_\mu}\left(\sum_\alpha\sum_{i_\mu^\alpha}^{N_\mu} g_{i_\mu^\alpha}\right)\delta\left(\sum_\alpha\sum_{i_\mu^\alpha}^{N_\mu^\alpha}\mathbf{p}_{i_\mu^\alpha} - \mathbf{P}_\mu\right)\delta\left(\sum_\alpha\sum_{i_\mu^\alpha}^{N_\mu^\alpha}\left(\frac{m_\alpha}{2}\left(\frac{\mathbf{p}_{i_\mu^\alpha}}{m_\alpha} - \mathbf{v}_\mu\right)^2 + \hat{\phi}_{i_\mu^\alpha}\right) - \hat{\mathscr{E}}_\mu\right)$$

where i_μ^α is the label of particles of type α that are in cell μ. By taking a Galilean transformation,

$$\langle G_\mu \rangle^x = \exp\{-\hat{S}(N_\mu^A, N_\mu^B, \hat{\mathscr{E}}_\mu, V_\mu)/k_B\}$$
$$\times \frac{1}{N_\mu^A!}\frac{1}{N_\mu^B!}\int_{\mathscr{V}_\mu}\underbrace{d\mathbf{q}^A \dots d\mathbf{q}^A}_{N_\mu^A}\int_{\mathscr{V}_\mu}\underbrace{d\mathbf{q}^B \dots d\mathbf{q}^B}_{N_\mu^B}\int\underbrace{d\mathbf{p}^A \dots d\mathbf{p}^A}_{N_\mu^A}\int\underbrace{d\mathbf{p}^B \dots d\mathbf{p}^B}_{N_\mu^B}$$
$$\times \frac{1}{\mathscr{V}_\mu}\left(\sum_\alpha\sum_{i_\mu^\alpha}^{N_\mu}\mathscr{G}_\mu g_{i_\alpha}\right)\delta\left(\sum_\alpha\sum_{i_\mu^\alpha}^{N_\mu^\alpha}\mathbf{p}_{i_\mu^\alpha}\right)\delta\left(\sum_\alpha\sum_{i_\mu^\alpha}^{N_\mu^\alpha}\left(\frac{\mathbf{p}_{i_\mu^\alpha}^2}{2m_\alpha} + \hat{\phi}_{i_\mu^\alpha}\right) - \hat{\mathscr{E}}_\mu\right)$$

In summary,

$$\langle G_\mu \rangle^x = \langle \mathscr{G}_\mu g_\mu(z) \rangle_\mu^{\mathrm{eq}}$$

where $\langle\cdots\rangle_\mu^{\rm eq}$ is a usual equilibrium microcanonical average of a system at rest containing N_μ^α molecules of specie $\alpha = 1, \ldots, r$ and a given energy $\hat{\mathscr{E}}_\mu$. Again, it should be remarked that the Hamiltonian that should be used in this equilibrium microcanonical average has only a hard core potential. The function $g_\mu(z)$ in (7.3.3) is

$$g_\mu(z) = \frac{1}{\mathscr{V}_\mu} \sum_\alpha \sum_{i_\alpha}^{N_\mu^\alpha} g_{i_\mu^\alpha}$$

and the Galilean operator $\mathscr{G}_\mu$ is defined through its action on an arbitrary phase function $\hat{A}(z)$ as follows

$$\mathscr{G}_\mu A(\mathbf{q}_{i_\alpha}, \mathbf{p}_{i_\alpha}, \mathbf{q}_{i_\beta}, \mathbf{p}_{i_\beta}) = A(\mathbf{q}_{i_\alpha}, \mathbf{p}_{i_\alpha} + m^\alpha \mathbf{v}_\mu, \mathbf{q}_{i_\beta}, \mathbf{p}_{i_\beta} + m^\beta \mathbf{v}_\mu)$$

Eqn. (7.3.3) is a very important result as it reflects the concept of *local equilibrium*. The constrained average of a local function can be computed as an equilibrium microcanonical average in the rest frame and with the local values of the energy and number of particles.

7.3.4   Reversible dynamics

The elements of the reversible matrix L defined in Eqn. (??) will have the following structure for a fluid mixture,

$$L_{\mathbf{r}\mathbf{r}'}^{xy} = \sum_\gamma \sum_{k_\gamma} \left\langle \frac{\partial x_{\mathbf{r}}}{\partial \mathbf{q}_{k_\gamma}} \cdot \frac{\partial y_{\mathbf{r}'}}{\partial \mathbf{p}_{k_\gamma}} - \frac{\partial x_{\mathbf{r}}}{\partial \mathbf{p}_{k_\gamma}} \cdot \frac{\partial y_{\mathbf{r}'}}{\partial \mathbf{q}_{k_\gamma}} \right\rangle^x$$

where $x_{\mathbf{r}}, y_{\mathbf{r}}$ are any of the hydrodynamic fields. In order to compute the reversible matrix as defined in Eqn. (??) it is necessary to compute previously the derivatives of the relevant variables with respect to the microstate. These derivatives are

$$\frac{\partial n_{\mathbf{r}}^\alpha(z)}{\partial \mathbf{q}_{k_\gamma}} = -\delta_{\alpha\gamma} \nabla \bar{\delta}(\mathbf{r} - \mathbf{q}_{k_\gamma})$$

$$\frac{\partial n_{\mathbf{r}}^\alpha(z)}{\partial \mathbf{p}_{k_\gamma}} = 0$$

$$\frac{\partial \mathbf{g}_{\mathbf{r}}(z)}{\partial \mathbf{q}_{k_\gamma}} = -\mathbf{p}_{k_\gamma} \nabla \bar{\delta}(\mathbf{r} - \mathbf{q}_{k_\gamma})$$

$$\frac{\partial \mathbf{g}_{\mathbf{r}}(z)}{\partial \mathbf{p}_{k_\gamma}} = \mathbf{1}\bar{\delta}(\mathbf{r} - \mathbf{q}_{k_\gamma})$$

$$\frac{\partial \hat{\epsilon}_{\mathbf{r}}(z)}{\partial \mathbf{p}_{i_\gamma}} = \bar{\delta}(\mathbf{r} - \mathbf{q}_{k_\gamma}) \left(\frac{\mathbf{p}_{k_\gamma}}{m_\gamma} - \mathbf{v}_{\mathbf{r}} \right)$$

where $\mathbf{1}$ is the unit tensor.

The calculation of the derivative of the internal energy density field with respect to the positions is a bit more involved. We first use

$$\frac{\partial \hat{\phi}_{i_\alpha j_\beta}}{\partial \mathbf{q}_{k_\gamma}} = -\hat{\mathbf{F}}_{i_\alpha j_\beta} \left(\delta_{\alpha\gamma} \delta_{i_\alpha k_\gamma} - \delta_{\beta\gamma} \delta_{j_\beta k_\gamma} \right)$$

where $\hat{\mathbf{F}}_{i_\alpha j_\beta}$ is the hard core force that particle j of specie β exerts on particle i of specie α. In this way,

$$\frac{\partial \hat{\epsilon}_{\mathbf{r}}(z)}{\partial \mathbf{q}_{k_\gamma}} = -\hat{\epsilon}_{k_\gamma} \nabla \overline{\delta}(\mathbf{r} - \mathbf{q}_{k_\gamma})$$

$$- \frac{1}{2} \sum_\beta \sum_{j_\beta} \hat{\mathbf{F}}_{k_\gamma j_\beta} [\overline{\delta}(\mathbf{r} - \mathbf{q}_{k_\gamma}) + \overline{\delta}(\mathbf{r} - \mathbf{q}_{j_\beta})]$$

We can now obtain the following elements of the matrix L

$$L_{\mathbf{rr'}}^{n^\alpha n^\beta} = 0$$
$$L_{\mathbf{rr'}}^{n^\alpha \mathbf{g}} = n_{\mathbf{r'}}^\alpha \nabla' \overline{\delta}_{\mathbf{rr'}}$$
$$L_{\mathbf{rr'}}^{n^\alpha \hat{\epsilon}} = 0$$
$$L_{\mathbf{rr'}}^{\mathbf{gg}} = \left[\mathbf{g_{r'}} \nabla' \overline{\delta}_{\mathbf{rr'}} + \nabla' \overline{\delta}_{\mathbf{rr'}} \mathbf{g_r} \right]$$
$$L_{\mathbf{rr'}}^{\mathbf{g}\hat{\epsilon}} = \hat{\epsilon}_{\mathbf{r}} \nabla' \overline{\delta}_{\mathbf{rr'}} + \hat{\mathbf{F}}_{\mathbf{rr'}}$$
$$L_{\mathbf{rr'}}^{\hat{\epsilon}\hat{\epsilon}} = 0$$

Here, $\overline{\delta}_{\mathbf{rr'}}$ is a shorthand for the coarse-grained delta function, whereas

$$\nabla' \overline{\delta}_{\mathbf{rr'}} = \frac{\partial}{\partial \mathbf{r'}} \overline{\delta}(\mathbf{r} - \mathbf{r'})$$

In order to obtain (7.3.4) we have used the following results,

$$\left\langle \sum_{k_\beta} \nabla \overline{\delta}(\mathbf{r} - \mathbf{q}_{k_\beta}) \overline{\delta}(\mathbf{r'} - \mathbf{q}_{k_\beta}) \right\rangle^x = \nabla \delta_{\mathbf{rr'}} \langle n_{\mathbf{r'}}^\beta(z) \rangle^x = \nabla \delta_{\mathbf{rr'}} n_{\mathbf{r'}}^\beta$$

$$\left\langle \sum_\beta \sum_{k_\beta} \overline{\delta}(\mathbf{r'} - \mathbf{q}_{k_\beta}) \left(\frac{\mathbf{p}_{k_\beta}}{m_\beta} - \mathbf{v_{r'}} \right) \right\rangle^x = 0$$

The first identity is due to the fact that we are computing the average of the density field constrained to produce a particular value of the density field (and the rest of hydrodynamic fields denoted symbolically by x). The second identity in (7.3.4) is an instance

of (7.3.3) together with the fact that the equilibrium average of the momentum is zero. The vanishing of $L_{\mathbf{rr}'}^{\hat{\epsilon}\hat{\epsilon}}$ in (7.3.4) is due to the same reason.

In Eqn. (7.3.4) we have introduced the following coarse grained force between two points of the fluid

$$
\hat{\mathbf{F}}_{\mathbf{rr}'} = \left\langle \frac{1}{2} \sum_{\gamma\beta} \sum_{k_\gamma j_\beta} \hat{\mathbf{F}}_{k_\gamma j_\beta} \delta(\mathbf{r} - \mathbf{q}_{k_\gamma}) \sum_{k_\gamma \hat{\mathbf{F}}_{\mathbf{r}}} \left(\overline{\delta}(\mathbf{r}' - \mathbf{q}_{k_\gamma}) + \overline{\delta}(\mathbf{r}' - \mathbf{q}_{j_\beta}) \right) \right\rangle^x
$$
$$
- \sum_{\gamma} \sum_{k_\gamma} \left\langle (\mathbf{p}_{k_\gamma} - m_\gamma \mathbf{v}_{\mathbf{r}'})(\mathbf{p}_{k_\gamma} - m_\gamma \mathbf{v}_{\mathbf{r}'})\overline{\delta}(\mathbf{r}' - \mathbf{q}_{k_\gamma}) \right\rangle^x \nabla \overline{\delta}_{\mathbf{rr}'}
$$

By following the pioneering work by Irwing and Kirkwood [?], the usual treatment of this term (7.3.4) is to perform a Taylor expansion of the delta function in the form

$$
\overline{\delta}(\mathbf{r} - \mathbf{q}_{k_\gamma}) - \overline{\delta}(\mathbf{r} - \mathbf{q}_{j_\beta}) = -\mathbf{q}_{k_\gamma j_\beta} \nabla \overline{\delta}(\mathbf{r} - \mathbf{q}_{k_\gamma})
$$

By inserting this expansion into Eqn. (7.3.4) we obtain

$$
\hat{\mathbf{F}}_{\mathbf{rr}'} = \langle \mathscr{G}^{-1} \hat{\sigma}_{\mathbf{r}'} \rangle^x \nabla' \overline{\delta}_{\mathbf{rr}'}
$$

Here $\mathscr{G}_{\mathbf{r}}^{-1}$ is the inverse of the Galilean operator introduced in Eqn. (7.3.3) (where we have changed the discrete label μ by the continuum label $\mathbf{r}$). The inverse operator is obtained by reversing the sign of the velocity field. We have introduced in Eqn. (7.3.4) the usual microscopic expression for the stress tensor

$$
\mathscr{G}_{\mathbf{r}}^{-1} \hat{\sigma}_{\mathbf{r}} = \sum_{\alpha} \sum_{i_\alpha} m_\alpha \left(\frac{\mathbf{p}_{i_\alpha}}{m_\alpha} - \mathbf{v}_{\mathbf{r}} \right) \left(\frac{\mathbf{p}_{i_\alpha}}{m_\alpha} - \mathbf{v}_{\mathbf{r}} \right) \overline{\delta}(\mathbf{r} - \mathbf{q}_{i_\alpha}) + \frac{1}{2} \sum_{\gamma\beta} \sum_{k_\gamma j_\beta} \hat{\mathbf{F}}_{k_\gamma j_\beta} \mathbf{q}_{k_\gamma j_\beta} \overline{\delta}(\mathbf{r} - r_{k_\gamma})
$$

By collecting all the elements of the matrix L in Eqns. (7.3.4), we can finally write

$$
L_{\mathbf{rr}'} = \begin{pmatrix} 0 & 0 & n_{\mathbf{r}'}^A \nabla' \overline{\delta}_{\mathbf{rr}'} & 0 \\ 0 & 0 & n_{\mathbf{r}'}^B \nabla' \overline{\delta}_{\mathbf{rr}'} & 0 \\ n_{\mathbf{r}}^A \nabla' \overline{\delta}_{\mathbf{rr}'} & n_{\mathbf{r}}^B \nabla' \overline{\delta}_{\mathbf{rr}'} & \mathbf{g}_{\mathbf{r}'} \nabla' \overline{\delta}_{\mathbf{rr}'} + \nabla' \overline{\delta}_{\mathbf{rr}'} \mathbf{g}_{\mathbf{r}} & \hat{\epsilon}_{\mathbf{r}} \nabla' \overline{\delta}_{\mathbf{rr}'} + \langle \mathscr{G}_{\mathbf{r}'}^{-1} \hat{\sigma}_{\mathbf{r}'} \rangle^x \nabla' \overline{\delta}_{\mathbf{rr}'} \\ 0 & 0 & \hat{\epsilon}_{\mathbf{r}'} \nabla' \overline{\delta}_{\mathbf{rr}'} + \langle \mathscr{G}_{\mathbf{r}}^{-1} \hat{\sigma}_{\mathbf{r}} \rangle^x \nabla' \overline{\delta}_{\mathbf{rr}'} & 0 \end{pmatrix}
$$

The only unknown quantity in this matrix is $\langle \mathscr{G}_{\mathbf{r}}^{-1} \hat{\sigma}_{\mathbf{r}'} \rangle^x \nabla' \overline{\delta}_{\mathbf{rr}'}$. We have two routes for computing this quantity. The first one is to use the result (7.3.3) in order to perform explicitly the constrained average of the microscopic stress tensor. The second is to use the degeneracy $L\nabla S = 0$ presented in (??). Both routes provide the same answer and we illustrate the second, which is the simplest one. The degeneracy $L\nabla S = 0$ becomes

in the fluid mixture case

$$\int d\mathbf{r}' \left[\sum_\alpha n_{\mathbf{r}}^\alpha \nabla' \overline{\delta}_{\mathbf{rr}'} \left(-\frac{\hat{\mu}_{\mathbf{r}'}^\alpha}{\hat{T}_{\mathbf{r}'}} \right) + \hat{\epsilon}_{\mathbf{r}} \nabla' \overline{\delta}_{\mathbf{rr}'} \frac{1}{\hat{T}_{\mathbf{r}'}} + \langle \mathscr{G}_{\mathbf{r}'}^{-1} \hat{\sigma}_{\mathbf{r}'} \rangle^x \nabla' \overline{\delta}_{\mathbf{rr}'} \frac{1}{\hat{T}_{\mathbf{r}'}} \right] = 0$$

or, by performing the integrals over the delta functions,

$$\sum_\alpha n_{\mathbf{r}}^\alpha \nabla \left(\frac{\hat{\mu}_{\mathbf{r}}}{\hat{T}_{\mathbf{r}}} \right) - \hat{\epsilon}_{\mathbf{r}} \nabla \left(\frac{1}{\hat{T}_{\mathbf{r}}} \right) - \nabla \left(\frac{\langle \mathscr{G}_{\mathbf{r}}^{-1} \hat{\sigma}_{\mathbf{r}} \rangle^x}{\hat{T}_{\mathbf{r}}} \right) = 0$$

By comparing with the Gibbs-Duhem relation (7.3.2) we readily obtain

$$\langle \mathscr{G}_{\mathbf{r}}^{-1} \hat{\sigma}_{\mathbf{r}} \rangle^x = \hat{P}_{\mathbf{r}} \mathbf{1}$$

We are now in position to write the reversible part of the dynamics $\dot{x}|_{\text{rev}} = L\nabla E$ by using (7.3.4) with (11.10), and (7.3.1). The balance of mass equations take the form

$$\partial_t n_{\mathbf{r}}^\alpha = -\nabla \mathbf{v_r} n_{\mathbf{r}}^\alpha$$

The momentum balance equation becomes

$$\partial_t \mathbf{g_r} = -\nabla \cdot (\mathbf{g_r v_r}) - \nabla \hat{P}_{\mathbf{r}} - \sum_\alpha n_{\mathbf{r}}^\alpha \nabla \frac{\delta \overline{\Phi}}{\delta n_{\mathbf{r}}^\alpha}$$

where the pressure is given by the equation of state $\hat{P}_{\mathbf{r}} = \hat{P}(n_{\mathbf{r}}^A, n_{\mathbf{r}}^B, \hat{\epsilon}_{\mathbf{r}})$. We have introduced in (7.3.4) the total mean field potential energy given by

$$\overline{\Phi} = \frac{1}{2} \sum_{\alpha\beta} \int d\mathbf{rr}' n_{\mathbf{r}}^\alpha n_{\mathbf{r}'}^\beta \overline{\phi}_{\mathbf{rr}'}^{\alpha\beta}$$

Note that Eqn. (7.3.4) can also be written as

$$\partial_t \mathbf{g_r} = -\nabla \cdot (\mathbf{g_r v_r}) - \nabla \hat{P}_{\mathbf{r}} + \sum_\alpha n_{\mathbf{r}}^\alpha \overline{\mathbf{F}}_{\mathbf{r}}^\alpha$$

where

$$\overline{\mathbf{F}}_{\mathbf{r}}^\alpha = -\nabla \frac{\delta \overline{\Phi}}{\delta n_{\mathbf{r}}^\alpha} = \sum_\beta \int d\mathbf{r}' \overline{\mathbf{F}}_{\mathbf{rr}'}^{\alpha\beta} n_{\mathbf{r}'}^\beta$$

and $\overline{\mathbf{F}}_{\mathbf{rr}'}^{\alpha\beta}$ is the long range attractive force that a molecule of specie β in $\mathbf{r}'$ exerts on a

molecule of specie α in $\mathbf{r}$. Finally, the energy equation is given by

$$\partial_t \hat{\epsilon}_{\mathbf{r}} = -\nabla\cdot(\mathbf{v_r}\hat{\epsilon}_{\mathbf{r}}) - \hat{P}_{\mathbf{r}}\nabla\cdot\mathbf{v_r}$$

Equations (7.3.4), (7.3.4), (7.3.4) are the corresponding Euler equations for a phase separating fluid mixture.

7.3.5 Irreversible dynamics

In order to compute the irreversible matrix M in Eqn. (**??**), we need to compute the time derivatives $i\mathcal{L}\hat{X}(z)$ of the relevant variables. A straightforward calculation leads to the microscopic mass balance equation.

$$i\mathcal{L}n_{\mathbf{r}}^{\alpha}(z) = -\nabla\cdot\frac{1}{m_\alpha}\mathbf{g}_{\mathbf{r}}^{\alpha}(z)$$

where we have introduced

$$\mathbf{g}_{\mathbf{r}}^{\alpha}(z) = \sum_{i_\alpha}\mathbf{p}_{i_\alpha}\overline{\delta}(\mathbf{r}-\mathbf{q}_{i_\alpha})$$

to be distinguished from $\mathbf{g_r}$ in Eqn. (7.3.1). Actually we have

$$\mathbf{g_r}(z) = \sum_{\alpha}^{r}\mathbf{g}_{\mathbf{r}}^{\alpha}(z)$$

The time derivative of the momentum density field can be written as

$$i\mathcal{L}\mathbf{g_r} = -\nabla\cdot\sum_{\alpha}\sum_{i_\alpha}\mathbf{p}_{i_\alpha}\mathbf{v}_{i_\alpha}\overline{\delta}(\mathbf{r}-\mathbf{q}_{i_\alpha}) + \sum_{\alpha\beta}\sum_{i_\alpha j_\beta}\mathbf{F}_{i_\alpha j_\beta}\overline{\delta}(\mathbf{r}-\mathbf{q}_{i_\alpha})$$

Let us analyze the force term in Eqn. (18.5). Under the separation of the potential into a short range repulsive core plus a long range attractive tail, we may write for the forces

$$\mathbf{F}_{i_\alpha j_\beta} = \hat{\mathbf{F}}_{i_\alpha j_\beta} + \overline{\mathbf{F}}_{i_\alpha j_\beta}$$

The last term in (18.5) can then be written as

$$\sum_{\alpha\beta}\sum_{i_\alpha j_\beta}\mathbf{F}_{i_\alpha j_\beta}\overline{\delta}(\mathbf{r}-\mathbf{q}_{i_\alpha}) = \sum_{\alpha\beta}\sum_{i_\alpha j_\beta}\hat{\mathbf{F}}_{i_\alpha j_\beta}\overline{\delta}(\mathbf{r}-\mathbf{q}_{i_\alpha}) + \sum_{\alpha\beta}\sum_{i_\alpha j_\beta}\overline{\mathbf{F}}_{i_\alpha j_\beta}\overline{\delta}(\mathbf{r}-\mathbf{q}_{i_\alpha})$$

$$\approx \sum_{\alpha\beta}\sum_{i_\alpha j_\beta}\hat{\mathbf{F}}_{i_\alpha j_\beta}\overline{\delta}(\mathbf{r}-\mathbf{q}_{i_\alpha}) + \sum_{\alpha\beta}\int d\mathbf{r}'\overline{\mathbf{F}}_{\mathbf{r}\mathbf{r}'}^{\alpha\beta}n_{\mathbf{r}}^{\alpha}(z)n_{\mathbf{r}'}^{\beta}(z)$$

where we have used the long range nature of the last term. Note that we are not allowed to perform a similar approximation for the short range part of the force, due to the finite

support of the coarse-grained delta functions.

The time derivative of the internal energy density field is straightforward to obtain. It can be expressed as follows,

$$i\mathcal{L}\hat{\epsilon}_\mathbf{r} = -\nabla\cdot\sum_\alpha\sum_{i_\alpha}\mathbf{v}_{i_\alpha}\hat{\epsilon}_{i_\alpha}\overline{\delta}(\mathbf{r}-\mathbf{q}_{i_\alpha}) - \sum_\alpha\sum i_\alpha m_\alpha(\mathbf{v}_{i_\alpha}-\mathbf{v_r})(\mathbf{v}_{i_\alpha}-\mathbf{v_r})\overline{\delta}(\mathbf{r}-\mathbf{q}_{i_\alpha}):\nabla\mathbf{v_r}$$

$$+\frac{1}{2}\sum_{\alpha\beta}\sum_{i_\alpha j_\beta}\hat{\mathbf{F}}_{i_\alpha j_\beta}\cdot(\mathbf{v}_{i_\alpha}+\mathbf{v}_{j_\beta})\overline{\delta}(\mathbf{r}-\mathbf{q}_{i_\alpha}) - \mathbf{v_r}\cdot\sum_{\alpha\beta}\sum_{i_\alpha j_\beta}\hat{\mathbf{F}}_{i_\alpha j_\beta}\overline{\delta}(\mathbf{r}-\mathbf{q}_{i_\alpha})$$

$$+\sum_\alpha\sum_{i_\alpha}(\mathbf{v}_{i_\alpha}-\mathbf{v_r})\cdot\overline{\mathbf{F}}_{i_\alpha}\overline{\delta}(\mathbf{r}-\mathbf{q}_{i_\alpha})$$

The second term in the right hand side of (7.3.5) can be written by using symmetry properties and the Taylor expansion (7.3.4) as

$$\frac{1}{2}\sum_{\alpha\beta}\sum_{i_\alpha j_\beta}\hat{\mathbf{F}}_{i_\alpha j_\beta}\cdot(\mathbf{v}_{i_\alpha}+\mathbf{v}_{j_\beta})\overline{\delta}(\mathbf{r}-\mathbf{q}_{i_\alpha}) = \frac{1}{4}\sum_{\alpha\beta}\sum_{i_\alpha j_\beta}\hat{\mathbf{F}}_{i_\alpha j_\beta}\cdot(\mathbf{v}_{i_\alpha}+\mathbf{v}_{j_\beta})\left(\overline{\delta}(\mathbf{r}-\mathbf{q}_{i_\alpha})-\overline{\delta}(\mathbf{r}-\mathbf{q}_{j_\beta})\right)$$

$$= -\nabla\cdot\frac{1}{4}\sum_{\alpha\beta}\sum_{i_\alpha j_\beta}\hat{\mathbf{F}}_{i_\alpha j_\beta}\cdot(\mathbf{v}_{i_\alpha}+\mathbf{v}_{j_\beta})\mathbf{q}_{i_\alpha j_\beta}\overline{\delta}(\mathbf{r}-\mathbf{q}_{i_\alpha})$$

We need now to compute the constrained averages $\langle i\mathcal{L}X\rangle^x$ that appear in $\delta i\mathcal{L}X$. The simplest procedure is to realize that these constrained averages are actually the reversible part of the dynamics, as it is shown in Eqn. (**??**). We have already computed this reversible part of the dynamics through Eqn. (**??**) which lead to the results (7.3.4),(7.3.4), and (7.3.4). Therefore, after some algebra, we have the following realization of $\delta i\mathcal{L}X = i\mathcal{L}X - \langle i\mathcal{L}X\rangle^x$ for the case of the hydrodynamic variables

$$\delta i\mathcal{L}n_\mathbf{r}^\alpha = -\nabla\cdot\left(\mathscr{G}_\mathbf{r}^{-1}\frac{\mathbf{g}_\mathbf{r}^\alpha(z)}{m_\alpha}\right)$$

$$\delta i\mathcal{L}\mathbf{g_r} = -\nabla\cdot\mathscr{G}_\mathbf{r}^{-1}\left(\hat{\sigma}_\mathbf{r}(z)-\hat{P}_\mathbf{r}\mathbf{1}\right) - \nabla\cdot\mathbf{v_r}\mathbf{v_r}\sum_\alpha[n_\mathbf{r}^\alpha(z)-n_\mathbf{r}^\alpha] - \nabla\mathbf{v_r}[\mathbf{g_r}(z)-\mathbf{g_r}]$$

$$+\int d\mathbf{r}\overline{\mathbf{F}}_{\mathbf{r}\mathbf{r}'}\left[n_\mathbf{r}^\alpha(z)n_{\mathbf{r}'}^\beta(z)-n_\mathbf{r}^\alpha n_{\mathbf{r}'}^\beta\right]$$

$$\delta i\mathcal{L}\hat{\epsilon}_\mathbf{r} = -\nabla\cdot\mathbf{v_r}\left(\hat{\epsilon}_\mathbf{r}(z)-\hat{\epsilon}_\mathbf{r}\right) + \left(\hat{\sigma}_\mathbf{r}(z)-\hat{P}_\mathbf{r}\mathbf{1}\right):\nabla\mathbf{v_r} - \nabla\cdot\left(\mathscr{G}^{-1}\mathbf{J}_\mathbf{r}^q\right) + \sum_\alpha\left(\mathscr{G}_\mathbf{r}^{-1}\frac{\mathbf{g}_\mathbf{r}^\alpha(z)}{m_\alpha}\right)\cdot\overline{\mathbf{F}}_\mathbf{r}^\alpha(z)$$

Note that these expressions have the form

$$\delta i\mathcal{L}X = \tilde{\delta}i\mathcal{L}X + F[\hat{X}(z)-X]$$

where F is some function. The last term in (7.3.5) that involves the CG variables

themselves will vanish in any constrained average and, in particular, in the calculation of the matrix M. Therefore, we can omit these terms. The final result can then be expressed in the form

$$\delta i\mathcal{L}n_{\mathbf{r}}^{\alpha} = -\nabla\cdot\left(\mathscr{G}_{\mathbf{r}}^{-1}\mathbf{J}_{\mathbf{r}}^{\alpha}(z)\right)$$

$$\delta i\mathcal{L}\mathbf{g}_{\mathbf{r}} = -\nabla\cdot\left(\mathscr{G}_{\mathbf{r}}^{-1}\left(\hat{\sigma}_{\mathbf{r}}(z) - \hat{P}_{\mathbf{r}}\mathbf{1}\right)\right)$$

$$\delta i\mathcal{L}\hat{\epsilon}_{\mathbf{r}} = \left(\mathscr{G}_{\mathbf{r}}^{-1}\left(\hat{\sigma}_{\mathbf{r}}(z) - \hat{P}_{\mathbf{r}}\mathbf{1}\right)\right):\nabla\mathbf{v}_{\mathbf{r}} - \nabla\cdot\left(\mathscr{G}_{\mathbf{r}}^{-1}\mathbf{J}_{\mathbf{r}}^{q}(z)\right) + \sum_{\alpha}\left(\mathscr{G}_{\mathbf{r}}^{-1}\mathbf{J}_{\mathbf{r}}^{\alpha}(z)\right)\cdot\overline{\mathbf{F}}_{\mathbf{r}}^{\alpha}(z)$$

We have introduced the following microscopic fluxes

$$\mathbf{J}_{\mathbf{r}}^{\alpha}(z) = \frac{\mathbf{g}_{\mathbf{r}}^{\alpha}(z)}{m_{\alpha}}$$

$$\hat{\sigma}_{\mathbf{r}}(z) = \sum_{\alpha}\sum_{i_{\alpha}}\mathbf{p}_{i_{\alpha}}\mathbf{v}_{i_{\alpha}}\overline{\delta}(\mathbf{r} - \mathbf{q}_{i_{\alpha}}) + \frac{1}{2}\sum_{\alpha\beta}\sum_{i_{\alpha}j_{\beta}}\hat{\mathbf{F}}_{i_{\alpha}j_{\beta}}\mathbf{q}_{i_{\alpha}j_{\beta}}\overline{\delta}(\mathbf{r} - \mathbf{q}_{i_{\alpha}})$$

$$\hat{\mathbf{J}}_{\mathbf{r}}^{q}(z) = \sum_{\alpha}\sum_{i_{\alpha}}\left(\frac{\mathbf{p}_{i_{\alpha}}^{2}}{2m_{\alpha}} + \hat{\phi}_{i_{\alpha}}\right)\mathbf{v}_{i_{\alpha}}\overline{\delta}(\mathbf{r} - \mathbf{q}_{i_{\alpha}}) + \frac{1}{4}\sum_{\alpha\beta}\sum_{i_{\alpha}j_{\beta}}(\mathbf{v}_{i_{\alpha}} + \mathbf{v}_{j_{\beta}})\hat{\mathbf{F}}_{i_{\alpha}j_{\beta}}\mathbf{q}_{i_{\alpha}j_{\beta}}\overline{\delta}(\mathbf{r} - \mathbf{q}_{i_{\alpha}})$$

Here $\mathbf{J}_{\mathbf{r}}^{\alpha}(z)$ is the microscopic mass flux, $\hat{\sigma}_{\mathbf{r}}(z)$ is the microscopic stress tensor and $\hat{\mathbf{J}}_{\mathbf{r}}^{q}(z)$ is the microscopic heat flux. It is quite remarkable that in these microscopic fluxes, only the short range part of the force appears. The long range part of the forces disappears when computing the constrained average of these fluxes.

We proceed now to the explicit calculation of the elements of the irreversible matrix M defined in Eqn. (**??**). This matrix will have the following form

$$M_{\mathbf{rr}'} = \begin{pmatrix} M_{\mathbf{rr}'}^{\alpha\beta} & M_{\mathbf{rr}'}^{\alpha\mathbf{g}} & M_{\mathbf{rr}'}^{\alpha\hat{\epsilon}} \\[2em] M_{\mathbf{rr}'}^{\mathbf{g}\beta} & M_{\mathbf{rr}'}^{\mathbf{gg}} & M_{\mathbf{rr}'}^{\mathbf{g}\hat{\epsilon}} \\[2em] M_{\mathbf{rr}'}^{\hat{\epsilon}\beta} & M_{\mathbf{rr}'}^{\hat{\epsilon}\mathbf{g}} & M_{\mathbf{rr}'}^{\hat{\epsilon}\hat{\epsilon}} \end{pmatrix},$$

where every element is a Green-Kubo formula involving the time integral of a correlation function as in Eqn. (**??**). We only need to consider the six elements of the upper triangular part, because M is symmetric. The first element $M_{\mathbf{rr}'}^{\alpha\beta}$ involves the following correlation

$$\langle \delta i \mathcal{L} n_{\mathbf{r}}^{\alpha} \exp\{Q i \mathcal{L} t\} \delta i \mathcal{L} n_{\mathbf{r}'}^{\beta} \rangle^x = \nabla \nabla' \langle \mathscr{G}_{\mathbf{r}}^{-1} \mathbf{J}_{\mathbf{r}}^{\alpha} \exp\{Q i \mathcal{L} t\} \mathscr{G}_{\mathbf{r}'}^{-1} \mathbf{J}_{\mathbf{r}'}^{\beta} \rangle^x$$

where $\nabla' = \partial/\partial \mathbf{r}'$. We will make in the following the assumption that the dynamics represented by $\exp Q i \mathcal{L} t$ in the Green-Kubo expression for the matrix M can be substituted by $\exp Q i \overset{\vee}{L} t$, as if only the short range part of the potential was present. The intuitive reasoning behind this approximation is that the long range forces are slowly varying (as they essentially depend on the density field, which is a slow variable) in the time scale of the correlation times of the microscopic fluxes. Then the projected dynamics systematically subtracts these slowly varying forces from the dynamics. From now on, every instance of a time dependence will be assumed to be generated by the hard core dynamics only.

Another approximation that we will take is to neglect the correlation of the projected fluxes of different cell. This amounts to neglect non-local effects due to the transport coefficients in the final hydrodynamic equations. Therefore, the constrained average in Eqn. (7.3.5) is over a local function, and we can apply Eqn. (7.3.3) in order to compute the constrained average. We end up with

$$\langle \delta i \mathcal{L} n_{\mathbf{r}}^{\alpha} \delta i \mathcal{L} n_{\mathbf{r}}^{\beta}(t) \rangle^x = \nabla \nabla' \delta_{\mathbf{r}\mathbf{r}'} \frac{1}{\mathscr{V}_{\mathbf{r}}} \langle \mathbf{V}^{\alpha} \mathbf{V}^{\beta}(t) \rangle_{\mathbf{r}}^{\mathrm{eq}}$$

where $\mathscr{V}_{\mathbf{r}}$ is the volume of the cell labeled with $\mathbf{r}$ and we have introduced the average velocity of specie α as

$$\mathbf{V}^{\alpha} = \sum_{i_{\alpha}}^{N^{\alpha}} \mathbf{v}_{i_{\alpha}}$$

The equilibrium ensemble is isotropic and this means that the above correlation function is isotropic too, that is,

$$\langle \delta i \mathcal{L} n_{\mathbf{r}}^{\alpha} \delta i \mathcal{L} n_{\mathbf{r}}^{\beta}(t) \rangle^x = \nabla \cdot \nabla' \delta_{\mathbf{r}\mathbf{r}'} \frac{1}{3 \mathscr{V}_{\mathbf{r}}} \langle \mathbf{V}^{\alpha} \cdot \mathbf{V}^{\beta}(t) \rangle_{\mathbf{r}}^{\mathrm{eq}}$$

The corresponding Green-Kubo expression that appears in the matrix M will be

$$M_{\mathbf{r}\mathbf{r}'}^{\alpha\beta} = \nabla \cdot \nabla (\delta_{\mathbf{r}\mathbf{r}'} D_{\mathbf{r}}^{\alpha\beta} \hat{T}_{\mathbf{r}})$$

where we have introduced the diffusion coefficients through [?],[?]

$$D_{\mathbf{r}}^{\alpha\beta} = \frac{1}{2 k_B \hat{T}_{\mathbf{r}}} \frac{1}{\mathscr{V}_{\mathbf{r}}} \int_{-\infty}^{\infty} dt \frac{1}{3} \langle \mathbf{V}^{\alpha} \cdot \mathbf{V}^{\beta}(t) \rangle_{\mathbf{r}}^{\mathrm{eq}}$$

Note that the equilibrium ensemble involved in (7.3.5) is a microcanonical one at rest. This means that $\sum_{\alpha} m_{\alpha} \mathbf{V}_{\alpha}$, which is the total momentum of the system is exactly zero at

all times. For this reason, we have that not all the diffusion coefficients are independent, but

$$\sum_\alpha m_\alpha D_{\mathbf{r}}^{\alpha\beta} = 0$$

The next element $M_{\mathbf{rr'}}^{\alpha\mathbf{g}}$ involves the correlation $\langle \delta i\mathcal{L}n_{\mathbf{r}}^\alpha \exp Qi\mathcal{L}t\delta i\mathcal{L}\mathbf{g}_{\mathbf{r'}}\rangle^x$. Under the same approximations used above, we can write

$$\langle \delta i\mathcal{L}n_{\mathbf{r}}^\alpha \delta i\mathcal{L}\mathbf{g}_{\mathbf{r'}}(t)\rangle^x = \nabla\nabla'\delta_{\mathbf{rr'}}\frac{1}{\mathscr{V}_{\mathbf{r}}}\langle \mathbf{V}^\alpha\left(\hat{\mathbf{\Sigma}}(t) - \hat{P}_{\mathbf{r}}\mathbf{1}\right)\rangle_{\mathbf{r}}^{\mathrm{eq}}$$

where the macroscopic stress tensor is given by

$$\hat{\mathbf{\Sigma}} = \sum_\alpha \sum_{i_\alpha}^{N^\alpha}\mathbf{p}_{i_\alpha}\mathbf{v}_{i_\alpha} + \frac{1}{2}\sum_{\alpha\beta}\sum_{i_\alpha j_\beta}^{N^\alpha N^\beta}\hat{\mathbf{F}}_{i_\alpha j_\beta}\mathbf{q}_{i_\alpha j_\beta}$$

Due to the isotropy of the equilibrium ensemble, the above correlation, which is a third order tensor, should vanish and then $M_{\mathbf{rr'}}^{\alpha\mathbf{g}} = 0$.

The next element to be computed is $M_{\mathbf{rr'}}^{\alpha\hat{\epsilon}}$ which involves the correlation

$$\langle \delta i\mathcal{L}n_{\mathbf{r}}^\alpha \delta i\mathcal{L}\hat{\epsilon}_{\mathbf{r'}}(t)\rangle^x = \nabla\nabla'\delta_{\mathbf{rr'}}\frac{1}{\mathscr{V}_{\mathbf{r}}}\langle \mathbf{V}^\alpha\hat{\mathbf{Q}}(t)\rangle_{\mathbf{r}}^{\mathrm{eq}} - \nabla\delta_{\mathbf{rr'}}\sum_\beta\frac{1}{\mathscr{V}_{\mathbf{r}}}\langle \mathbf{V}^\alpha\mathbf{V}^\beta(t)\rangle_{\mathbf{r}}^{\mathrm{eq}}\overline{\mathbf{F}}_{\mathbf{r}}^\beta$$

where we have introduced the macroscopic heat flux

$$\hat{\mathbf{Q}} = \sum_\alpha \sum_{i_\alpha}^{N^\alpha}\left(\frac{\mathbf{p}_{i_\alpha}^2}{2m_\alpha} + \hat{\phi}_{i_\alpha}\right)\mathbf{v}_{i_\alpha} + \frac{1}{4}\sum_{\alpha\beta}\sum_{i_\alpha j_\beta}^{N^\alpha N^\beta}(\mathbf{v}_{i_\alpha} + \mathbf{v}_{j_\beta})\hat{\mathbf{F}}_{i_\alpha j_\beta}\mathbf{q}_{i_\alpha j_\beta}$$

In Eqn. (7.3.5) we have omitted a third order tensor that vanishes by isotropy. The corresponding element of the matrix M will be

$$M_{\mathbf{rr'}}^{\alpha\hat{\epsilon}} = \nabla\cdot\nabla'(\delta_{\mathbf{rr'}}S_{\mathbf{r}}^\alpha\hat{T}_{\mathbf{r}}^2) - \nabla\delta_{\mathbf{rr'}}\sum_\beta D_{\mathbf{r}}^{\alpha\beta}\overline{\mathbf{F}}_{\mathbf{r}}^\beta$$

where the cross-coefficient $S_{\mathbf{r}}^\alpha$ is defined through the Green-Kubo formula [?],[?]

$$S_{\mathbf{r}}^\alpha = \frac{1}{2k_B\hat{T}_{\mathbf{r}}^2}\frac{1}{\mathscr{V}_{\mathbf{r}}}\int_{-\infty}^\infty dt\frac{1}{3}\langle \mathbf{V}^\alpha\cdot\hat{\mathbf{Q}}(t)\rangle_{\mathbf{r}}^{\mathrm{eq}}$$

Again, we have the identity

$$\sum_{\alpha} m_\alpha S_{\mathbf{r}}^{\alpha} = 0$$

due to momentum conservation.

The next correlation is

$$\langle \delta i \mathcal{L} \mathbf{g_r} \delta i \mathcal{L} \mathbf{g_{r'}}(t) \rangle^x = \nabla \nabla' \delta_{\mathbf{rr'}} \frac{1}{\mathscr{V}_{\mathbf{r}}} \langle \hat{\mathbf{\Sigma}} \hat{\mathbf{\Sigma}}(t) \rangle_{\mathbf{r}}^{\mathrm{eq}}$$

where we have omitted some third order tensors that vanish by isotropy. The corresponding element of the matrix M is an isotropic fourth order tensor

$$M_{\mathbf{r}}^{\mathbf{gg}} = \nabla \nabla' : \mathbf{\Theta_r} \hat{T}_{\mathbf{r}} \delta_{\mathbf{rr'}}$$

where the isotropic fourth order tensor is given by

$$\mathbf{\Theta}_{\mathbf{r}}^{\mu\nu\mu'\nu'} = \hat{\eta}_{\mathbf{r}} \left(\delta^{\mu\mu'} \delta^{\nu\nu'} + \delta^{\mu\nu'} \delta^{\nu\mu'} \right) + \left(\hat{\zeta}_{\mathbf{r}} - \frac{2}{3} \hat{\eta}_{\mathbf{r}} \right) \delta^{\mu\nu} \delta^{\mu'\nu'}$$

where the usual Green-Kubo expressions for the shear η and bulk ζ viscosities appear

$$\hat{\eta}_{\mathbf{r}} = \frac{1}{2 k_B \hat{T}_{\mathbf{r}}} \frac{1}{\mathscr{V}_{\mathbf{r}}} \int_{-\infty}^{\infty} dt \langle \hat{\mathbf{\Sigma}}^{xy} \hat{\mathbf{\Sigma}}^{xy}(t) \rangle_{\mathbf{r}}^{\mathrm{eq}}$$

$$\hat{\zeta}_{\mathbf{r}} = \frac{1}{2 k_B \hat{T}_{\mathbf{r}}} \frac{1}{\mathscr{V}_{\mathbf{r}}} \int_{\infty}^{-\infty} dt \langle (\hat{\mathbf{\Sigma}}^{xx} - \hat{P}_{\mathbf{r}})(\hat{\mathbf{\Sigma}}^{xx} - \hat{P}_{\mathbf{r}})(t) \rangle_{\mathbf{r}}^{\mathrm{eq}}$$

The next correlation is

$$\langle \delta i \mathcal{L} \mathbf{g_r} \delta i \mathcal{L} \hat{\epsilon}_{\mathbf{r'}}(t) \rangle^x = \nabla \left(\delta_{\mathbf{rr'}} \frac{1}{\mathscr{V}_{\mathbf{r}}} \langle \hat{\mathbf{\Sigma}} \hat{\mathbf{\Sigma}}(t) \rangle_{\mathbf{r}}^{\mathrm{eq}} : \nabla \mathbf{v_r} \right)$$

where we have neglected again some third order tensors. The corresponding element of the matrix M is

$$M_{\mathbf{r}}^{\mathbf{g}\hat{\epsilon}} = \nabla \left(\delta_{\mathbf{rr'}} \hat{T}_{\mathbf{r}} \mathbf{\Theta} : \nabla \mathbf{v_r} \right)$$

The last correlation is given by

$$
\begin{aligned}
\langle \delta i \mathcal{L} \hat{\epsilon}_{\mathbf{r}} \delta i \mathcal{L} \hat{\epsilon}_{\mathbf{r}'}(t) \rangle^x &= \nabla \nabla' \left(\delta_{\mathbf{rr}'} \frac{1}{\mathscr{V}_{\mathbf{r}}} \langle \hat{\mathbf{Q}} \hat{\mathbf{Q}}(t) \rangle_{\mathbf{r}}^{\mathrm{eq}} \right) \\
&\quad + \delta_{\mathbf{rr}'} \frac{1}{\mathscr{V}_{\mathbf{r}}} \nabla \mathbf{v}_{\mathbf{r}} : \langle \hat{\mathbf{\Sigma}} \mathbf{\Sigma}(t) \rangle_{\mathbf{r}}^{\mathrm{eq}} : \nabla \mathbf{v}_{\mathbf{r}} + \delta_{\mathbf{rr}'} \frac{1}{\mathscr{V}_{\mathbf{r}}} \sum_{\alpha\beta} \langle \mathbf{V}^{\alpha} \mathbf{V}^{\beta}(t) \rangle_{\mathbf{r}}^{\mathrm{eq}} \overline{\mathbf{F}}_{\mathbf{r}}^{\alpha} \overline{\mathbf{F}}_{\mathbf{r}}^{\beta} \\
&\quad - \nabla \left(\sum_{\alpha} \delta_{\mathbf{rr}'} \langle \mathbf{V}^{\alpha} \hat{\mathbf{Q}}(t) \rangle_{\mathbf{r}}^{\mathrm{eq}} \overline{\mathbf{F}}_{\mathbf{r}}^{\alpha} \right) - \nabla' \left(\sum_{\alpha} \delta_{\mathbf{rr}'} \langle \hat{\mathbf{Q}} \mathbf{V}^{\alpha}(t) \rangle_{\mathbf{r}}^{\mathrm{eq}} \overline{\mathbf{F}}_{\mathbf{r}}^{\alpha} \right)
\end{aligned}
$$

and the corresponding element of the matrix M is

$$
\begin{aligned}
M_{\mathbf{rr}'}^{\hat{\epsilon}\hat{\epsilon}} &= \nabla \cdot \nabla' \left(\hat{\kappa}_{\mathbf{r}} \hat{T}_{\mathbf{r}}^2 \delta_{\mathbf{rr}'} \right) + \delta_{\mathbf{rr}'} \nabla \mathbf{v}_{\mathbf{r}} : \mathbf{\Theta}_{\mathbf{r}} : \nabla \mathbf{v}_{\mathbf{r}} \hat{T}_{\mathbf{r}} - (\nabla + \nabla') \left(\delta_{\mathbf{rr}'} \sum_{\alpha} S_{\mathbf{r}}^{\alpha} \overline{\mathbf{F}}_{\mathbf{r}}^{\alpha} \right) \\
&\quad + \delta_{\mathbf{rr}'} \sum_{\alpha\beta} D_{\mathbf{r}}^{\alpha\beta} \overline{\mathbf{F}}_{\mathbf{r}}^{\alpha} \cdot \overline{\mathbf{F}}_{\mathbf{r}}^{\alpha} \hat{T}_{\mathbf{r}}
\end{aligned}
$$

where the usual Green-Kubo expression for the thermal conductivity $\hat{\kappa}$ has been introduced

$$
\hat{\kappa}_{\mathbf{r}} = \frac{1}{2 k_B \hat{T}_{\mathbf{r}}^2} \frac{1}{\mathscr{V}_{\mathbf{r}}} \int_{-\infty}^{\infty} dt \frac{1}{3} \langle \hat{\mathbf{Q}} \cdot \hat{\mathbf{Q}}(t) \rangle_{\mathbf{r}}^{\mathrm{eq}}
$$

By collecting all the elements of the matrix M we note that we can write it as the sum of two matrices $M_{\mathbf{rr}'} = D_{\mathbf{rr}'} + H_{\mathbf{rr}'}$ where $D_{\mathbf{rr}'}$ contains all those transport coefficients related to diffusion of mass and heat, and $H_{\mathbf{rr}'}$ contains the viscosity transport coefficients. More explicitly, we can write for the matrices $D_{\mathbf{rr}'}$ and $H_{\mathbf{rr}'}$,

$$
D_{\mathbf{rr}'} =
\begin{pmatrix}
\nabla\cdot\nabla'\left(\delta_{\mathbf{rr}'}D_{\mathbf{r}}^{\alpha\beta}\hat{T}_{\mathbf{r}}\right) & 0 & -\nabla\cdot\left(\delta_{\mathbf{rr}'}\sum_{\beta}D_{\mathbf{r}}^{\alpha\beta}\hat{T}_{\mathbf{r}}\overline{\mathbf{F}}_{\mathbf{r}}^{\beta}\right)+\nabla\cdot\nabla'\left(\delta_{\mathbf{rr}'}S_{\mathbf{r}}^{\alpha}\hat{T}_{\mathbf{r}}^{2}\right) \\[2em]
0 & 0 & 0 \\[2em]
-\nabla'\cdot\left(\delta_{\mathbf{rr}'}\sum_{\beta}D_{\mathbf{r}}^{\alpha\beta}\hat{T}_{\mathbf{r}}\overline{\mathbf{F}}_{\mathbf{r}}^{\beta}\right)+\nabla\cdot\nabla'\left(\delta_{\mathbf{rr}'}S_{\mathbf{r}}^{\alpha}\hat{T}_{\mathbf{r}}^{2}\right) & 0 & \sum_{\alpha\beta}\delta_{\mathbf{rr}'}D_{\mathbf{r}}^{\alpha\beta}\hat{T}_{\mathbf{r}}\overline{\mathbf{F}}_{\mathbf{r}}^{\alpha}\cdot\overline{\mathbf{F}}_{\mathbf{r}}^{\beta}-(\nabla+\nabla')\cdot\left(\sum_{\alpha}S_{\mathbf{r}}^{\alpha}\delta_{\mathbf{rr}'}\hat{T}_{\mathbf{r}}^{2}\overline{\mathbf{F}}_{\mathbf{r}}^{\alpha}\right) \\
 & & +\nabla\cdot\nabla'\left(\delta_{\mathbf{rr}'}\hat{\kappa}_{\mathbf{r}}\hat{T}_{\mathbf{r}}^{2}\right)
\end{pmatrix},
$$

$$(7.3.\text{-}50)$$

$$
H_{\mathbf{rr}'} =
\begin{pmatrix}
0 & 0 & 0 \\[1.5em]
0 & (\nabla'\nabla+\mathbf{1}\nabla\cdot\nabla')\hat{\eta}_{\mathbf{r}}\hat{T}_{\mathbf{r}}\delta_{\mathbf{rr}'}+\nabla\nabla'\left(\hat{\zeta}_{\mathbf{r}}-\tfrac{2}{3}\eta_{\mathbf{r}}\right)\hat{T}_{\mathbf{r}}\delta_{\mathbf{rr}'} & \nabla\hat{\eta}_{\mathbf{r}}\hat{T}_{\mathbf{r}}\dot{\gamma}_{\mathbf{r}}\delta_{\mathbf{rr}'}+\nabla\left(\hat{\zeta}_{\mathbf{r}}-\tfrac{2}{3}\eta_{\mathbf{r}}\right)\hat{T}_{\mathbf{r}}\mathrm{tr}\dot{\gamma}\delta_{\mathbf{rr}'} \\[1.5em]
0 & \nabla'\hat{\eta}_{\mathbf{r}}\hat{T}_{\mathbf{r}}\dot{\gamma}_{\mathbf{r}}\delta_{\mathbf{rr}'}+\nabla'\left(\hat{\zeta}_{\mathbf{r}}-\tfrac{2}{3}\eta_{\mathbf{r}}\right)\hat{T}_{\mathbf{r}}\mathrm{tr}\dot{\gamma}\delta_{\mathbf{rr}'} & \tfrac{1}{2}\hat{\eta}_{\mathbf{r}}\hat{T}_{\mathbf{r}}\dot{\gamma}_{\mathbf{r}}:\dot{\gamma}_{\mathbf{r}}\delta_{\mathbf{rr}'}+\left(\hat{\zeta}_{\mathbf{r}}-\tfrac{2}{3}\eta_{\mathbf{r}}\right)\hat{T}_{\mathbf{r}}(\mathrm{tr}\dot{\gamma})^{2}\delta_{\mathbf{rr}'}
\end{pmatrix},
$$

$$(7.3.\text{-}49)$$

Liquid-liquid: Fluid mixtures $\rho_{\mathbf{r}}^{1}, \rho_{\mathbf{r}}^{2}, \mathbf{g}_{\mathbf{r}}, e_{\mathbf{r}}$

where $\dot{\gamma}_{\mathbf{r}} = \nabla \mathbf{v_r} + (\nabla \mathbf{v_r})^T$ is the symmetrized velocity gradient tensor.

It is possible to write the matrix $M_{\mathbf{rr'}}$ in a more compact way. Eqs. (7.3.5) suggest to introduce the following fluxes

$$\delta i \mathcal{L} n_{\mathbf{r}}^{\alpha} = -\nabla \tilde{\mathbf{J}}_{\mathbf{r}}^{\alpha}$$
$$\delta i \mathcal{L} \mathbf{g_r} = -\nabla \tilde{\sigma}_{\mathbf{r}}$$
$$\delta i \mathcal{L} \hat{\epsilon}_{\mathbf{r}} = \tilde{\sigma}_{\mathbf{r}} : \nabla \mathbf{v_r} - \nabla \tilde{\mathbf{Q}}_{\mathbf{r}} + \sum_{\alpha} \tilde{\mathbf{J}}_{\mathbf{r}}^{\alpha} \cdot \overline{\mathbf{F}}_{\mathbf{r}}^{\alpha}$$

where we have introduced the "stochastic" mass flux $\tilde{\mathbf{J}}_{\mathbf{r}}^{\alpha}$, the "stochastic" stress tensor $\tilde{\sigma}_{\mathbf{r}}$ and the "stochastic" flux $\tilde{\mathbf{Q}}_{\mathbf{r}}$. These "stochastic" fluxes are actually phase functions with definite microscopic expressions. They are not stochastic at all but deterministic. We will understand the time evolution of $\delta i \mathcal{L} X$ to be generated by the projected dynamics, this is, $\delta i \mathcal{L} X(t) = \exp\{Q i \mathcal{L} t\} \delta i \mathcal{L} X$. Of course, even though the projected dynamics is deterministic, the correlation times of the projected currents $\delta i \mathcal{L} X(t)$ are very short as compared with the time scales of the CG variables. This is only possible if these functions change rapidly in time, allowing for a modelization in terms of random noise.

Note that we can write (7.3.5) in compact form as follows

$$\begin{pmatrix} \delta i \mathcal{L} n_{\mathbf{r}}^{\alpha} \\ \\ \delta i \mathcal{L} \mathbf{g_r} \\ \\ \delta i \mathcal{L} \hat{\epsilon}_{\mathbf{r}} \end{pmatrix} = \begin{pmatrix} -\nabla_{\mathbf{r}} & 0 & 0 \\ \\ 0 & -\nabla_{\mathbf{r}} & 0 \\ \\ \overline{\mathbf{F}}_{\mathbf{r}}^{\alpha} & \nabla_{\mathbf{r}} \mathbf{v_r} & -\nabla_{\mathbf{r}} \end{pmatrix} \begin{pmatrix} \tilde{\mathbf{J}}_{\mathbf{r}}^{\alpha} \\ \\ \tilde{\sigma}_{\mathbf{r}} \\ \\ \tilde{\mathbf{Q}}_{\mathbf{r}} \end{pmatrix}$$

In this way, we have separated the vector of projected currents in two bits, one which is strictly kinematic and that depends only on the CG variables, and another that contains the "stochastic" fluxes. These fluxes are, actually, what enters into the definition of the transport coefficients through the Green-Kubo expressions.

It is now quite simple to rewrite the Green-Kubo expression (**??**) for M in the form

$$M_{\mathbf{rr'}} = \begin{pmatrix} -\nabla_{\mathbf{r}} & 0 & 0 \\ \\ 0 & -\nabla_{\mathbf{r}} & 0 \\ \\ \overline{\mathbf{F}}_{\mathbf{r}}^{\alpha} & \nabla_{\mathbf{r}} \mathbf{v_r} & -\nabla_{\mathbf{r}} \end{pmatrix} \begin{pmatrix} D_{\mathbf{r}}^{\alpha\beta} \hat{T}_{\mathbf{r}} & 0 & S_{\mathbf{r}}^{\alpha} \hat{T}_{\mathbf{r}}^2 \\ \\ 0 & \theta_{\mathbf{r}} \hat{T}_{\mathbf{r}} & 0 \\ \\ S_{\mathbf{r}}^{\alpha} \hat{T}_{\mathbf{r}}^2 & 0 & \kappa_{\mathbf{r}} \hat{T}_{\mathbf{r}}^2 \end{pmatrix} \begin{pmatrix} -\nabla_{\mathbf{r'}} & 0 & \overline{\mathbf{F}}_{\mathbf{r'}}^{\alpha} \\ \\ 0 & -\nabla_{\mathbf{r'}} & \nabla_{\mathbf{r'}} \mathbf{v_{r'}} \\ \\ 0 & 0 & -\nabla_{\mathbf{r'}} \end{pmatrix} \delta_{\mathbf{rr'}}$$

The fact that the M matrix can be decomposed as $M = CDC^T$ in terms of a purely mechanic matrix C and purely thermodynamic matrix D has been discovered in Refs. [**?**]. From the microscopic example presented here, the splitting can be traced back to the particular splitting of the projected currents $\delta i \mathcal{L} X$ in terms of the stochastic fluxes that enter into the definition of the Green-Kubo expression for the matrix M. It is apparent that the symmetry of the the matrix M is ensured if D is symmetric, and that

the positive semidefinite character of D also ensures that M is positive semidefinite. We discuss the positive semidefinite character of D in section 7.4. As a final remark, we note that one of the merits of the $M = CDC^T$ decomposition is that it facilitates the task of constructing new models for complex fluids. We see, therefore, that for macroscopic modeling purposes, it may be very convenient to follow the "noise route to dissipation", as we can call it, where one first compute the time derivative of the microscopically defined CG variables, identify the "stochastic fluxes" that will produce transport coefficients in the Green-Kubo formula, and then construct the matrix M which, automatically, will have the CDC^T structure.

We are now in position of writing the irreversible part of the dynamics $M\nabla S$ by multiplying the matrix M with the functional derivatives of the entropy in (7.3.2) and integrating over $\mathbf{r}'$. The matrix H will produce the well-known terms of the Navier-Stokes equations that contain the viscosity coefficients. We write with some detail the part of the equations that involve the diffusion of mass and heat

$$\partial_t n^\alpha|_{\text{diff}} = \nabla\left(\sum_\beta D_{\mathbf{r}}^{\alpha\beta}\hat{T}_{\mathbf{r}}\nabla\left(\frac{\hat{\mu}_{\mathbf{r}}^\beta}{\hat{T}_{\mathbf{r}}}\right)\right) - \nabla\left(S_{\mathbf{r}}^\alpha\hat{T}_{\mathbf{r}}^2\nabla\left(\frac{1}{\hat{T}_{\mathbf{r}}}\right)\right) - \nabla\left(\sum_\beta D_{\mathbf{r}}^{\alpha\beta}\overline{\mathbf{F}}_{\mathbf{r}}^\beta\right)$$

$$\partial_t\hat{\epsilon}|_{\text{diff}} = \nabla\left(\sum_\alpha S_{\mathbf{r}}^\alpha\hat{T}_{\mathbf{r}}^2\nabla\left(\frac{\hat{\mu}_{\mathbf{r}}^\alpha}{\hat{T}_{\mathbf{r}}}\right)\right) - \nabla\left(\hat{\kappa}_{\mathbf{r}}\hat{T}_{\mathbf{r}}^2\nabla\left(\frac{1}{\hat{T}_{\mathbf{r}}}\right)\right) - \sum_{\alpha\beta}\left[\hat{T}_{\mathbf{r}}\nabla\left(\frac{\hat{\mu}_{\mathbf{r}}^\alpha}{\hat{T}_{\mathbf{r}}}\right) - \overline{\mathbf{F}}_{\mathbf{r}}^\alpha\right]D_{\mathbf{r}}^{\alpha\beta}\overline{\mathbf{F}}_{\mathbf{r}}^\beta$$

$$- \nabla\left(\sum_\alpha S_{\mathbf{r}}^\alpha\overline{\mathbf{F}}_{\mathbf{r}}^\alpha\hat{T}_{\mathbf{r}}\right) - \sum_\alpha S_{\mathbf{r}}^\alpha\overline{\mathbf{F}}_{\mathbf{r}}^\alpha\nabla\hat{T}_{\mathbf{r}}$$

By collecting Eqns. (7.3.5) with the usual viscous terms, and the reversible part of the dynamics in Eqns. (7.3.4)-(7.3.4), we obtain the final hydrodynamic equations for a phase separating mixture given in Eqns. (7.2).

7.4   Positive transport matrix

Although we know in advance that the transport matrix is positive, we check under which conditions the matrix D introduced in Eqn. (7.3.-50) is positive semidefinite. For the sake of simplicity, we study the binary mixture case. We double contract that matrix D with an arbitrary vector function $G_{\mathbf{r}} = (G_{\mathbf{r}}^A, G_{\mathbf{r}}^B, G_{\mathbf{r}}^g, G_{\mathbf{r}}^e)$, understanding that a contraction of the continuous matrix $M_{\mathbf{rr}'}$ involves integrals over the continuous indices. After some

algebra that involves integration by parts one easily arrives at the following expression.

$$\int d\mathbf{r}d\mathbf{r}' G_\mathbf{r} M_{\mathbf{r}\mathbf{r}'} G_{\mathbf{r}'}$$

$$= \int d\mathbf{r}\hat{T}\left(\nabla G_\mathbf{r}^A + \overline{F}_\mathbf{r}^A G_\mathbf{r}^\epsilon, \nabla G_\mathbf{r}^B + \overline{F}_\mathbf{r}^B G_\mathbf{r}^\epsilon, \nabla G_\mathbf{r}^\epsilon\right) \begin{pmatrix} D_\mathbf{r}^{AA} & D_\mathbf{r}^{AB} & \hat{T}S_\mathbf{r}^A \\ D_\mathbf{r}^{BA} & D_\mathbf{r}^{BB} & \hat{T}S_\mathbf{r}^B \\ \hat{T}S_\mathbf{r}^A & \hat{T}S_\mathbf{r}^B & \hat{T}\hat{\kappa}_\mathbf{r} \end{pmatrix} \begin{pmatrix} \nabla G_\mathbf{r}^A + \overline{F}_\mathbf{r}^A G_\mathbf{r}^\epsilon \\ \nabla G_\mathbf{r}^B + \overline{F}_\mathbf{r}^B G_\mathbf{r}^\epsilon \\ \nabla G_\mathbf{r}^\epsilon \end{pmatrix}$$

It is apparent that in order for this quantity to be positive (or zero), we need that the inner matrix is positive *semi*-definite. Note that the vector $(m_A, m_B, 0)$ is an eigenvector of the above matrix with null eigenvalue, due to Eqns. (7.3.5) and (7.3.5). Actually, by using these equations we can write the matrix as

$$\begin{pmatrix} D & -rD & \hat{T}S \\ -rD & r^2D & -r\hat{T}S \\ \hat{T}S & -r\hat{T}S & \hat{T}\hat{\kappa} \end{pmatrix}$$

where $r = m_A/m_B$ is the ratio of molecular mass of the two species, $D = D_\mathbf{r}^{AA}$, and $S = S_\mathbf{r}^A$. By multiplying (7.4) by the right and the left with an arbitrary vector (x, y, z) we obtain

$$(x, y, z) \begin{pmatrix} D & -rD & \hat{T}S \\ -rD & r^2D & -r\hat{T}S \\ \hat{T}S & -r\hat{T}S & \hat{T}\hat{\kappa} \end{pmatrix} \begin{pmatrix} x \\ y \\ z \end{pmatrix}$$
$$= D(x - ry)^2 + \hat{T}S2(x - ry)z + \hat{T}\hat{\kappa}z^2$$

For this quantity to be positive for arbitrary x, y, z we need D and $\hat{\kappa}$ to be positive. If we define $x' = D^{1/2}(x - ry)$, $z' = S/D^{1/2}z$, the quadratic form (7.4) becomes

$$(x' + z')^2 + \left(\frac{D\hat{\kappa}}{\hat{T}S^2} - 1\right)z'^2$$

which will be positive if and only if $D\hat{\kappa} > \hat{T}S^2$.

The conditions $D > 0$, $\hat{\kappa} > 0$, and $D\hat{\kappa} > \hat{T}S^2$ are actually the conditions for the following matrix to be definite positive

$$\begin{pmatrix} D & \hat{T}S \\ \hat{T}S & \hat{T}\hat{\kappa} \end{pmatrix}$$

By forming a quadratic form with an arbitrary vector (x, y) we can write

$$(x, y) \begin{pmatrix} D & \hat{T}S \\ \hat{T}S & \hat{T}\hat{\kappa} \end{pmatrix} \begin{pmatrix} x \\ y \end{pmatrix} = \frac{1}{2k_B\hat{T}} \int_{-\infty}^{\infty} \langle (xV^A + yQ)(xV^A + yQ)(t) \rangle$$

The right hand side of this equation is the time integral of an autocorrelation function. By recalling the Wiener-Khinchine theorem that states that the Fourier transform of a stationary autocorrelation function is positive [?], we conclude that the quadratic form is positive or, in other words, that the matrix (7.4) is a positive matrix [?].

8

Fluid-fluid systems: miscible-immiscible phase transition in mixtures

- Diffusion in mixtures
- Miscible-inmiscible fluid phase transition
- Liquid-Vapour phase transition

9

Isothermal Two fluid model $\hat{\rho}_{\mathbf{r}}^1, \hat{\rho}_{\mathbf{r}}^2, \hat{\mathbf{g}}_{\mathbf{r}}^1, \hat{\mathbf{g}}_{\mathbf{r}}^2, \hat{e}_{\mathbf{r}}$ (Boundary conditions for immiscible fluids)

[Boundary conditions in immiscible fluids]

144Isothermal Two fluid model $\hat{\rho}_{\mathbf{r}}^1, \hat{\rho}_{\mathbf{r}}^2, \hat{\mathbf{g}}_{\mathbf{r}}^1, \hat{\mathbf{g}}_{\mathbf{r}}^2, \hat{e}_{\mathbf{r}}$ (Boundary conditions for immiscible fluids)

10

Fluid-solid interaction: $n_{\mathbf{r}}, \mathbf{g}_{\mathbf{r}}, \mathbf{R}, \mathbf{P}$ (Boundary conditions)

Consider a liquid system of N monoatomic molecules described with the position and momenta of their center of mass. For simplicity, we consider that the system is in a volume $\mathscr{V}$ with periodic boundary conditions. Interacting with that sea of liquid molecules there is a group of N' bonded atoms forming a solid object of spherical shape. At the *microscopic level* the system is described by the set of all positions $\mathbf{q}_i$ and momenta $\mathbf{p}_i = m_i \mathbf{v}_i$ ($i = 1, \cdots, N$) of the liquid atoms plus the positions $\mathbf{r}_{i'}$ and momenta $\mathbf{p}_{i'} = m_{i'} \mathbf{v}_{i'}$ ($i' = 1, \cdots, N'$) of the atoms of the solid sphere. For compactness we will denote the microstate in either of the following forms z or q, p, q', p'. We will distinguish with a prime the labels of the atoms of the solid sphere from the unprimed labels of the liquid atoms. The microstate of the system evolves according to Hamilton's equations with a Hamiltonian given by

$$\hat{H}(z) = \sum_i^N \frac{p_i^2}{2m_i} + \sum_{i'}^{N'} \frac{p_{i'}^2}{2m_{i'}} + U(z)$$

where the potential energy $U(z)$ is given by

$$U(z) = V^l(q) + V^{ls}(q, q') + V^s(q')$$

We assume a pair-wise potential energy, where $V^l(q) = \frac{1}{2} \sum_{ij}^N \phi_{ij}^{ll}$ is the potential of interaction between liquid atoms, $V^{ls}(q, q') = \sum_{ii'}^{NN'} \phi_{ii'}^{ls}$ is the potential of interaction between liquid atoms and solid atoms, while $V^s(q') = \frac{1}{2} \sum_{i'j'}^{N'} \phi_{i'j'}^{ss}$ is the potential of interaction between the atoms of the solid object. Self interaction of the atoms is not considered, so $\phi_{ii} = 0$, etc.

We describe the system at a *coarse grained level* by selecting as CG variables the mass

and momentum density fields of the fluid and the center of mass position and momentum of the solid sphere. These are given by the following set of phase functions

$$\hat{\rho}_{\mathbf{r}}(z) = \sum_i^N m\delta(\mathbf{r} - \mathbf{q}_i), \qquad\qquad \hat{\mathbf{R}} = \frac{1}{N'} \sum_{i'}^{N'} \mathbf{r}_{i'}$$

$$\hat{\mathbf{g}}_{\mathbf{r}}(z) = \sum_i^N \mathbf{p}_i \delta(\mathbf{r} - \mathbf{q}_i), \qquad\qquad \hat{\mathbf{P}} = \sum_{i'}^{N'} \mathbf{p}_{i'}$$

For the sake of simplicity, we do not include orientational degrees of freedom of the solid for the time being. Note that by selecting the center of mass variables of the solid as the only ones necessary to describe the state of the solid we are implicitly assuming that the remaining solid degrees of freedom are much faster than the hydrodynamic fields. Otherwise the resulting dynamic equations would not be Markovian. Phase functions are denoted with a hat, while its actual values will be unhatted.

The relevant ensemble (**??**) now becomes

$$\overline{\rho}(z) = \frac{1}{Z[\lambda]} \rho^{\mathrm{eq}}(z)$$

$$\times \exp\left\{ -\beta \int d\mathbf{r} \left(\lambda_\rho(\mathbf{r}) \hat{\rho}_{\mathbf{r}}(z) + \boldsymbol{\lambda}_g(\mathbf{r}, t) \hat{\mathbf{g}}_{\mathbf{r}}(z) \right) \right\}$$

$$\times \exp\left\{ -\beta \boldsymbol{\lambda}_R \cdot \hat{\mathbf{R}} - \beta \boldsymbol{\lambda}_P \cdot \hat{\mathbf{P}} \right\}$$

The normalization factor is the λ-dependent grand-canonical partition function defined as

$$\Xi^H[\lambda] \equiv \sum_{N=0}^{\infty} \frac{1}{N! h^{3N}} \int dq\, dp\, dq'\, dp'$$

$$\times \exp\left\{ -\beta \hat{H}(z_N) - \beta \sum_{i=1}^N m\lambda_\rho(\mathbf{q}_i) - \beta \sum_{i=1}^N \mathbf{p}_i \cdot \boldsymbol{\lambda}_g(\mathbf{q}_i) \right\}$$

$$\times \exp\left\{ -\beta \boldsymbol{\lambda}_R \cdot \hat{\mathbf{R}} - \beta \boldsymbol{\lambda}_P \cdot \hat{\mathbf{P}} \right\}$$

Note that for the trace in phase space we are using a macrocanonical trace concerning the fluid degrees of freedom and a canonical trace for the solid degrees of freedom. The use of the macrocanonical ensemble for the liquid is standard in DFT as it solves some technical problems that appear when using the canonical ensemble. The conjugate fields λ of the CG variables (11.1.1) are fixed by the condition that the averages of the relevant variables (11.1.1) with the relevant ensemble coincide with the averages $\rho(\mathbf{r}), \mathbf{g}(\mathbf{r}), \mathbf{R}, \mathbf{P}$ computed with the actual ensemble, solution of the Liouville equation. This condition

can be expressed as in Eqs. (**??**) as

$$\rho(\mathbf{r}) = \frac{\delta \Omega^H[\lambda]}{\delta \lambda_\rho(\mathbf{r})} \qquad\qquad \mathbf{R} = \frac{\partial \Omega^H[\lambda]}{\partial \boldsymbol{\lambda}_R}$$

$$\mathbf{g}(\mathbf{r}) = \frac{\delta \Omega^H[\lambda]}{\delta \boldsymbol{\lambda}_g(\mathbf{r})} \qquad\qquad \mathbf{P} = \frac{\partial \Omega^H[\lambda]}{\partial \boldsymbol{\lambda}_P}$$

where the λ-dependent grand-canonical potential is given by

$$\Omega^H[\lambda] \equiv -k_B T \ln \Xi^H[\lambda]$$

We use the superscript H to denote that these quantities refer to the hydrodynamic level of description. Because the functional $\Omega^H[\lambda]$ is convex the conjugate variables $\lambda_\rho, \boldsymbol{\lambda}_g, \boldsymbol{\lambda}_R, \boldsymbol{\lambda}_P$ are in one to one connection with $\rho, \mathbf{g}, \mathbf{R}, \mathbf{P}$. Therefore, the functionals $\lambda_\rho[\rho, \mathbf{g}, \mathbf{R}, \mathbf{P}], \boldsymbol{\lambda}_g[\rho, \mathbf{g}, \mathbf{R}, \mathbf{P}], \boldsymbol{\lambda}_R[\rho, \mathbf{g}, \mathbf{R}, \mathbf{P}], \boldsymbol{\lambda}_P[\rho, \mathbf{g}, \mathbf{R}, \mathbf{P}]$ exist and are unique. We can therefore switch from the conjugate variables λ to the relevant variables a and construct the corresponding *hydrodynamic functional*. The hydrodynamic functional is given by the Legendre transform of the λ-dependent grand canonical potential, this is

$$\hat{H}[\rho, \mathbf{g}, \mathbf{R}, \mathbf{P}] = \Omega^H[\lambda_\rho, \boldsymbol{\lambda}_g, \boldsymbol{\lambda}_R, \boldsymbol{\lambda}_P]$$
$$- \int d\mathbf{r} \rho(\mathbf{r}) \lambda_\rho(\mathbf{r}) - \int d\mathbf{r} \mathbf{g}(\mathbf{r}) \boldsymbol{\lambda}_g(\mathbf{r})$$
$$- \boldsymbol{\lambda}_R \mathbf{R} - \boldsymbol{\lambda}_P \mathbf{P}$$

where here the λ are to be understood as functionals of the a. The hydrodynamic functional is the negative of the corresponding entropy (**??**) for the present level of description. Being a Legendre transform, the hydrodynamic functional satisfies the following relationships (see Eq. (2.1.7)), conjugate of those in Eq. (11.1.1),

$$\lambda_\rho(\mathbf{r}) = -\frac{\delta \hat{H}}{\delta \rho(\mathbf{r})} \qquad\qquad \boldsymbol{\lambda}_R = -\frac{\partial \hat{H}}{\partial \mathbf{R}}$$

$$\boldsymbol{\lambda}_g(\mathbf{r}) = -\frac{\delta \hat{H}}{\delta \mathbf{g}(\mathbf{r})} \qquad\qquad \boldsymbol{\lambda}_P = -\frac{\partial \hat{H}}{\partial \mathbf{P}}$$

In fact, it is possible to find the explicit expression of $\boldsymbol{\lambda}_g, \boldsymbol{\lambda}_P$ by performing the momentum integrals in Eq. (18.4). One obtains

$$\Xi^H[\lambda] \equiv \sum_{N=0}^{\infty} \frac{1}{N!} \int \frac{dq}{\Lambda^{3N}} \frac{dq'}{\Lambda^{3N'}} e^{-\beta U}$$
$$\times \exp\left\{ -\beta \sum_{i=1}^{N} \left(m\lambda_\rho(\mathbf{q}_i) - \frac{m}{2}\boldsymbol{\lambda}_g^2(\mathbf{q}_i) \right) \right\}$$
$$\times \exp\left\{ -\beta \left(\boldsymbol{\lambda}_R \hat{\mathbf{R}} - \frac{M'}{2}\boldsymbol{\lambda}_P^2 \right) \right\}$$

where Λ is the thermal wavelength. Then take the functional derivative of Eq. (18.4) with respect to the conjugate field $\boldsymbol{\lambda}_g(\mathbf{r})$, and the derivative with respect to $\boldsymbol{\lambda}_P$. Together with Eqs. (22.4), (22.5), this leads directly to the explicit form of the conjugate variables

$$\boldsymbol{\lambda}_g(\mathbf{r}) = -\frac{\mathbf{g}(\mathbf{r})}{\rho(\mathbf{r})} = -\mathbf{v}(\mathbf{r})$$

$$\boldsymbol{\lambda}_P = -\frac{\mathbf{P}}{M'}$$

and allows one to interpret these conjugate variables as (negative) velocities. The grand potential (22.5) takes now the form

$$\Omega^H[\lambda] = \Omega^{\mathrm{pos}}[\mu, \boldsymbol{\lambda}_R] - \frac{M'}{2}\boldsymbol{\lambda}_P{}^2$$

where we have defined the following grand potential

$$\Omega^{\mathrm{pos}}[\mu, \boldsymbol{\lambda}_R] \equiv -k_B T \ln \sum_{N=0}^{\infty} \frac{1}{N!} \int \frac{dq}{\Lambda^{3N}} \frac{dq'}{\Lambda^{3N'}}$$

$$\times \exp\left\{-\beta\left(U - \sum_{i=1}^{N} m\mu(\mathbf{q}_i) + \boldsymbol{\lambda}_R\hat{\mathbf{R}}\right)\right\}$$

and the chemical potential per unit mass has been introduced as

$$\mu(\mathbf{r}) \equiv \frac{1}{2}\lambda_g^2(\mathbf{r}) - \lambda_\rho(\mathbf{r})$$

The grand potential $\Omega^{\mathrm{pos}}[\mu, \boldsymbol{\lambda}_R]$ is similar to the macrocanonical grand potential of a fluid, except for the presence of the solid degrees of freedom and the corresponding conjugate variable $\boldsymbol{\lambda}_R$. The Legendre transform of the grand potential for a simple liquid gives the classic (free energy) density functional and we may pursue now the same route in order to define the free energy density functional for a fluid in the presence of a solid sphere. We need first to compute the derivatives of the functional (10) that give

$$\frac{\delta\Omega^{\mathrm{pos}}}{\delta\mu(\mathbf{r})}[\mu, \boldsymbol{\lambda}_R] = \langle\hat{\rho}_{\mathbf{r}}\rangle^{\mu, \boldsymbol{\lambda}_R}$$

$$\frac{\partial\Omega^{\mathrm{pos}}}{\partial\boldsymbol{\lambda}_R}[\mu, \boldsymbol{\lambda}_R] = \langle\hat{\mathbf{R}}\rangle^{\mu, \boldsymbol{\lambda}_R}$$

where the averages $\langle\cdots\rangle^{\mu, \boldsymbol{\lambda}_R}$ are defined in these equations. The second derivatives of Ω^{pos} are given by covariances and this implies that $\Omega^{\mathrm{pos}}[\mu, \boldsymbol{\lambda}_R]$ is a convex function(al). Therefore, the connection between $\langle\hat{\rho}_{\mathbf{r}}\rangle^{\mu, \boldsymbol{\lambda}_R}, \langle\hat{\mathbf{R}}\rangle^{\mu, \boldsymbol{\lambda}_R}$ and $\mu(\mathbf{r}), \boldsymbol{\lambda}_R$ is one to one. Note also that because the phase functions $\hat{\rho}_{\mathbf{r}}, \hat{\mathbf{R}}$ are velocity independent, we have that the

averages are given by

$$\langle \hat{\rho}_{\mathbf{r}} \rangle^{\mu, \boldsymbol{\lambda}_R} = \mathrm{Tr}[\overline{\rho} \hat{\rho}_{\mathbf{r}}] = \rho_{\mathbf{r}}$$
$$\langle \hat{\mathbf{R}} \rangle^{\mu, \boldsymbol{\lambda}_R} = \mathrm{Tr}[\overline{\rho} \hat{\mathbf{R}}] = \mathbf{R}$$

Therefore, we have a one to one connection between the conjugate variables $\mu(\mathbf{r}), \boldsymbol{\lambda}_R$ and the averages $\rho(\mathbf{r}), \mathbf{R}$ of the CG variables. The free energy functional $F[\rho, \mathbf{R}]$ of a structured fluid in the presence of a solid sphere is obtained as the following Legendre transform

$$F[\rho, \mathbf{R}] \equiv \Omega^{\mathrm{pos}}[\mu, \boldsymbol{\lambda}_R] + \int d\mathbf{r} \rho(\mathbf{r}) \mu(\mathbf{r}) - \boldsymbol{\lambda}_R \mathbf{R}$$

whose derivatives are given by

$$\frac{\delta F}{\delta \rho(\mathbf{r})}[\rho, \mathbf{R}] = \mu(\mathbf{r})$$
$$\frac{\partial F}{\partial \mathbf{R}}[\rho, \mathbf{R}] = -\boldsymbol{\lambda}_R$$

We may now express the hydrodynamic functional (10) as

$$\hat{H}[\rho, \mathbf{g}, \mathbf{R}, \mathbf{P}] = \int \frac{\mathbf{g}^2(\mathbf{r})}{2\rho(\mathbf{r})} d\mathbf{r} + \frac{\mathbf{P}^2}{2M'} + F[\rho, \mathbf{R}]$$

The expression (22.5) of the hydrodynamic functional $\hat{H}$ as the sum of a kinetic part and a "potential" part that depends on both the density and the positon of the solid is a non-trivial exact result.

We may compute the functional derivative of the hydrodynamic functional (22.5) with respect to the position $\mathbf{R}$ and we obtain

$$\frac{\partial \hat{H}}{\partial \mathbf{R}}[\rho, \mathbf{g}, \mathbf{R}, \mathbf{P}] = \frac{\partial F}{\partial \mathbf{R}}[\rho, \mathbf{R}] = -\boldsymbol{\lambda}_R$$

As we will see below, $\boldsymbol{\lambda}_R$ is just the average force on the solid due to the fluid. Therefore, the "potential" part $F[\rho, \mathbf{R}]$ of the hydrodynamic functional really acts as a potential energy whose negative gradient gives the actual force on the sphere. For future reference, we may also compute the functional derivative of the hydrodynamic functional $\hat{H}$ with respect to the density field with the result

$$\frac{\delta \hat{H}}{\delta \rho(\mathbf{r})}[\rho, \mathbf{g}, \mathbf{R}, \mathbf{P}] = -\frac{\mathbf{v}^2(\mathbf{r})}{2} + \frac{\delta F}{\delta \rho(\mathbf{r})}[\rho, \mathbf{R}]$$

10.1 The time derivatives

The time derivatives of the coarse variables play a fundamental role in the final structure of the dynamic equations (12.2). The time derivative $i\mathcal{L}X$ is the result of applying the

Liouville operator (12.2) to the CG variables. In this section, we discuss the particular form of $i\mathcal{L}X$ for the case of selected CG variables (11.1.1). It proves convenient to use the well-known results for the time derivatives of the microscopic densities introduced in Eq. (11.1.1). They are

$$i\mathcal{L}\hat{\rho}_\mathbf{r}(z) = -\boldsymbol{\nabla}\cdot\hat{\mathbf{g}}_\mathbf{r}(z)$$

$$i\mathcal{L}\hat{\mathbf{g}}_\mathbf{r}(z) = -\boldsymbol{\nabla}\hat{\Pi}_\mathbf{r} + \hat{\mathbf{F}}_\mathbf{r}^l(z)$$

Here, the kinetic stress tensor is

$$\hat{\Pi}_\mathbf{r} = \sum_i^N \mathbf{p}_i\mathbf{v}_i\delta(\mathbf{r} - \mathbf{q}_i)$$

and the total force density $\hat{\mathbf{F}}_\mathbf{r}^l(z)$ on the liquid is defined as

$$\hat{\mathbf{F}}_\mathbf{r}^l(z) = \sum_i^N -\frac{\partial U}{\partial \mathbf{q}_i}\delta(\mathbf{r} - \mathbf{q}_i)$$

We may decompose this force density in the two parts coming from the forces that the liquid exerts on the liquid and the forces that the solid exerts on the liquid, this is, $\hat{\mathbf{F}}_\mathbf{r}^l(z) = \hat{\mathbf{F}}_\mathbf{r}^{l\rightarrow l}(z) + \hat{\mathbf{F}}_\mathbf{r}^{s\rightarrow l}(z)$ with

$$\hat{\mathbf{F}}_\mathbf{r}^{l\rightarrow l}(z) \equiv \sum_{ij}^{NN} \hat{\mathbf{F}}_{ij}\delta(\mathbf{r} - \mathbf{q}_i)$$

$$\hat{\mathbf{F}}_\mathbf{r}^{s\rightarrow l}(z) \equiv \sum_{ij'}^{NN'} \hat{\mathbf{F}}_{ij'}\delta(\mathbf{r} - \mathbf{q}_i)$$

where $\hat{\mathbf{F}}_{ij'}$ is the force that atom j' of the molecule exerts on atom i of the liquid. This is, $\hat{\mathbf{F}}_\mathbf{r}^{l\rightarrow l}(z)$ is the force density that the liquid exerts on the liquid molecules that are around the point $\mathbf{r}$ and $\hat{\mathbf{F}}_\mathbf{r}^{s\rightarrow l}(z)$ is the force density that the solid object exerts on the liquid at the point $\mathbf{r}$.

By using a standard trick [?, ?, ?]

$$\delta(\mathbf{r} - \mathbf{q}_i) - \delta(\mathbf{r} - \mathbf{q}_j) = -\boldsymbol{\nabla}\int_0^1 d\epsilon\mathbf{q}_{ij}\delta(\mathbf{r} - \mathbf{q}_j - \epsilon\mathbf{q}_{ij})$$

the liquid force density $\hat{\mathbf{F}}_\mathbf{r}^{l\rightarrow l}(z)$ can be expressed as the divergence of the potential

microscopic stress tensor, this is

$$\hat{\mathbf{F}}_{\mathbf{r}}^{l\to l}(z) = -\boldsymbol{\nabla}\hat{\boldsymbol{\Sigma}}_{\mathbf{r}}(z)$$

$$\hat{\boldsymbol{\Sigma}}_{\mathbf{r}}(z) \equiv \frac{1}{2}\sum_{ij}^{N}\mathbf{e}_{ij}\hat{\mathbf{F}}_{ij}\int_{0}^{r_{ij}}dx\delta(\mathbf{r} - \mathbf{q}_i + x\mathbf{e}_{ij})$$

In this way, we may also express the time derivative of the momentum density (10.1) in the form

$$i\mathcal{L}\hat{\mathbf{g}}_{\mathbf{r}} = -\boldsymbol{\nabla}\hat{\boldsymbol{\sigma}}_{\mathbf{r}} + \mathbf{F}_{\mathbf{r}}^{s\to l}$$

where $\hat{\boldsymbol{\sigma}}_{\mathbf{r}}$ is the total microscopic stress tensor of the fluid, this is

$$\hat{\boldsymbol{\sigma}}_{\mathbf{r}} = \hat{\boldsymbol{\Pi}}_{\mathbf{r}} + \hat{\boldsymbol{\Sigma}}_{\mathbf{r}}$$

$$= \sum_{i}^{N}\mathbf{p}_i\mathbf{v}_i\delta(\mathbf{r} - \mathbf{q}_i) + \frac{1}{2}\sum_{ij}^{N}\mathbf{e}_{ij}\hat{\mathbf{F}}_{ij}\int_{0}^{r_{ij}}dx\delta(\mathbf{r} - \mathbf{q}_i + x\mathbf{e}_{ij})$$

In this way, we make the fundamental observation that the force density on the fluid (10.1) has two components, one which is the force done by the fluid itself and that has the form of a divergence of a stress tensor and another one due to the solid that cannot be expressed as the divergence of a stress.

For the solid object we have

$$i\mathcal{L}\hat{\mathbf{R}} = \frac{\hat{\mathbf{P}}}{M}$$

$$i\mathcal{L}\hat{\mathbf{P}} = -\int d\mathbf{r}\hat{\mathbf{F}}_{\mathbf{r}}^{s\to l}(z)$$

Note that the total momentum, which is defined in terms of the coarse-grained variables as

$$\hat{\mathbf{P}}_T = \int \hat{\mathbf{g}}_{\mathbf{r}}(z)d\mathbf{r} + \hat{\mathbf{P}}(z)$$

satisfies $i\mathcal{L}\hat{\mathbf{P}}_T = 0$ and is, therefore, a conserved quantity of the microscopic dynamics.

10.2 Reversible dynamics

We consider in this subsection the reversible part $v_i(t)$ in Eq. (12.2) for the case that the CG variables are (11.1.1). For the mass density we have

$$\partial_t\rho(\mathbf{r},t)|_{\text{rev}} = \text{Tr}[\overline{\rho}_t i\mathcal{L}\hat{\rho}_{\mathbf{r}}] = -\boldsymbol{\nabla}\mathbf{g}(\mathbf{r},t)$$

where we have used Eq. (10.1) and the fact that the relevant ensemble average of $\hat{\mathbf{g}}_{\mathbf{r}}$ is precisely the momentum density field $\mathbf{g}_{\mathbf{r}}$. On the other hand, the reversible part of the

momentum density evolution equation is

$$\partial_t \mathbf{g}(\mathbf{r},t)|_{\text{rev}} = \text{Tr}[\overline{\rho}_t i\mathcal{L}\hat{\mathbf{g}}_\mathbf{r}]$$
$$= -\boldsymbol{\nabla}\text{Tr}[\overline{\rho}_t \hat{\boldsymbol{\Pi}}_\mathbf{r}] + \text{Tr}[\overline{\rho}_t \hat{\mathbf{F}}_\mathbf{r}]$$

We introduce the Galilean operator $\mathscr{G}$ that when applied to any phase function changes its velocity arguments from $\mathbf{v}_i \to \mathbf{v}_i + \mathbf{v}(\mathbf{q}_i)$ for i a fluid particle. Within any trace this is just a change of variables. Therefore, we have the property

$$\text{Tr}[\overline{\rho}_t \hat{F}] = \text{Tr}[(\mathscr{G}\overline{\rho}_t)(\mathscr{G}\hat{F})]$$

The action of the Galilean operator on the relevant ensemble is

$$\mathscr{G}\overline{\rho}_t = \frac{1}{\Xi[\lambda(t)]}\rho^{\text{eq}}(z)\exp\left\{\beta\int d\mathbf{r}\mu(\mathbf{r})\hat{\rho}_\mathbf{r}(z)\right\}$$
$$\times \exp\left\{-\beta\boldsymbol{\lambda}_R(t)\cdot\hat{\mathbf{R}} - \beta\boldsymbol{\lambda}_P(t)\cdot\hat{\mathbf{P}}\right\}$$

where the chemical potential per unit mass has been introduced in Eq. (10). The action of the Galilean operator on the microscopic kinetic stress tensor is

$$\mathscr{G}\hat{\boldsymbol{\Pi}}_\mathbf{r} = \hat{\boldsymbol{\Pi}}_\mathbf{r} + \mathbf{v}(\mathbf{r})\hat{\mathbf{g}}_\mathbf{r} + \hat{\mathbf{g}}_\mathbf{r}\mathbf{v}(\mathbf{r}) + \mathbf{v}(\mathbf{r})\mathbf{v}(\mathbf{r})\hat{\rho}_\mathbf{r}$$

By noting that the ensemble (10.2) is Gaussian in momenta, we have finally

$$\text{Tr}[\overline{\rho}_t \hat{\boldsymbol{\Pi}}_\mathbf{r}] = \frac{k_BT}{m}\rho(\mathbf{r})\boldsymbol{\delta} + \mathbf{v}(\mathbf{r})\mathbf{v}(\mathbf{r})\rho(\mathbf{r})$$

The last term $\text{Tr}[\overline{\rho}_t \hat{\mathbf{F}}_\mathbf{r}]$ in Eq. (11.3) is computed in Eq. (10.12) of the appendix. By collecting (10.2) and (10.12) into the momentum density equation (11.3) we obtain

$$\partial_t \mathbf{g}(\mathbf{r},t)|_{\text{rev}} = -\boldsymbol{\nabla}\mathbf{v}(\mathbf{r})\mathbf{g}(\mathbf{r}) - \rho(\mathbf{r})\boldsymbol{\nabla}\mu(\mathbf{r})$$

Finally, the averages with the relevant ensemble of the solid object variables are

$$\text{Tr}[\overline{\rho}_t i\mathcal{L}\hat{\mathbf{R}}] = \frac{\mathbf{P}}{M}$$
$$\text{Tr}[\overline{\rho}_t i\mathcal{L}\hat{\mathbf{P}}] = -\frac{\partial F}{\partial\mathbf{R}}[\rho,\mathbf{R}]$$

where we have used Eq. (10.12) in the Appendix.

The reversible part of the dynamics has the form

$$\partial_t \rho(\mathbf{r})|_{\text{rev}} = -\boldsymbol{\nabla} \cdot \mathbf{g}(\mathbf{r})$$

$$\partial_t \mathbf{g}(\mathbf{r})|_{\text{rev}} = -\boldsymbol{\nabla} \cdot \mathbf{g}(\mathbf{r})\mathbf{v}(\mathbf{r}) - \rho(\mathbf{r})\boldsymbol{\nabla}\mu(\mathbf{r})$$

$$\partial_t \left. \mathbf{R}\right|_{\text{rev}} = \frac{\mathbf{P}}{M}$$

$$\partial_t \left. \mathbf{P}\right|_{\text{rev}} = -\frac{\partial F}{\partial \mathbf{R}}[\rho, \mathbf{R}]$$

10.3 Irreversible dynamics

Because the time derivatives of $\rho(\mathbf{r})$ and $\mathbf{R}$ are given in terms of CG variables themselves, it is apparent that the effect of the projection operator in (20.2.1) is simply $\mathcal{Q}i\mathcal{L}\rho_{\mathbf{r}} = 0$ and $\mathcal{Q}i\mathcal{L}\mathbf{R}_\mu = 0$ resulting in a large simplification of the friction matrix. The irreversible part of the dynamics $\sum_j D_{ij}\lambda_j$ in Eq. (12.2) now takes the form

$$\partial_t \begin{pmatrix} \rho(\mathbf{r}) \\ \\ \mathbf{g}(\mathbf{r}) \\ \\ \mathbf{R} \\ \\ \mathbf{P} \end{pmatrix}_{\text{irr}} = - \begin{pmatrix} 0 & 0 & 0 & 0 \\ 0 & \int d\mathbf{r}' M_{\mathbf{rr}'}^{gg} & 0 & M_{\mathbf{r}}^{gP} \\ 0 & 0 & 0 & 0 \\ 0 & \int d\mathbf{r}' M_{\mathbf{r}'}^{Pg} & 0 & M^{PP} \end{pmatrix} \begin{pmatrix} \frac{\delta \hat{H}}{\delta \rho_{\mathbf{r}'}} \\ \\ \frac{\delta \hat{H}}{\delta \mathbf{g}_{\mathbf{r}'}} \\ \\ \frac{\partial \hat{H}}{\delta \mathbf{R}} \\ \\ \frac{\partial \hat{H}}{\delta \mathbf{P}} \end{pmatrix}$$

where the non-zero elements are defined as

$$M_{\mathbf{rr}'}^{gg} = \frac{1}{k_B T}\int_0^\infty dt \langle \delta i \mathcal{L}\hat{\mathbf{g}}_{\mathbf{r}}(t)\delta i \mathcal{L}\hat{\mathbf{g}}_{\mathbf{r}'}\rangle^\lambda$$

$$M_{\mathbf{r}}^{gP} = \frac{1}{k_B T}\int_0^\infty dt \langle \delta i \mathcal{L}\hat{\mathbf{g}}_{\mathbf{r}}(t)\delta i \mathcal{L}\hat{\mathbf{P}}\rangle^\lambda$$

$$M_{\mathbf{r}'}^{Pg} = \frac{1}{k_B T}\int_0^\infty dt \langle \delta i \mathcal{L}\hat{\mathbf{P}}(t)\delta i \mathcal{L}\hat{\mathbf{g}}_{\mathbf{r}'}\rangle^\lambda$$

$$M^{PP} = \frac{1}{k_B T}\int_0^\infty dt \langle \delta i \mathcal{L}\hat{\mathbf{P}}(t)\delta i \mathcal{L}\hat{\mathbf{P}}\rangle^\lambda$$

We now use the decomposition (10.1) of the force density in terms of liquid and solid contributions. Then

$$M_{\mathbf{rr'}}^{gg} = \frac{1}{k_B T} \int_0^\infty dt \langle \delta i \mathcal{L} \hat{\mathbf{g}}_{\mathbf{r}}(t) \delta i \mathcal{L} \hat{\mathbf{g}}_{\mathbf{r'}} \rangle^\lambda = \frac{1}{k_B T} \int_0^\infty dt \langle (-\boldsymbol{\nabla} \delta \hat{\boldsymbol{\sigma}}_{\mathbf{r}} + \delta \hat{\mathbf{F}}_{\mathbf{r}}^{\mathrm{s \to l}})(t)(-\boldsymbol{\nabla}' \delta \hat{\boldsymbol{\sigma}}_{\mathbf{r'}} + \delta \hat{\mathbf{F}}_{\mathbf{r'}}^{\mathrm{s \to l}}) \rangle^\lambda$$

$$= \frac{1}{k_B T} \int_0^\infty dt \langle \boldsymbol{\nabla} \delta \hat{\boldsymbol{\sigma}}_{\mathbf{r}}(t) \boldsymbol{\nabla}' \delta \hat{\boldsymbol{\sigma}}_{\mathbf{r'}} \rangle^\lambda - \frac{1}{k_B T} \int_0^\infty dt \langle \delta \hat{\mathbf{F}}_{\mathbf{r}}^{\mathrm{s \to l}}(t) \boldsymbol{\nabla}' \delta \hat{\boldsymbol{\sigma}}_{\mathbf{r'}} \rangle^\lambda$$

$$- \frac{1}{k_B T} \int_0^\infty dt \langle \boldsymbol{\nabla} \delta \hat{\boldsymbol{\sigma}}_{\mathbf{r}}(t) \delta \hat{\mathbf{F}}_{\mathbf{r'}}^{\mathrm{s \to l}} \rangle^\lambda + \frac{1}{k_B T} \int_0^\infty dt \langle \delta \hat{\mathbf{F}}_{\mathbf{r}}^{\mathrm{s \to l}}(t) \delta \hat{\mathbf{F}}_{\mathbf{r'}}^{\mathrm{s \to l}} \rangle^\lambda$$

$$= \boldsymbol{\nabla} \boldsymbol{\nabla}' \boldsymbol{\eta}_{\mathbf{rr'}} - \boldsymbol{\nabla}' \mathbf{G}_{\mathbf{rr'}} - \boldsymbol{\nabla} \mathbf{H}_{\mathbf{rr'}} + \boldsymbol{\gamma}_{\mathbf{rr'}}$$

$$M_{\mathbf{r}}^{gP} = \frac{1}{k_B T} \int_0^\infty dt \langle \delta i \mathcal{L} \hat{\mathbf{g}}_{\mathbf{r}}(t) \delta i \mathcal{L} \hat{\mathbf{P}} \rangle^\lambda = -\frac{1}{k_B T} \int_0^\infty dt \left\langle \int d\mathbf{r'} (-\boldsymbol{\nabla} \delta \hat{\boldsymbol{\sigma}}_{\mathbf{r}}(t) + \delta \hat{\mathbf{F}}_{\mathbf{r}}^{\mathrm{s \to l}}(t)) \delta \hat{\mathbf{F}}_{\mathbf{r'}}^{\mathrm{s \to l}} \right\rangle^\lambda$$

$$= \int d\mathbf{r'} \boldsymbol{\nabla} \mathbf{H}_{\mathbf{rr'}} - \int d\mathbf{r'} \boldsymbol{\gamma}_{\mathbf{rr'}}$$

$$M_{\mathbf{r'}}^{Pg} = \frac{1}{k_B T} \int_0^\infty dt \langle \delta i \mathcal{L} \hat{\mathbf{P}}(t) \delta i \mathcal{L} \hat{\mathbf{g}}_{\mathbf{r'}} \rangle^\lambda = -\frac{1}{k_B T} \int_0^\infty dt \left\langle \int d\mathbf{r} \mathbf{F}_{\mathbf{r}}^{\mathrm{s \to l}}(t)(-\boldsymbol{\nabla}' \delta \hat{\boldsymbol{\sigma}}_{\mathbf{r'}} + \delta \hat{\mathbf{F}}_{\mathbf{r'}}^{\mathrm{s \to l}}) \right\rangle^\lambda$$

$$= \int d\mathbf{r} \boldsymbol{\nabla}' \mathbf{G}_{\mathbf{rr'}} - \int d\mathbf{r} \boldsymbol{\gamma}_{\mathbf{rr'}}$$

$$M^{PP} = \frac{1}{k_B T} \int_0^\infty dt \langle \delta i \mathcal{L} \hat{\mathbf{P}}(t) \delta i \mathcal{L} \hat{\mathbf{P}} \rangle^\lambda = \frac{1}{k_B T} \int d\mathbf{r} \int d\mathbf{r'} \int_0^\infty dt \langle \hat{\mathbf{F}}_{\mathbf{r}}^{\mathrm{s \to l}}(t) \delta \hat{\mathbf{F}}_{\mathbf{r'}}^{\mathrm{s \to l}} \rangle^\lambda$$

$$= \int d\mathbf{r} \int d\mathbf{r'} \boldsymbol{\gamma}_{\mathbf{rr'}}$$

In these expressions we have introduced the following non-local transport coefficients: the viscosity fourth order tensor $\boldsymbol{\eta}_{\mathbf{rr'}}$, the coupling third order tensors $\mathbf{H}_{\mathbf{rr'}}, \mathbf{G}_{\mathbf{rr'}}$ and the friction second order tensor $\boldsymbol{\gamma}_{\mathbf{rr'}}$. They are defined by the Green-Kubo formulas

$$\boldsymbol{\eta}_{\mathbf{rr'}} = \frac{1}{k_B T} \int_0^\infty dt \langle \delta \hat{\boldsymbol{\sigma}}_{\mathbf{r}}(t) \delta \hat{\boldsymbol{\sigma}}_{\mathbf{r'}} \rangle^\lambda$$

$$\mathbf{H}_{\mathbf{rr'}} = \frac{1}{k_B T} \int_0^\infty dt \langle \delta \hat{\boldsymbol{\sigma}}_{\mathbf{r}}(t) \delta \hat{\mathbf{F}}_{\mathbf{r'}}^{\mathrm{s \to l}} \rangle^\lambda$$

$$\mathbf{G}_{\mathbf{rr'}} = \frac{1}{k_B T} \int_0^\infty dt \langle \delta \hat{\mathbf{F}}_{\mathbf{r}}^{\mathrm{s \to l}}(t) \delta \hat{\boldsymbol{\sigma}}_{\mathbf{r'}} \rangle^\lambda$$

$$\boldsymbol{\gamma}_{\mathbf{rr'}} = \frac{1}{k_B T} \int_0^\infty dt \langle \delta \hat{\mathbf{F}}_{\mathbf{r}}^{\mathrm{s \to l}}(t) \delta \hat{\mathbf{F}}_{\mathbf{r'}}^{\mathrm{s \to l}} \rangle^\lambda$$

By using these expressions (10.14) for the friction matrix elements into the irreversible part of the dynamics (11.4) one obtains

$$
\partial_t \mathbf{g}^\mu(\mathbf{r})|_{\mathrm{irr}} = -\int d\mathbf{r}' M^{gg}_{\mathbf{rr}'} \frac{\delta \hat{H}}{\delta \mathbf{g}_{\mathbf{r}'}} + M^{gP}_{\mathbf{r}} \frac{\partial \hat{H}}{\partial \mathbf{P}}
$$

$$
= -\int d\mathbf{r}' \left[\boldsymbol{\nabla}^\nu \boldsymbol{\nabla}^{\mu'}_{\mathbf{r}'} \eta^{\mu\nu\mu'\nu'}_{\mathbf{rr}'} - \boldsymbol{\nabla}^{\nu'}_{\mathbf{r}'} \mathbf{G}^{\mu\mu'\nu'}_{\mathbf{rr}'} - \boldsymbol{\nabla}^\nu \mathbf{H}^{\mu\nu\mu'}_{\mathbf{rr}'} + \gamma^{\mu\mu'}_{\mathbf{rr}'} \right] \mathbf{v}^{\mu'}(\mathbf{r}') - \int d\mathbf{r}' \left[\boldsymbol{\nabla}^\nu \mathbf{H}^{\mu\nu\mu'}_{\mathbf{rr}'} - \gamma^{\mu\mu'}_{\mathbf{rr}'} \right] \mathbf{V}^{\mu'}
$$

$$
\partial_t \mathbf{P}^\mu|_{\mathrm{irr}} = -\int d\mathbf{r}' M^{Pg}_{\mathbf{r}'} \frac{\delta \hat{H}}{\delta \mathbf{g}_{\mathbf{r}'}} - M^{PP} \frac{\partial \hat{H}}{\partial \mathbf{P}}
$$

$$
= \int d\mathbf{r} \int d\mathbf{r}' \left[\boldsymbol{\nabla}^{\nu'}_{\mathbf{r}'} \mathbf{G}^{\mu\mu'\nu'}_{\mathbf{rr}'} + \gamma^{\mu\mu'}_{\mathbf{rr}'} \right] \mathbf{v}^{\mu'}(\mathbf{r}') - \int d\mathbf{r} \int d\mathbf{r} \gamma^{\mu\mu'}_{\mathbf{rr}'} \mathbf{V}^{\mu'}
$$

By collecting the reversible part of the dynamics (11.3) and the irreversible part (11.10) we obtain the final dynamic equations for the CG variables

$$
\partial_t \rho(\mathbf{r}) = -\boldsymbol{\nabla} \cdot \mathbf{g}(\mathbf{r})
$$

$$
\partial_t \mathbf{g}^\mu(\mathbf{r}) = -\boldsymbol{\nabla}^{\mu'} \mathbf{g}^\mu(\mathbf{r}) \mathbf{v}^{\mu'}(\mathbf{r}) - \rho(\mathbf{r}) \boldsymbol{\nabla}^\mu \mu(\mathbf{r})
$$

$$
- \int d\mathbf{r}' \left[\boldsymbol{\nabla}^\nu_{\mathbf{r}} \boldsymbol{\nabla}^{\nu'}_{\mathbf{r}'} \eta^{\mu\nu\mu'\nu'}_{\mathbf{rr}'} - \boldsymbol{\nabla}^{\nu'}_{\mathbf{r}'} \mathbf{G}^{\mu\mu'\nu'}_{\mathbf{rr}'} - \boldsymbol{\nabla}^\nu_{\mathbf{r}} \mathbf{H}^{\mu\nu\mu'}_{\mathbf{rr}'} + \gamma^{\mu\mu'}_{\mathbf{rr}'} \right] \mathbf{v}^{\mu'}(\mathbf{r}') - \int d\mathbf{r}' \left[\boldsymbol{\nabla}^\nu_{\mathbf{r}} \mathbf{H}^{\mu\nu\mu'}_{\mathbf{rr}'} - \gamma^{\mu\mu'}_{\mathbf{rr}'} \right] \mathbf{V}^{\mu'}
$$

$$
\dot{\mathbf{R}} = \frac{\mathbf{P}}{M}
$$

$$
\dot{\mathbf{P}}^\mu = -\frac{\partial F}{\partial \mathbf{R}^\mu} + \int d\mathbf{r} \int d\mathbf{r}' \left[\boldsymbol{\nabla}^{\nu'}_{\mathbf{r}'} \mathbf{G}^{\mu\mu'\nu'}_{\mathbf{rr}'} + \gamma^{\mu\mu'}_{\mathbf{rr}'} \right] \mathbf{v}^{\mu'}(\mathbf{r}') - \int d\mathbf{r} \int d\mathbf{r} \gamma^{\mu\mu'}_{\mathbf{rr}'} \mathbf{V}^{\mu'}
$$

Greek indices stand for components of vectors and tensors. In order to have equations in a way that manifestly conserves momentum it is useful to introduce a vanishing term of the form $\int d\mathbf{r} \boldsymbol{\nabla}_{\mathbf{r}} f_{\mathbf{rr}'} = 0$ in the momentum equation of the sphere that it is therefore written as

$$
\dot{\mathbf{P}}^\mu = -\frac{\partial F}{\partial \mathbf{R}^\mu} + \int d\mathbf{r} \int d\mathbf{r}' \left[\boldsymbol{\nabla}^{\nu'}_{\mathbf{r}'} \mathbf{G}^{\mu\mu'\nu'}_{\mathbf{rr}'} - \boldsymbol{\nabla}^{\nu'}_{\mathbf{r}} \mathbf{H}^{\mu\mu'\nu'}_{\mathbf{rr}'} + \gamma^{\mu\mu'}_{\mathbf{rr}'} \right] \mathbf{v}^{\mu'}(\mathbf{r}') + \int d\mathbf{r} \int d\mathbf{r}' \left[\boldsymbol{\nabla}^\nu_{\mathbf{r}} \mathbf{H}^{\mu\nu\mu'}_{\mathbf{rr}'} - \gamma^{\mu\mu'}_{\mathbf{rr}'} \right] \mathbf{V}^{\mu'}
$$

The final equations have a compact form when written in the form (several integration by parts are done)

$$
\partial_t \rho(\mathbf{r}) = -\boldsymbol{\nabla} \cdot \mathbf{g}(\mathbf{r})
$$

$$
\partial_t \mathbf{g}^\mu(\mathbf{r}) = -\boldsymbol{\nabla}^{\mu'} \mathbf{g}^\mu(\mathbf{r}) \mathbf{v}^{\mu'}(\mathbf{r}) - \rho(\mathbf{r}) \boldsymbol{\nabla}^\mu \mu(\mathbf{r}) + \boldsymbol{\nabla}^\nu_{\mathbf{r}} \int d\mathbf{r}' \eta^{\mu\nu\mu'\nu'}_{\mathbf{rr}'} \boldsymbol{\nabla}^{\nu'}_{\mathbf{r}'} \mathbf{v}^{\mu'}(\mathbf{r}') + \phi^\mu(\mathbf{r})
$$

$$
\dot{\mathbf{R}}^\mu = \frac{\mathbf{P}^\mu}{M}
$$

$$
\dot{\mathbf{P}}^\mu = -\frac{\partial F}{\partial \mathbf{R}^\mu} - \int d\mathbf{r} \phi^\mu(\mathbf{r})
$$

where we have introduced the irreversible coupling force per unit volume $\phi^\mu(\mathbf{r})$ as

$$
\phi^\mu(\mathbf{r}) = \int d\mathbf{r}' \left[\boldsymbol{\nabla}_{\mathbf{r}'}^{\nu'} \mathbf{G}_{\mathbf{rr}'}^{\mu\mu'\nu'} + \boldsymbol{\nabla}_{\mathbf{r}}^{\nu'} \mathbf{H}_{\mathbf{rr}'}^{\mu\mu'\nu'} - \boldsymbol{\gamma}_{\mathbf{rr}'}^{\mu\mu'} \right] \mathbf{v}^{\mu'}(\mathbf{r}') - \int d\mathbf{r}' \left[\boldsymbol{\nabla}_{\mathbf{r}}^{\nu} \mathbf{H}_{\mathbf{rr}'}^{\mu\nu\mu'} - \boldsymbol{\gamma}_{\mathbf{rr}'}^{\mu\mu'} \right] \mathbf{V}^{\mu'}
$$

$$
= - \int d\mathbf{r}' \mathbf{G}_{\mathbf{rr}'}^{\mu\mu'\nu'} \boldsymbol{\nabla}_{\mathbf{r}'}^{\nu'} \mathbf{v}^{\mu'}(\mathbf{r}') + \boldsymbol{\nabla}_{\mathbf{r}}^{\nu} \int d\mathbf{r}' \mathbf{H}_{\mathbf{rr}'}^{\mu\nu\mu'} (\mathbf{v}^{\mu'}(\mathbf{r}') - \mathbf{V}^{\mu'}) - \int d\mathbf{r}' \boldsymbol{\gamma}_{\mathbf{rr}'}^{\mu\mu'} (\mathbf{v}^{\mu'}(\mathbf{r}') - \mathbf{V}^{\mu'})
$$

Eqs. (10.3) are one of the main results of the present paper. They describe the non-local hydrodynamics of a simple isothermal fluid coupled with the motion of an immersed structureless solid sphere. The only approximation that has been taken is the Markovian approximation that neglects memory effects.

The equation for the evolution of the mass density field is just the continuity equation. The equation for the momentum density field involves the usual convective term, and a term $-\rho \boldsymbol{\nabla} \mu$ which, for the case when the free energy functional can be well approximated with a local functional, can be expressed as the gradient of the pressure field (see Eq. (10.5.1) below). The following irreversible term involving second derivatives is the usual viscosity term of the Navier-Stokes equations, which is here expressed in a non-local form. The use of non-local viscosities has been advocated recently in the field of nano-hydrodynamics [?]. The irreversible coupling force $\phi(\mathbf{r})$ involving the non-local transport coefficients $\mathbf{H_{rr'}}, \mathbf{G_{rr'}}, \boldsymbol{\gamma}_{\mathbf{rr'}}$ describe the irreversible coupling of the dynamics of the fluid with the solid sphere. Note that these transport coefficients are defined in terms of correlations involving the force density $\hat{\mathbf{F}}_{\mathbf{r}}^{s \to l}$ that the solid sphere exerts on the liquid molecules. These terms should be understood, therefore, as the responsible for transmitting the forces that exert the solid sphere on the fluid. In a macroscopic phenomenological theory, the effect of these terms is taken into account through boundary conditions applied to the fluid equations. We will consider in section 10.5 the necessary approximation in which the effect of these forces can be understood as induced forces, according to the method first introduced by Mazur and Bedeaux in order to include the boundary conditions into the dynamic equations themselves.

10.4   Conserved quantities, H-theorem and the equilibrium state

The equations (10.3) are the equations of hydrodynamics in the presence of a solid spherical particle. We will give a full discussion of the equations in Sec. **??** once we present specific models for the transport coefficients. In this section, we simply stress that the above equations conserve total mass and momentum, given by

$$M_T = M' + \int d\mathbf{r}\rho(\mathbf{r})$$

$$\mathbf{P}_T = \mathbf{P} + \int d\mathbf{r}\mathbf{g}(\mathbf{r})$$

Mass conservation follows inmediately from the continuity equation. Momentum conservation is a consequence of the invariance under translations of the free energy functional, this is

$$F[T_{\mathbf{c}}\rho, T_{\mathbf{c}}\mathbf{R}] = F[\rho, \mathbf{R}]$$

where the translation operator applied to any function is defined as

$$T_{\mathbf{c}}f(\mathbf{r}) = f(\mathbf{r} + \mathbf{c})$$

By taking the derivative with respect to $\mathbf{c}$ in both sides of Eq. (10.4) and setting afterwards $\mathbf{a} = 0$ we obtain the identity

$$\int d\mathbf{r}\frac{\delta F}{\delta\rho_{\mathbf{r}}}\boldsymbol{\nabla}\rho_{\mathbf{r}} + \frac{\partial F}{\partial\mathbf{R}} = 0$$

This identity is crucial in order to show that total momentum is conserved by the reversible part of the dynamics. The irreversible part conserves also total momentum because, appart from a global divergence term, the momentum lost by the fluid is gained by the solid sphere. In addition, the function $\hat{H}$ evolves in time in a strictly decreasing way, this is

$$\frac{d\hat{H}}{dt}(t) \geq 0$$

where the equality sign occurs when the system has reached its equilibrium state. This is because, while the reversible part of the dynamics conserves $\hat{H}$, the irreversible part of the dynamics fullfils (11.10.2), due to the positive semidefinite character of the friction matrix. As a consequence, the equilibrium state of Eqs. (10.3) is the one that maximizes $\hat{H}$ subject to give the actual values of the total mass and momentum. One should minimize the following functional without constraints

$$\hat{H} - \mu_0 \int d\mathbf{r}\rho(\mathbf{r}) - \mathbf{V}_0 \left[\int d\mathbf{r}\mathbf{g}(\mathbf{r}) + \mathbf{P}\right]$$

where $\mu_0, \mathbf{V}_0$ are the corresponding Lagrange multipliers. Setting to zero the derivatives of the above functional gives

$$\frac{\mathbf{v}^2(\mathbf{r})}{2} + \frac{\delta F}{\delta \rho(\mathbf{r})}[\rho, \mathbf{R}] - \mu_0 = 0, \qquad\qquad \frac{\partial F}{\partial \mathbf{R}}[\rho, \mathbf{R}] = 0$$

$$\mathbf{v}(\mathbf{r}) - \mathbf{V}_0 = 0, \qquad\qquad \mathbf{V} - \mathbf{V}_0 = 0$$

This means that the state of equilibrium has a constant velocity field equal to the velocity of the solid particle and, without losing generality, we may take $\mathbf{V}_0 = 0$. We then have the following two coupled equations for the equilibrium value that take the density field and the position of the sphere

$$\frac{\delta F}{\delta \rho(\mathbf{r})}[\rho, \mathbf{R}] = \mu_0, \qquad\qquad \frac{\partial F}{\partial \mathbf{R}}[\rho, \mathbf{R}] = 0$$

From Eqs. (10), the first equation (10.4) simply states that the equilibrium state has a constant value of the chemical potential $\mu(\mathbf{r}) = \mu_0$ while the second equation states that the total force on the solid sphere vanishes at equilibrium. This set of two coupled equations should be understood as a set of nonlinear equations for the equilibrium density field $\rho(\mathbf{r})$ and the equilibrium value of the center of mass of the sphere. Translational invariance of the system implies that if $\mathbf{R}, \rho(\mathbf{r})$ is a solution of (10.4), then $\mathbf{R} + \mathbf{c}, \rho(\mathbf{r} + \mathbf{c})$ is also a solution. Therefore, without loose of generality we may chose the origin of coordinates at the center of the sphere an $\mathbf{R} = 0$. Then the equilibrium density field is the solution of the first equation. Note that, in principle, the density field will display oscillations at short length scales due to the packing of the fluid near the solid sphere.

10.5   The singular boundary model

The equations (10.3) are general and should allow one to describe fluids in which microstructure effects are important, as it is expected when one goes towards nanoscales. However, from a *macroscopic point of view*, a fluid should be appropriately described as a featureless continuum in which the molecular correlations are negligible. We explore in this section a model for the fluid and fluid/solid interaction in which all the effects of the latter are regarded as happening at the *boundary* of the solid sphere. This should be adequate when considering smooth flows around a macroscopic sphere.

10.5.1   The free energy functional

According to Eq. (10), the free energy functional $F[\rho, \mathbf{R}]$ is the Legendre transform of the grand potential (10). In order to get some physical intuition about this free energy functional, let us assume for a moment that there is no interaction between the liquid atoms and the solid atoms, this is, $V^{ls} = 0$ in Eq. (12.3). In this case, the grand potential (10) becomes simply

$$\Omega^{\mathrm{pos}}[\mu, \boldsymbol{\lambda}_R] = \Omega^l[\mu] + \Omega^s[\boldsymbol{\lambda}_R]$$

where

$$\Omega^l[\mu] \equiv -k_B T \ln \sum_{N=0}^{\infty} \frac{1}{N!} \int \frac{dq}{\Lambda^{3N}} e^{-\beta V^l}$$

$$\times \exp\left\{-\beta\left(\sum_{i=1}^{N} m\mu(\mathbf{q}_i)\right)\right\}$$

$$\Omega^s[\boldsymbol{\lambda}_R] \equiv -k_B T \ln \int \frac{dq'}{\Lambda^{3N'}} e^{-\beta V^s} \exp\left\{-\beta\boldsymbol{\lambda}_R\hat{\mathbf{R}}\right\}$$

The Legendre transform (10) is therefore of the form

$$F[\rho, \mathbf{R}] = F[\rho] + F[\mathbf{R}]$$

where $F[\rho]$ is the usual (free energy) density functional. This simple argument shows that in the general case where there is liquid solid interaction, we should understand $F[\rho, \mathbf{R}]$ as the (free energy) density functional of a fluid in the presence of a solid sphere located at $\mathbf{R}$.

There are many approximate expressions for the density functional of a simple structured liquid that range from the simplest local approximation, through the square gradient approximation, and weighted density approximations. The *local approximation*, that neglects correlations in the fluid and is, therefore, valid only on length scales much larger than molecular length scales, takes the form

$$F[\rho] = \int d\mathbf{r} f(\rho(\mathbf{r}))$$

where $f(\rho)$ is the thermodynamic free energy density. In the presence of a spherical solid, perhaps the simplest model for the free energy functional is given by

$$F[\rho, \mathbf{R}] = \int d\mathbf{r} f_0(\rho(\mathbf{r})) + \frac{V_0}{m} \int d\mathbf{r} \rho(\mathbf{r})\theta(|\mathbf{r} - \mathbf{R}| - a)$$

where $f_0(\rho)$ is the free energy density of the fluid in the absence of the sphere, V_0 is an energy scale much larger than $k_B T$, m is the mass of a fluid molecule, and $\theta(x)$ is the Heaviside step function. In this model, we assume that the fluid particles may enter the solid particle, and once inside they have a constant potential energy V_0. When $V_0 \to \infty$ (or, actually, $V_0 \gg k_B T$) we have a hard-core potential. In this way, the last term in Eq. (10.5.1) gives a penalty of free energy for those density fields that happen to be non-zero inside the solid sphere. Therefore, there are no liquid molecules inside the solid sphere, according to this model. This model, that neglects all molecular correlations as any local model, is expected to work only in situations in which these efects are not important. Hydrodynamic problems with smooth spatial variations, and regarded at large length scales, are expected to be well represented by the above functional. On the other hand, nanoscopic flows will require improved descriptions of the free energy functional $F[\rho, \mathbf{R}]$.

In the reversible part of the dynamics, we will need the derivatives of the free energy functional with respect to $\rho(\mathbf{r})$ and $\mathbf{R}$. For the hard core model (10.5.1) these are given

by

$$\mu(\mathbf{r}) = \frac{\delta F}{\delta \rho(\mathbf{r})}[\rho, \mathbf{R}] = \mu_0(\mathbf{r}) + \frac{V_0}{m}\theta(|\mathbf{r} - \mathbf{R}| - a)$$

where $\mu_0(\rho) = f_0'(\rho)$ is the chemical potential of the liquid in the absence of the solid sphere. Note that the chemical potential field $\mu(\mathbf{r})$ is a discontinuous function of space. This will produce singular forces in the dynamic equations. Also, we have

$$\begin{aligned}
\frac{\partial F}{\partial \mathbf{R}}[\rho, \mathbf{R}] &= -\frac{\partial}{\partial \mathbf{R}} V_0 \int d\mathbf{r}\, n(\mathbf{r})\theta(|\mathbf{r} - \mathbf{R}| - a) \\
&= V_0 \int d\mathbf{r}\, n(\mathbf{r})\delta(|\mathbf{r} - \mathbf{R}| - a)\frac{\mathbf{r} - \mathbf{R}}{|\mathbf{r} - \mathbf{R}|} \\
&= \frac{V_0}{m} \int d\mathbf{r}\, \rho(\mathbf{r})\delta(|\mathbf{r} - \mathbf{R}| - a)\mathbf{n}
\end{aligned}$$

It is illustrative at this point to look at the equilibrium state for the present hard core model. It is obtained from the conditions (10.4) that for the present model become simply

$$\mu_0(\rho(\mathbf{r})) + \frac{V_0}{m}\Theta(|\mathbf{r} - \mathbf{R}| - a) = \mu_0$$

$$\frac{\partial}{\partial \mathbf{R}}\frac{V_0}{m}\int d\mathbf{r}\, \rho(\mathbf{r})\theta(|\mathbf{r} - \mathbf{R}| - a) = 0$$

This is a set of two equations for the equilibrium values of $\rho(\mathbf{r}), \mathbf{R}$. Of course, an explicit solution requires an explicit model for the fluid chemical potential $\mu_0(\rho)$. For example, for an ideal gas, the above equations become

$$-k_B T \ln \rho(\mathbf{r}) + \frac{V_0}{m}\Theta(|\mathbf{r} - \mathbf{R}| - a) = \mu_0$$

$$\frac{\partial}{\partial \mathbf{R}}\frac{V_0}{m}\int d\mathbf{r}\, \rho(\mathbf{r})\theta(|\mathbf{r} - \mathbf{R}| - a) = 0$$

These equations have as solution a density field $\rho(\mathbf{r}) = \rho_0$ for $|\mathbf{r} - \mathbf{R}| > a$ and $\rho(\mathbf{r}) = \rho_0 e^{-\beta V_0}$ for $|\mathbf{r} - \mathbf{R}| < a$, while any value of $\mathbf{R}$ is a solution of the above equations, as expected. It is apparent that when $V_0 \gg k_B T$, the density inside the sphere is negligible.

The hard-core model is highly singular and it may be useful to consider situations in which the coarse-grained interaction between the solid and the fluid is reflected by a singular contribution, albeit one with a finite range. For example, we may model the free energy functional in the form

$$F[\rho, \mathbf{R}] = \int d\mathbf{r}\, f_0(\rho(\mathbf{r})) + \int d\mathbf{r}\, \frac{1}{m}\rho(\mathbf{r})V(|\mathbf{r} - \mathbf{R}|)$$

where $V(|\mathbf{r} - \mathbf{R}|)$ is a coarse-grained potential that models the interaction between the fluid and the solid. This potential captures the repulsive interaction between solid and fluid atoms and is, therefore, of the Lennard-Jones type form. The reversible part of the

momentum equation now becomes

$$\partial_t \mathbf{g}^\mu(\mathbf{r}) = -\boldsymbol{\nabla}^{\mu'}\mathbf{g}^\mu(\mathbf{r})\mathbf{v}^{\mu'}(\mathbf{r}) - \rho(\mathbf{r})\boldsymbol{\nabla}^\mu \mu_0(\mathbf{r})$$
$$- \frac{1}{m}\rho(\mathbf{r})\boldsymbol{\nabla}^\mu V(\mathbf{r} - \mathbf{R})$$

It is apparent that in those regions near the surface of the sphere where the potential is very large, the density field needs to be, necessarily, very small, in order for the product $\rho\boldsymbol{\nabla}V$ to remain finite in Eq. (10.5.1). Otherwise the time derivative of the momentum density field would be very large, thus producing enormous motion in the direction of reducing the forces. In particular, this argument shows that there can be no fluid inside the solid at any time and, therefore, $\rho(\mathbf{r}) = 0$ for $|\mathbf{r} - \mathbf{R}| < a$. We will explore the consequences of this fact in section 10.7.

Finally, note that the we may rewrite the term

$$\rho(\mathbf{r})\boldsymbol{\nabla}\mu_0(\mathbf{r}) = \rho(\mathbf{r})\boldsymbol{\nabla}f_0'(\rho(\mathbf{r})) = \boldsymbol{\nabla}P_0(\rho(\mathbf{r}))$$

where we have introduced the usual definition of the pressure in terms of the free energy density

$$P_0(\rho) = \rho f_0'(\rho) - f_0(\rho)$$

10.5.2   The transport coefficients

In this section, we present models for the transport coefficients that are expected to be appropriate for macroscopic hydrodynamic problems. We first present an approximation of the *canonical* averages in terms of *microcanonical* averages, this is conditional expectations at fixed values of the position and momentum of the solid sphere.

Canonical versus microcanonical averages

Note that the averages with respect to the relevant ensemble (**??**) can be understood as generalized canonical averages, to be compared with microcanonical averages performed with a generalized microcanonical ensemble of the form

$$\rho^{\mathrm{mic}}(z) = \frac{1}{\Omega}\rho^{\mathrm{eq}}(z)\delta(\hat{A}(z) - a)$$

For the case that the CG variables are (11.1.1) that include the hydrodynamic fields, the definition of a microcanonical ensemble is not possible because of the singular nature of the hydrodynamic fields (we would need to evaluate Dirac delta functions, those of the hydrodynamic fields, *inside* a Dirac delta function). This is essentially the reason for considering the Kawasaki-Gunton projector instead of Zwanzig's in the present work.

Nevertheless we may consider a mixed canonical microcanonical ensemble of the form

$$\overline{\rho}^{\mathrm{mic}}(z) = \frac{1}{\Xi[\lambda]} \rho^{\mathrm{eq}}(z) \delta(\mathbf{R} - \hat{\mathbf{R}}(z)) \delta(\mathbf{P} - \hat{\mathbf{P}}(z))$$

$$\times \exp\left\{ -\beta \int d\mathbf{r}\, (\lambda_\rho(\mathbf{r}) \hat{\rho}_{\mathbf{r}}(z) + \boldsymbol{\lambda}_g(\mathbf{r}, t) \hat{\mathbf{g}}_{\mathbf{r}}(z)) \right\}$$

which is microcanonical in the center of mass variables and canonical in the hydrodynamic variables. The relationship between purely canonical averages $\langle \cdots \rangle^{\lambda_\rho, \boldsymbol{\lambda}_g, \boldsymbol{\lambda}_R, \boldsymbol{\lambda}_P}$ performed with (12.4) and the mixed canonical microcanonical averages $\langle \cdots \rangle^{\lambda_\rho, \boldsymbol{\lambda}_g, \mathbf{R}, \mathbf{P}}$ performed with (10.5.2) is as follows

$$\langle \cdots \rangle^{\lambda_\rho, \boldsymbol{\lambda}_g, \boldsymbol{\lambda}_R, \boldsymbol{\lambda}_P} = \int d\mathbf{R} d\mathbf{P} P(\mathbf{R}, \mathbf{P}, \lambda) \langle \cdots \rangle^{\lambda_\rho, \boldsymbol{\lambda}_g, \mathbf{R}, \mathbf{P}}$$

where the function $P(\mathbf{R}, \mathbf{P}, \lambda)$ is defined as

$$P(\mathbf{R}, \mathbf{P}, \lambda) = \exp\{-\beta(\boldsymbol{\lambda}_R \mathbf{R} + \boldsymbol{\lambda}_P \mathbf{P})\} \mathrm{Tr} \left[\frac{\rho^{\mathrm{eq}}}{\Xi[\lambda]} \exp\left\{ -\beta \int d\mathbf{r}\, (\lambda_\rho(\mathbf{r}) \hat{\rho}_{\mathbf{r}} + \boldsymbol{\lambda}_g(\mathbf{r}, t) \hat{\mathbf{g}}_{\mathbf{r}}) \right\} \delta(\mathbf{R} - \hat{\mathbf{R}}) \delta(\mathbf{P} - \hat{\mathbf{P}}) \right]$$

This function is normalized to unity and, therefore, may be interpreted as a probability distribution of $\mathbf{R}, \mathbf{P}$. We expect that this function is highly peaked because the number of degrees of freedom of the solid is very large. For this reason, we may approximate the canonical averages with respect to the relevant ensemble with an average performed with the mixed canonical/microcanonical average (10.5.2). These averages can be understood as conditional averages in which the solid sphere is fixed at $\mathbf{R}$ with a given momentum $\mathbf{P}$. This observation is relevant when considering the modelling of the transport coefficients in Sec 10.5.2. In particular, we will assume that the averages $\langle \cdots \rangle^\lambda$ can be understood as conditional averages in which the solid sphere is fixed in space. In addition, we will assume that we are in near equilibrium situations in such a way that we may evaluate the above averages in the correlation functions with the hydrodynamic conjugate variables λ set to its equilibrium values (i.e. $\lambda = 0$).

The Green-Kubo integrands

The transport coefficients defined in (12.6) are expressed in terms of averages with respect to the relevant ensemble. As such, they are functions of the CG variables and they depend on the state of the system. If we were about to compute these transport coefficients from MD simulations, we would need to perform a huge number of simulations in order to explore the whole functional form of these transport coefficients as functions of the state space. This is certainly unfeasible. It is necessary that we use our intuition in order to *model* in the best possible way these transport coefficients. In order to do this it helps to have a good understanding of the meaning of the different microscopic objects entering the correlations in the Green-Kubo expressions.

Let us first consider the force density $\mathbf{F}_{\mathbf{r}}^{\mathrm{s} \rightarrow \mathrm{l}}(z)$ in (10.1). This is the force per unit

volume that the atoms of the solid sphere exert on the liquid atoms that are around the point $\mathbf{r}$ in space. Only for those points $\mathbf{r}$ that are near the surface of the solid sphere this force density will be different from zero. In general this force density will be a fluctuating vector on the surface of the solid sphere. If the interaction between fluid and solid atoms is purely repulsive, this force will be most of the time directed outwards the surface of the solid sphere. In a similar way, the stress tensor $\boldsymbol{\sigma_r}$ that depends only on fluid atom coordinates will be non-zero only outside the solid sphere because the interaction with the solid sphere refrains to have liquid molecules inside the solid sphere (more on this later). The force density and the stress tensor are assumed to vary in time in a time scale much shorter than the typical time scale in which the mass and momentum density of the solvent, and the position and momentum of the solid sphere particle appreciably changes. This separation of time scales is at the core of the Markovian form of the evolution of the CG dynamics in the projection operator technique. It is for this reason that we have to consider averages that contain the state dependence of the system through the relevant ensemble.

Let us heuristically analyze the form of the correlations in the Green-Kubo formulae.

The viscosity tensor

Let us start with the viscosity tensor $\boldsymbol{\eta_{rr'}}$ involving the stress-stress correlation $\langle \delta\boldsymbol{\sigma_r}\delta\boldsymbol{\sigma_{r'}}(t)\rangle^\lambda$. We expect that this stress will be uncorrelated beyond a length scale of molecular size. If the velocity field $\mathbf{v(r)}$ does not change appreciably on these molecular length scales, then we may take a local approximation in the following term of Eq. (10.3)

$$\int d\mathbf{r}'\eta^{\mu\nu\mu'\nu'}_{\mathbf{rr}'}\boldsymbol{\nabla}^{\nu'}_{\mathbf{r}'}\mathbf{v}^{\mu'}(\mathbf{r}') \approx \left[\int d\mathbf{r}'\eta^{\mu\nu\mu'\nu'}_{\mathbf{rr}'}\right]\boldsymbol{\nabla}^{\nu'}_{\mathbf{r}}\mathbf{v}^{\mu'}(\mathbf{r})$$

which amounts to approximate

$$\boldsymbol{\eta_{rr'}} = \boldsymbol{\eta_r}\delta(\mathbf{r}-\mathbf{r}')$$

where

$$\boldsymbol{\eta_r} = \int d\mathbf{r}'\boldsymbol{\eta_{rr'}}$$

Of course, if $\mathbf{r}$ is inside the solid sphere the stress tensor vanishes and, consequently, also the transport coefficient $\boldsymbol{\eta_r}$. Outside the sphere, we do not expect a strong variation of $\boldsymbol{\eta_r}$ with respect to $\mathbf{r}$, although near the sphere the interaction with the solid sphere may induce modification with respect to bulk values. The bulk value of $\boldsymbol{\eta_r}$, being independent of the position of space can also be obtained from a space average of the form

$$\boldsymbol{\eta} = \frac{1}{V}\int d\mathbf{r}\boldsymbol{\eta_r}$$
$$= \frac{1}{Vk_BT}\int_0^\infty dt\langle \delta\hat{\boldsymbol{\sigma}}\delta\hat{\boldsymbol{\sigma}}(t)\rangle^\lambda$$

where the total fluid stress tensor is defined as

$$\hat{\boldsymbol{\sigma}} = \sum_i^N m\hat{\mathbf{v}}_i\hat{\mathbf{v}}_i + \frac{1}{2}\sum_{ij}^N \hat{\mathbf{q}}_{ij}\hat{\mathbf{F}}_{ij}$$

In near equilibrium situations we may simply assume that the hydrodynamic fields $\lambda_\rho, \boldsymbol{\lambda_g}$ take the equilibrium value (which is zero) and therefore, the averages $\langle\cdots\rangle^\lambda$ become ordinary equilibrium averages conditional to the position of the solid sphere. In this way, we obtain the usual expression for the viscosity tensor, which is a completely isotropic fourth order tensor

$$\boldsymbol{\eta}^{\mu\nu\mu'\nu'} = \eta\left[\delta^{\mu\mu'}\delta^{\nu\nu'} + \delta^{\mu\nu'}\delta^{\nu\mu'} - \frac{2}{3}\delta^{\mu\nu}\delta^{\mu'\nu'}\right] + \zeta\delta^{\mu\nu}\delta^{\mu'\nu'}$$

where η and ζ are the usual shear and bulk viscosities, respectively. The above arguments break down near the solid sphere. In this region the viscosity tensor is no longer fully isotropic because the presence of the sphere breaks the isotropy of space. In addition, the dynamics of the fluid stress tensor near the solid surface is affected by the interactions with the solid atoms, leading to a modification of the actual value of the viscosity near the solid surface. However, we will assume that these effects are negligible as compared with the direct effects due to the correlation of the stress tensor and the force $\mathbf{F}_{\mathbf{r}}^{s\to l}$ that the sphere exerts on the fluid and that are represented by the transport coefficients $\mathbf{H_{r,r'}}$, $\mathbf{G_{r,r'}}$.

The friction tensor

Now, let us move to the non-local friction coefficient $\boldsymbol{\gamma_{rr'}}$ involving the conditional correlation of the force density $\langle\delta\mathbf{F}_{\mathbf{r}}^{s\to l}\delta\mathbf{F}_{\mathbf{r'}}^{s\to l}(t)\rangle^\lambda$. The force per unit volume that the solid sphere exerts on the molecules of fluid that happen to be in $\mathbf{r}$ will be zero unless we are considering points that are near the surface of the solid. In addition, consider two points $\mathbf{r}, \mathbf{r'}$ that are both near the surface of the solid sphere. The changes of the force that the particle exert on the fluid are due exclusively to the motion of the solvent molecules, because the particle is held fixed in space due to the conditional expectation. Therefore, we will assume that the correlation of the forces at different locations will be zero unless both locations are the same. Only if $\mathbf{r}$ is at the surface of the solid sphere we should have non-vanishing forces of the solid sphere atoms onto the fluid and, therefore, a non-vanishing friction coefficient. Finally, the conditional correlation of the force should account for the fact that the solid sphere surface breaks the isotropic symmetry. In fact, we expect that the second order friction tensor will be isotropic with respect to any rotation around an axis $\mathbf{n}$ perpendicular to the solid sphere surface. By collecting all these intuitions into an explicit model for the friction tensor, we propose that the transport coefficient $\boldsymbol{\gamma_{rr'}}$ can be modeled as

$$\boldsymbol{\gamma_{rr'}} = \delta^S(\mathbf{r})\delta(\mathbf{r} - \mathbf{r'})\left[\gamma_{||}(\boldsymbol{\delta} - \mathbf{nn}^T) + \gamma_\perp\mathbf{nn}^T\right]$$

where the surface Dirac delta function is

$$\delta^S(\mathbf{r}) = \delta(|\mathbf{r} - \mathbf{R}| - a)$$

and the normal vector $\mathbf{n}$ is defined as

$$\mathbf{n} = \frac{\mathbf{r} - \mathbf{R}}{|\mathbf{r} - \mathbf{R}|}$$

which is a unit normal vector to the surface of the solid sphere. The surface area of the sphere in the denominator has been introduced for convenience, thus providing the dimensionality of the constants $\gamma_\perp, \gamma_{||}$ equal to an ordinary friction coefficient. In fact, let us have a look now to the term $\int d\mathbf{r} \int d\mathbf{r}' \gamma_{\mathbf{rr}'}$ in the dynamic equations (11.10). The integral of the force density is just the total force that the solid sphere exerts on the fluid, this is

$$\hat{\mathbf{F}}^{s\to l} \equiv \int d\mathbf{r} \hat{\mathbf{F}}_{\mathbf{r}}^{s\to l}(z) = \sum_{ij'}^{NN'} \hat{\mathbf{F}}_{ij'}$$

Therefore, we may introduce the friction coefficient in the usual way, as the time integral of the force-force (force that the liquid exerts on the solid) autocorrelation, this is

$$\boldsymbol{\gamma} = \int d\mathbf{r} \int d\mathbf{r}' \gamma_{\mathbf{rr}'} = \frac{1}{k_B T} \int_0^\infty dt \langle \mathbf{F}\mathbf{F}(t) \rangle^\lambda$$

By isotropy, this second order tensor needs to be isotropic and, therefore,

$$\boldsymbol{\gamma} = \gamma \boldsymbol{\delta}$$

where we have introduced the scalar friction coefficient γ. We may relate the constants $\gamma_{||}, \gamma_\perp$ in Eq. (10.5.2) with the friction tensor

$$\boldsymbol{\gamma} = \int d\mathbf{r} \int d\mathbf{r}' \delta(\mathbf{r} - \mathbf{r}') \delta(|\mathbf{r} - \mathbf{R}| - a)$$
$$\times \left[\gamma_{||}(\boldsymbol{\delta} - \mathbf{n}\mathbf{n}^T) + \gamma_\perp \mathbf{n}\mathbf{n}^T \right]$$

By taking the trace of this tensor we obtain

$$\gamma = \frac{4\pi a^2}{3} \left[2\gamma_{||} + \gamma_\perp \right]$$

which is a relationship between the friction coefficient of the sphere and the slip coefficients $\gamma_{||}, \gamma_\perp$ (see below for the interpretation of these coefficients as slip coefficients).

Of course, the calculation of the friction coefficient is straightforward in an MD simulation. However, we would also like to obtain both coefficients $\gamma_{||}, \gamma_\perp$. This can be achieved by looking at the model (10.5.2) and fully contract the second order tensor $\boldsymbol{\gamma}_{\mathbf{rr}'}$

with the dyadic $\mathbf{nn}^T$ in order to get the following scalar

$$\mathbf{n}\cdot\boldsymbol{\gamma}_{\mathbf{rr'}}\cdot\mathbf{n} = \delta(|\mathbf{r}-\mathbf{R}|-a)\delta(\mathbf{r}-\mathbf{r'})\gamma_\perp$$

By integrating Eq. (10.5.2)with respect to $\mathbf{r}$ and $\mathbf{r'}$, and dividing by $4\pi a^2$ we obtain

$$\gamma_\perp = \frac{1}{4\pi a^2 k_B T}$$

$$\times \int_0^\infty dt \left\langle \left(\int d\mathbf{r}\,\mathbf{n}\cdot\delta\hat{\mathbf{F}}_{\mathbf{r}}^{\mathrm{s}\to\mathrm{l}}\right)\left(\int d\mathbf{r'}\,\mathbf{n'}\cdot\delta\hat{\mathbf{F}}_{\mathbf{r'}}^{\mathrm{s}\to\mathrm{l}}(t)\right)\right\rangle^\lambda$$

where in the last equation we have used the molecular expression (12.6). By using the explicit form (10.1) for $\hat{\mathbf{F}}_{\mathbf{r}}^{\mathrm{s}\to\mathrm{l}}$ we obtain the phase function that we are correlating here

$$\delta\hat{F}_\perp \equiv \int d\mathbf{r}\,\mathbf{n}\cdot\delta\hat{\mathbf{F}}_{\mathbf{r}}^{\mathrm{s}\to\mathrm{l}} = \sum_{ij'}^{NN'} \hat{\mathbf{F}}_{ij'}\cdot\frac{\mathbf{q}_i-\mathbf{R}}{|\mathbf{q}_i-\mathbf{R}|}$$

which is the sum of the normal component of the force done by the solid atoms on every fluid particle. Eqs. (10.5.2), (10.5.2), together with (10.5.2) allow one to compute the transport coefficients $\gamma, \gamma_\perp, \gamma_{||}$ from MD simulations.

The slip tensors

Finally, it remains to consider the transport coefficient $\mathbf{G_{rr'}}$ involving the conditional cross correlation of force density and stress tensor in Eq. (10.14). The force $\hat{\mathbf{F}}_{\mathbf{r}}^{\mathrm{s}\to\mathrm{l}}$ is only different from zero in the spheric shell $\Delta\Sigma$ defined by $a < |\mathbf{r}| < a+\sigma$ where σ is the range of interaction of the force between a solid atom and a fluid atom. On the other hand, we expect that the force $\hat{\mathbf{F}}_{\mathbf{r}}^{\mathrm{s}\to\mathrm{l}}$ and the stress tensor $\hat{\boldsymbol{\sigma}}_{\mathbf{r}}$ will be correlated only when the distance $|\mathbf{r}-\mathbf{r'}|$ is of molecular size. Therefore, a *local* model for the transport coefficient $\mathbf{G_{rr'}}$ is

$$\mathbf{G_{rr'}} = \delta(\mathbf{r}-\mathbf{r'})\delta(|\mathbf{r}-\mathbf{R}|-a)\mathbf{G}$$

Here, $\mathbf{G}$ is a third order tensor which is symmetric with respect to its last two indices, i.e. $\mathbf{G}_{\alpha\beta\gamma} = \mathbf{G}_{\alpha\gamma\beta}$, because the microscopic stress tensor is symmetric. This tensor must also be invariant under a rotation around $\mathbf{n}$, because we assume that there is no preferred direction on the surface of the sphere. In the appendix **??** we show that the most general tensor fulfilling the above symmetries has the following structure

$$\mathbf{G}_{\alpha\beta\gamma} = g_1(\boldsymbol{\delta}_{\alpha\beta}\mathbf{n}_\gamma + \boldsymbol{\delta}_{\alpha\gamma}\mathbf{n}_\beta) + g_2\mathbf{n}_\alpha\boldsymbol{\delta}_{\beta\gamma} + g_3(\mathbf{n}_{\alpha\beta}^{(2)}\mathbf{n}_\gamma + \mathbf{n}_{\alpha\gamma}^{(2)}\mathbf{n}_\beta) + g_4\mathbf{n}_\alpha\mathbf{n}_\beta\mathbf{n}_\gamma$$

The coeficients g_1, g_2, g_3, g_4 can be obtained from full contractions of the third order tensor $\mathbf{G_{rr'}}$ with the tensors in (10.13.2) and integration over $\mathbf{r}, \mathbf{r'}$. Consider for example

the following contraction

$$\int d\mathbf{r} \int d\mathbf{r}' \mathbf{n}_\alpha \boldsymbol{\delta}_{\beta\gamma} \mathbf{G}_{\alpha\beta\gamma,\mathbf{r},\mathbf{r}'} = \int d\mathbf{r} \int d\mathbf{r}' \delta(\mathbf{r} - \mathbf{r}')\delta(|\mathbf{r} - \mathbf{R}| - a)(2g_1 + 3g_2 + g_4)$$
$$= (2g_1 + 3g_2 + g_4)4\pi a^2$$

In a similar way we may construct all the contractions

$$\frac{1}{4\pi a^2} \int d\mathbf{r} \int d\mathbf{r}' \text{Tr}[\mathbf{n}\mathbf{G}_{\mathbf{rr}'}\boldsymbol{\delta}] = \frac{1}{4\pi a^2} \int d\mathbf{r} \int d\mathbf{r}' \mathbf{n}_\alpha \mathbf{G}_{\alpha\beta\gamma\mathbf{rr}'}\boldsymbol{\delta}_{\beta\gamma} \qquad = 2g_1 + 3g_2 + g_4$$

$$\frac{1}{4\pi a^2} \int d\mathbf{r} \int d\mathbf{r}' \text{Tr}[\boldsymbol{\delta}\mathbf{G}_{\mathbf{rr}'}\mathbf{n}] = \frac{1}{4\pi a^2} \int d\mathbf{r} \int d\mathbf{r}' \boldsymbol{\delta}_{\alpha\beta} \mathbf{G}_{\alpha\beta\gamma\mathbf{rr}'}\mathbf{n}_\gamma \qquad = 4g_1 + g_2 + g_4$$

$$\frac{1}{4\pi a^2} \int d\mathbf{r} \int d\mathbf{r}' \text{Tr}[\mathbf{nn}\mathbf{G}_{\mathbf{rr}'}\mathbf{n}] = \frac{1}{4\pi a^2} \int d\mathbf{r} \int d\mathbf{r}' \mathbf{n}_\alpha\mathbf{n}_\beta \mathbf{G}_{\alpha\beta\gamma\mathbf{rr}'}\mathbf{n}_\gamma \quad = 2g_1 + g_2 + g_4$$

$$\frac{1}{4\pi a^2} \int d\mathbf{r} \int d\mathbf{r}' \text{Tr}[\mathbf{n}^{(2)}\mathbf{G}_{\mathbf{rr}'}\mathbf{n}] = \frac{1}{4\pi a^2} \int d\mathbf{r} \int d\mathbf{r}' \mathbf{n}^{(2)}_{\alpha\beta} \mathbf{G}_{\alpha\beta\gamma\mathbf{rr}'}\mathbf{n}_\gamma \qquad = 2g_3$$

where in the last identity we have used the well-known property $\epsilon_{\alpha\beta\mu}\epsilon_{\alpha\beta\mu'} = 2\delta_{\mu\mu'}$. We may solve for the coefficients g_1, g_2, g_3, g_4. The inverse matrix is

$$\frac{1}{2} \begin{pmatrix} 0 & 1 & -1 \\ 1 & 0 & -1 \\ -1 & -2 & 5 \end{pmatrix}$$

and the result is

$$g_1 = \frac{1}{8\pi a^2} \int d\mathbf{r} \int d\mathbf{r}' \left[\text{Tr}[\boldsymbol{\delta}\mathbf{G}_{\mathbf{rr}'}\mathbf{n}] - \text{Tr}[\mathbf{nn}\mathbf{G}_{\mathbf{rr}'}\mathbf{n}] \right]$$

$$g_2 = \frac{1}{8\pi a^2} \int d\mathbf{r} \int d\mathbf{r}' \left[\text{Tr}[\mathbf{n}\mathbf{G}_{\mathbf{rr}'}\boldsymbol{\delta}] - \text{Tr}[\mathbf{nn}\mathbf{G}_{\mathbf{rr}'}\mathbf{n}] \right]$$

$$g_4 = \frac{1}{8\pi a^2} \int d\mathbf{r} \int d\mathbf{r}' \left[5\text{Tr}[\mathbf{nn}\mathbf{G}_{\mathbf{rr}'}\mathbf{n}] - 2\text{Tr}[\boldsymbol{\delta}\mathbf{G}_{\mathbf{rr}'}\mathbf{n}] - \text{Tr}[\mathbf{n}\mathbf{G}_{\mathbf{rr}'}\boldsymbol{\delta}] \right]$$

$$g_3 = \frac{1}{8\pi a^2} \int d\mathbf{r} \int d\mathbf{r}' \text{Tr}[\mathbf{n}^{(2)}\mathbf{G}_{\mathbf{rr}'}\mathbf{n}]$$

These coefficients can be expressed as Green-Kubo formulae as follows

$$\int d\mathbf{r} \int d\mathbf{r}' \mathrm{Tr}[\mathbf{n}\mathbf{G}_{\mathbf{rr}'}\boldsymbol{\delta}] = \int d\mathbf{r} \int d\mathbf{r}' \mathbf{n}_\alpha \mathbf{G}_{\alpha\beta\gamma\mathbf{rr}'}\boldsymbol{\delta}_{\beta\gamma} = \frac{1}{8\pi a^2 k_B T} \int_0^\infty dt \left\langle \left(\int d\mathbf{r}' \mathbf{n}' \delta\hat{\mathbf{F}}_{\mathbf{r}'}^{\mathrm{s}\to\mathrm{l}}(t) \right) \left(\int d\mathbf{r} \delta\mathrm{Tr}[\hat{\boldsymbol{\sigma}}_\mathbf{r}] \right) \right\rangle^\lambda$$

$$= \frac{1}{8\pi a^2 k_B T} \int_0^\infty dt \left\langle \delta F_\perp^{\mathrm{s}\to\mathrm{l}}(t) \mathrm{Tr}[\delta\hat{\boldsymbol{\sigma}}] \right\rangle^\lambda$$

$$\int d\mathbf{r} \int d\mathbf{r}' \mathrm{Tr}[\boldsymbol{\delta}\mathbf{G}_{\mathbf{rr}'}\mathbf{n}] = \int d\mathbf{r} \int d\mathbf{r}' \boldsymbol{\delta}_{\alpha\beta} \mathbf{G}_{\alpha\beta\gamma\mathbf{rr}'}\mathbf{n}_\gamma = \frac{1}{8\pi a^2 k_B T} \int_0^\infty dt \left\langle \left(\int d\mathbf{r}' \delta\hat{\mathbf{F}}_{\mathbf{r}'}^{\mathrm{s}\to\mathrm{l}}(t) \right) \left(\int d\mathbf{r} \delta\hat{\boldsymbol{\sigma}}_\mathbf{r}\mathbf{n} \right) \cdot \right\rangle^\lambda$$

$$= \frac{1}{8\pi a^2 k_B T} \int_0^\infty dt \left\langle \delta\mathbf{F}^{\mathrm{s}\to\mathrm{l}}(t)\cdot\delta\hat{\boldsymbol{\sigma}}_\perp \right\rangle^\lambda$$

$$\int d\mathbf{r} \int d\mathbf{r}' \mathrm{Tr}[\mathbf{n}\mathbf{G}_{\mathbf{rr}'}\mathbf{n}\mathbf{n}] = \int d\mathbf{r} \int d\mathbf{r}' \mathbf{n}_\alpha \mathbf{G}_{\alpha\beta\gamma\mathbf{rr}'}\mathbf{n}_\beta\mathbf{n}_\gamma = \frac{1}{8\pi a^2 k_B T} \int_0^\infty dt \left\langle \left(\int d\mathbf{r}' \mathbf{n}' \delta\hat{\mathbf{F}}_{\mathbf{r}'}^{\mathrm{s}\to\mathrm{l}}(t) \right) \left(\int d\mathbf{r} \mathbf{n}\cdot\delta\hat{\boldsymbol{\sigma}}_\mathbf{r}\cdot\mathbf{n} \right) \right\rangle^\lambda$$

$$= \frac{1}{8\pi a^2 k_B T} \int_0^\infty dt \left\langle \delta F_\perp^{\mathrm{s}\to\mathrm{l}}(t)\hat{\sigma}_{\perp\perp} \right\rangle^\lambda$$

$$\int d\mathbf{r} \int d\mathbf{r}' \mathrm{Tr}[\mathbf{n}^{(2)}\mathbf{G}_{\mathbf{rr}'}\mathbf{n}] = \int d\mathbf{r} \int d\mathbf{r}' \mathbf{n}_{\alpha\beta}^{(2)} \mathbf{G}_{\alpha\beta\gamma\mathbf{rr}'}\mathbf{n}_\gamma = \frac{1}{8\pi a^2 k_B T} \int_0^\infty dt \left\langle \left(\int d\mathbf{r}' (\delta\hat{\mathbf{F}}_{\mathbf{r}'}^{\mathrm{s}\to\mathrm{l}}(t) \times \mathbf{n}') \right) \cdot \left(\int d\mathbf{r} \delta\hat{\boldsymbol{\sigma}}_\mathbf{r}\cdot\mathbf{n} \right) \right\rangle^\lambda$$

$$= \frac{1}{8\pi a^2 k_B T} \int_0^\infty dt \left\langle \delta\mathbf{F}_\times^{\mathrm{s}\to\mathrm{l}}(t)\cdot\delta\hat{\boldsymbol{\sigma}}_\perp \right\rangle^\lambda$$

Let us make explicit what phase functions are those by using the definitions of $\hat{\mathbf{F}}_\mathbf{r}^{\mathrm{s}\to\mathrm{l}}$ and $\hat{\boldsymbol{\sigma}}_\mathbf{r}$ in (10.1), (10.1), this is

$$\hat{\mathbf{F}}^{\mathrm{s}\to\mathrm{l}} \equiv \int d\mathbf{r} \hat{\mathbf{F}}_\mathbf{r}^{\mathrm{s}\to\mathrm{l}} = \sum_{ij'}^{NN'} \hat{\mathbf{F}}_{ij'}$$

$$\hat{F}_\perp^{\mathrm{s}\to\mathrm{l}} \equiv \int d\mathbf{r}\mathbf{n}\cdot\hat{\mathbf{F}}_\mathbf{r}^{\mathrm{s}\to\mathrm{l}} = \sum_{ij'}^{NN'} \hat{\mathbf{F}}_{ij'}\cdot\frac{\mathbf{q}_i - \mathbf{R}}{|\mathbf{q}_i - \mathbf{R}|}$$

$$\hat{\mathbf{F}}_\times^{\mathrm{s}\to\mathrm{l}} \equiv \int d\mathbf{r}(\hat{\mathbf{F}}_\mathbf{r}^{\mathrm{s}\to\mathrm{l}} \times \mathbf{n}) = \sum_{ij'}^{NN'} \hat{\mathbf{F}}_{ij'} \times \frac{\mathbf{q}_i - \mathbf{R}}{|\mathbf{q}_i - \mathbf{R}|}$$

$$\mathrm{Tr}\hat{\boldsymbol{\sigma}} \equiv \int d\mathbf{r}' \mathrm{Tr}[\hat{\boldsymbol{\sigma}}_{\mathbf{r}'}] = \sum_i^N \mathbf{p}_i\cdot\mathbf{v}_i + \frac{1}{2}\sum_{ij}^N \mathbf{e}_{ij}\cdot\hat{\mathbf{F}}_{ij}$$

$$\hat{\sigma}_{\perp\perp} \equiv \int d\mathbf{r}\mathbf{n}\cdot\hat{\boldsymbol{\sigma}}_\mathbf{r}\cdot\mathbf{n} = \sum_i^N \frac{\mathbf{q}_i - \mathbf{R}}{|\mathbf{q}_i - \mathbf{R}|}\cdot\mathbf{p}_i\mathbf{v}_i\cdot\frac{\mathbf{q}_i - \mathbf{R}}{|\mathbf{q}_i - \mathbf{R}|} + \frac{1}{2}\sum_{ij}^N \mathbf{e}_{ij}\cdot\frac{\mathbf{q}_i - \mathbf{R}}{|\mathbf{q}_i - \mathbf{R}|}\hat{\mathbf{F}}_{ij}\cdot\frac{\mathbf{q}_i - \mathbf{R}}{|\mathbf{q}_i - \mathbf{R}|}$$

$$\hat{\boldsymbol{\sigma}}_\perp \equiv \int d\mathbf{r}' \hat{\boldsymbol{\sigma}}_{\mathbf{r}'}\cdot\mathbf{n}' = \sum_i^N \mathbf{p}_i\mathbf{v}_i\cdot\frac{\mathbf{q}_i - \mathbf{R}}{|\mathbf{q}_i - \mathbf{R}|} + \frac{1}{2}\sum_{ij}^N \mathbf{e}_{ij}\hat{\mathbf{F}}_{ij}\cdot\frac{\mathbf{q}_i - \mathbf{R}}{|\mathbf{q}_i - \mathbf{R}|}$$

It may be of some concern that the total stress tensor, involving the N fluid particles in the whole space, appears in the correlations defining $\mathbf{G}_{\mathbf{rr}'}$. Note, however, that because

the range of the force that a solid atom exerts on a fluid atom is short ranged by assumption, the only fluid atoms in the sum defining the total stress tensor $\boldsymbol{\sigma}$ that actually correlate with this force are those that are close to the surface of the solid sphere. In this way, we could equally restrict the sum defining the stress tensor in (10.5.2) to those $N_{\Delta\Sigma}$ atoms in the spheric shell $\Delta\Sigma$.

Finally we have the following explicit form for the transport coefficients

$$
\begin{aligned}
g_1 &= \frac{1}{8\pi a^2} \int d\mathbf{r} \int d\mathbf{r}' \left[\text{Tr}[\boldsymbol{\delta}\mathbf{G}_{\mathbf{rr}'}\mathbf{n}] - \text{Tr}[\mathbf{nn}\mathbf{G}_{\mathbf{rr}'}\mathbf{n}] \right] \\
&= \frac{1}{8\pi a^2 k_B T} \int_0^\infty dt \left\langle \delta\mathbf{F}^{\text{s}\to 1}(t)\cdot\delta\hat{\boldsymbol{\sigma}}_\perp - \delta F_\perp^{\text{s}\to 1}(t)\hat{\sigma}_{\perp\perp} \right\rangle^\lambda \\
&= \frac{1}{8\pi a^2 k_B T} \int_0^\infty dt \left\langle \delta\mathbf{F}^{\text{s}\to 1}(t)(\boldsymbol{\delta} - \mathbf{nn})\cdot\delta\hat{\boldsymbol{\sigma}}_\perp \right\rangle^\lambda \\
g_2 &= \frac{1}{8\pi a^2} \int d\mathbf{r} \int d\mathbf{r}' \left[\text{Tr}[\mathbf{n}\mathbf{G}_{\mathbf{rr}'}\boldsymbol{\delta}] - \text{Tr}[\mathbf{nn}\mathbf{G}_{\mathbf{rr}'}\mathbf{n}] \right] \\
&= \frac{1}{8\pi a^2 k_B T} \int_0^\infty dt \left\langle \delta F_\perp^{\text{s}\to 1}(t)\text{Tr}[\delta\hat{\boldsymbol{\sigma}}] - \delta\mathbf{F}^{\text{s}\to 1}(t)\cdot\delta\hat{\boldsymbol{\sigma}}_\perp \right\rangle^\lambda \\
&= \frac{1}{8\pi a^2 k_B T} \int_0^\infty dt \left\langle \delta\mathbf{F}^{\text{s}\to 1}(t)\cdot\left[\delta\hat{\boldsymbol{\sigma}} - \boldsymbol{\delta}\text{Tr}[\delta\hat{\boldsymbol{\sigma}}]\right]\cdot\mathbf{n} \right\rangle^\lambda \\
g_4 &= \frac{1}{8\pi a^2} \int d\mathbf{r} \int d\mathbf{r}' \left[5\text{Tr}[\mathbf{nn}\mathbf{G}_{\mathbf{rr}'}\mathbf{n}] - 2\text{Tr}[\boldsymbol{\delta}\mathbf{G}_{\mathbf{rr}'}\mathbf{n}] - \text{Tr}[\mathbf{n}\mathbf{G}_{\mathbf{rr}'}\boldsymbol{\delta}] \right] \\
g_3 &= \frac{1}{8\pi a^2 k_B T} \int_0^\infty dt \left\langle \delta\mathbf{F}_\times^{\text{s}\to 1}(t)\cdot\delta\hat{\boldsymbol{\sigma}}_\perp \right\rangle^\lambda
\end{aligned}
$$

In a similar way, we may now compute the third order tensor $\mathbf{H}_{\mathbf{rr}'}$ in Eq. (12.6). A *local* model for the transport coefficient $\mathbf{H}_{\mathbf{rr}'}$ is

$$
\mathbf{H}_{\mathbf{rr}'} = \delta(\mathbf{r} - \mathbf{r}')\delta(|\mathbf{r} - \mathbf{R}| - a)\mathbf{H}
$$

Here, $\mathbf{H}$ is a third order tensor which is symmetric with respect to its first two indices, i.e. $\mathbf{H}_{\alpha\beta\gamma} = \mathbf{H}_{\beta\alpha\gamma}$, because the microscopic stress tensor is symmetric. This tensor must also be invariant under a rotation around $\mathbf{n}$, because we assume that there is no preferred direction on the surface of the sphere. It should have the following form

$$
\mathbf{H}_{\alpha\beta\gamma} = h_1(\mathbf{n}_\alpha\boldsymbol{\delta}_{\beta\gamma} + \mathbf{n}_\beta\boldsymbol{\delta}_{\alpha\gamma}) + h_2\boldsymbol{\delta}_{\alpha\beta}\mathbf{n}_\gamma + h_3(\mathbf{n}_\alpha\mathbf{n}_{\beta\gamma}^{(2)} + \mathbf{n}_\beta\mathbf{n}_{\alpha\gamma}^{(2)}) + h_4\mathbf{n}_\alpha\mathbf{n}_\beta\mathbf{n}_\gamma
$$

We may now construct the contractions

$$\int d\mathbf{r} \int d\mathbf{r}' \mathrm{Tr}[\mathbf{n}\mathbf{H_{rr'}}\boldsymbol{\delta}] = \int d\mathbf{r} \int d\mathbf{r}' \mathbf{n}_\alpha \mathbf{H}_{\alpha\beta\gamma\mathbf{rr'}}\boldsymbol{\delta}_{\beta\gamma} \qquad = (4h_1 + h_2 + h_4)4\pi a^2$$

$$\int d\mathbf{r} \int d\mathbf{r}' \mathrm{Tr}[\boldsymbol{\delta}\mathbf{H_{rr'}}\mathbf{n}] = \int d\mathbf{r} \int d\mathbf{r}' \boldsymbol{\delta}_{\alpha\beta} \mathbf{H}_{\alpha\beta\gamma\mathbf{rr'}}\mathbf{n}_\gamma \qquad = (2h_1 + 3h_2 + h_4)4\pi a^2$$

$$\int d\mathbf{r} \int d\mathbf{r}' \mathrm{Tr}[\mathbf{nn}\mathbf{H_{rr'}}\mathbf{n}] = \int d\mathbf{r} \int d\mathbf{r}' \mathbf{n}_\alpha \mathbf{n}_\beta \mathbf{H}_{\alpha\beta\gamma\mathbf{rr'}}\mathbf{n}_\gamma \qquad = (2h_1 + h_2 + h_4)4\pi a^2$$

$$\int d\mathbf{r} \int d\mathbf{r}' \mathrm{Tr}[\mathbf{n}\mathbf{H_{rr'}}\mathbf{n}^{(2)}] = \int d\mathbf{r} \int d\mathbf{r}' \mathbf{n}_\alpha \mathbf{H}_{\alpha\beta\gamma\mathbf{rr'}}\mathbf{n}^{(2)}_{\beta\gamma} \qquad = 2h_3$$

The inverse matrix is

$$\frac{1}{2}\begin{pmatrix} 1 & 0 & -1 \\ 0 & 1 & -1 \\ -2 & -1 & 5 \end{pmatrix}$$

and the solution is

$$h_1 = \int d\mathbf{r} \int d\mathbf{r}' \frac{1}{2} \left[\mathrm{Tr}[\mathbf{n}\mathbf{H_{rr}}\boldsymbol{\delta}] - \mathrm{Tr}[\mathbf{nn}\mathbf{H_{rr}}\mathbf{n}] \right]$$

$$h_2 = \int d\mathbf{r} \int d\mathbf{r}' \frac{1}{2} \left[\mathrm{Tr}[\boldsymbol{\delta}\mathbf{H_{rr}}\mathbf{n}] - \mathrm{Tr}[\mathbf{nn}\mathbf{H_{rr}}\mathbf{n}] \right]$$

$$h_4 = \int d\mathbf{r} \int d\mathbf{r}' \frac{1}{2} \left[5\mathrm{Tr}[\mathbf{nn}\mathbf{H_{rr}}\mathbf{n}] - 2\mathrm{Tr}[\mathbf{n}\mathbf{H_{rr}}\boldsymbol{\delta}] - \mathrm{Tr}[\boldsymbol{\delta}\mathbf{H_{rr}}\mathbf{n}] \right]$$

$$h_3 = \int d\mathbf{r} \int d\mathbf{r}' \frac{1}{2} \mathrm{Tr}[\mathbf{n}\mathbf{H_{rr}}\mathbf{n}^{(2)}]$$

These coefficients can be expressed as Green-Kubo expressions as follows

$$\int d\mathbf{r} \int d\mathbf{r}' \text{Tr}[\mathbf{n}\mathbf{H}_{\mathbf{r}\mathbf{r}'}\boldsymbol{\delta}] = \int d\mathbf{r} \int d\mathbf{r}' \mathbf{n}_\alpha \mathbf{H}_{\alpha\beta\gamma\mathbf{r}\mathbf{r}'}\boldsymbol{\delta}_{\beta\gamma} = \frac{1}{k_B T} \int_0^\infty dt \left\langle \left(\int d\mathbf{r}\delta\hat{\boldsymbol{\sigma}}_{\mathbf{r}}(t)\mathbf{n} \right) \left(\int d\mathbf{r}' \delta\hat{\mathbf{F}}_{\mathbf{r}'}^{\text{s}\to\text{l}} \right) \right\rangle^\lambda$$

$$= \frac{1}{k_B T} \int_0^\infty dt \left\langle \delta\hat{\boldsymbol{\sigma}}_\perp(t)\cdot\delta\mathbf{F}^{\text{s}\to\text{l}} \right\rangle^\lambda$$

$$\int d\mathbf{r} \int d\mathbf{r}' \text{Tr}[\boldsymbol{\delta}\mathbf{H}_{\mathbf{r}\mathbf{r}'}\mathbf{n}] = \int d\mathbf{r} \int d\mathbf{r}' \boldsymbol{\delta}_{\alpha\beta} \mathbf{H}_{\alpha\beta\gamma\mathbf{r}\mathbf{r}'}\mathbf{n}_\gamma = \frac{1}{k_B T} \int_0^\infty dt \left\langle \left(\int d\mathbf{r}\delta\text{Tr}[\hat{\boldsymbol{\sigma}}_{\mathbf{r}}(t)] \right) \left(\int d\mathbf{r}'\mathbf{n}' \delta\hat{\mathbf{F}}_{\mathbf{r}'}^{\text{s}\to\text{l}} \right) \right\rangle^\lambda$$

$$= \frac{1}{k_B T} \int_0^\infty dt \left\langle \text{Tr}[\delta\hat{\boldsymbol{\sigma}}(t)]\delta F_\perp^{\text{s}\to\text{l}} \right\rangle^\lambda$$

$$\int d\mathbf{r} \int d\mathbf{r}' \text{Tr}[\mathbf{n}\mathbf{n}\mathbf{H}_{\mathbf{r}\mathbf{r}'}\mathbf{n}] = \int d\mathbf{r} \int d\mathbf{r}' \mathbf{n}_\alpha \mathbf{n}_\beta \mathbf{H}_{\alpha\beta\gamma\mathbf{r}\mathbf{r}'}\mathbf{n}_\gamma = \frac{1}{k_B T} \int_0^\infty dt \left\langle \left(\int d\mathbf{r}\mathbf{n}\cdot\delta\hat{\boldsymbol{\sigma}}_{\mathbf{r}}(t)\cdot\mathbf{n} \right) \left(\int d\mathbf{r}'\mathbf{n}' \delta\hat{\mathbf{F}}_{\mathbf{r}'}^{\text{s}\to\text{l}} \right) \right\rangle^\lambda$$

$$= \frac{1}{k_B T} \int_0^\infty dt \left\langle \hat{\sigma}_{\perp\perp}(t)\delta F_\perp^{\text{s}\to\text{l}} \right\rangle^\lambda$$

$$\int d\mathbf{r} \int d\mathbf{r}' \text{Tr}[\mathbf{n}\mathbf{H}_{\mathbf{r}\mathbf{r}'}\mathbf{n}^{(2)}] = \int d\mathbf{r} \int d\mathbf{r}' \mathbf{n}_\alpha \mathbf{H}_{\alpha\beta\gamma\mathbf{r}\mathbf{r}'}\mathbf{n}_{\beta\gamma}^{(2)} = \frac{1}{k_B T} \int_0^\infty dt \left\langle \left(\int d\mathbf{r}\delta\hat{\boldsymbol{\sigma}}_{\mathbf{r}}(t)\cdot\mathbf{n} \right) \right) \left(\int d\mathbf{r}'(\delta\hat{\mathbf{F}}_{\mathbf{r}'}^{\text{s}\to\text{l}} \times \mathbf{n}') \right\rangle^\lambda$$

$$= \frac{1}{k_B T} \int_0^\infty dt \left\langle \delta\hat{\boldsymbol{\sigma}}_\perp(t)\cdot\delta\mathbf{F}_\times^{\text{s}\to\text{l}} \right\rangle^\lambda$$

By comparing this coefficients with the ones corresponding to the $\mathbf{H}_{\mathbf{r}\mathbf{r}'}$ we conclude that $g_1 = h_1, g_2 = h_2, g_3 = h_3, g_4 = h_4$.

10.6 The dynamic equations for the singular boundary model

We now consider what form take the dynamic equations (10.3) when we introduce both, the hard-core model for the free energy and the models for the transport coefficients given in the previous section. The model of the free energy only enters the reversible part of the dynamics while the model of the transport coefficients only enters the irreversible part of the dynamics. We discuss each part separately.

10.6.1 Reversible part

By using the derivatives (10.5.1), (10.5.1) of the free energy, together with (10.5.1) we obtain the following reversible contribution to the dynamic equations

$$\partial_t \rho_{\mathbf{r}}\big|_{\text{rev}} = -\boldsymbol{\nabla} \cdot \mathbf{g}_{\mathbf{r}}$$

$$\partial_t \mathbf{g}_{\mathbf{r}}\big|_{\text{rev}} = -\boldsymbol{\nabla}\mathbf{g}_{\mathbf{r}}\mathbf{v}_{\mathbf{r}} - \boldsymbol{\nabla}P_0(\mathbf{r}) + V_0 n(\mathbf{r})\delta^S(\mathbf{r})$$

$$\partial_t \mathbf{R}\big|_{\text{rev}} = \frac{\mathbf{P}}{M}$$

$$\partial_t \mathbf{P}\big|_{\text{rev}} = -V_0 \int d\mathbf{r} n(\mathbf{r})\delta^S(\mathbf{r})\mathbf{n}$$

In the hard core model the reversible part of the dynamics is that of a simple liquid (i.e. Euler equations) that are subject to singular forces that occur at the boundary of the spherical solid particle. This singular force is purely repulsive and directed towards the fluid, and is the responsible for forbiding the entrance of fluid inside the solid particle. The force on the solid sphere is the result of the imbalance of the density of the fluid around the surface of the sphere.

10.6.2   Irreversible part

Let us consider now the result of adopting the singular boundary model for the transport coefficients in the different terms of the irreversible part of the dynamics in (10.3). The first term is the viscosity term

$$\boldsymbol{\nabla}_\mathbf{r}^\nu \int d\mathbf{r}' \eta_{\mathbf{r}\mathbf{r}'}^{\mu\nu\mu'\nu'} \boldsymbol{\nabla}_{\mathbf{r}'}^{\nu'} \mathbf{v}^{\mu'}(\mathbf{r}') = \boldsymbol{\nabla}_\mathbf{r}^\nu \int d\mathbf{r}' \delta(\mathbf{r}-\mathbf{r}') \left(\eta \left[\delta^{\mu\mu'}\delta^{\nu\nu'} + \delta^{\mu\nu'}\delta^{\nu\mu'} - \frac{2}{3}\delta^{\mu\nu}\delta^{\mu'\nu'} \right] + \zeta \delta^{\mu\nu}\delta^{\mu'\nu'} \right) \boldsymbol{\nabla}_{\mathbf{r}'}^{\nu'}\mathbf{v}^{\mu'}(\mathbf{r}')$$

$$= \eta\boldsymbol{\nabla}^2\mathbf{v}^\mu + \left(\frac{\eta}{3}+\zeta\right)\boldsymbol{\nabla}^\mu(\boldsymbol{\nabla}\cdot\mathbf{v})$$

$$= \boldsymbol{\nabla}^\nu\boldsymbol{\sigma}^{\mu\nu}$$

This is the usual viscous term in the Navier-Stokes equations.

The boundary coupling term (10.3) involves

$$\phi^\mu(\mathbf{r}) = -\int d\mathbf{r}' \mathbf{G}_{\mathbf{r}\mathbf{r}'}^{\mu\nu'\mu'} \boldsymbol{\nabla}_{\mathbf{r}'}^{\nu'} \mathbf{v}^{\mu'}(\mathbf{r}') + \boldsymbol{\nabla}_\mathbf{r}^\nu \int d\mathbf{r}' \mathbf{H}_{\mathbf{r}\mathbf{r}'}^{\mu\nu\mu'}\left(\mathbf{v}^{\mu'}(\mathbf{r}') - \mathbf{V}^{\mu'}\right) - \int d\mathbf{r}' \gamma_{\mathbf{r}\mathbf{r}'}^{\mu\mu'}\left(\mathbf{v}^{\mu'}(\mathbf{r}') - \mathbf{V}^{\mu'}\right)$$

The first term is

$$\int d\mathbf{r}' \mathbf{G}_{\mathbf{r}\mathbf{r}'}^{\mu\mu'\nu'} \boldsymbol{\nabla}_{\mathbf{r}'}^{\nu'} \mathbf{v}^{\mu'}(\mathbf{r}') = -\int d\mathbf{r}' \delta(\mathbf{r}-\mathbf{r}')\delta(|\mathbf{r}-\mathbf{R}|-a)\mathbf{G}^{\mu\mu'\nu'} \boldsymbol{\nabla}_{\mathbf{r}'}^{\nu'}\mathbf{v}^{\mu'}(\mathbf{r}')$$

$$= -\delta_\mathbf{r}^S \mathbf{G}^{\mu\mu'\nu'} \boldsymbol{\nabla}_\mathbf{r}^{\nu'} \mathbf{v}^{\mu'}(\mathbf{r})$$

The second term is

$$\boldsymbol{\nabla}_\mathbf{r}^\nu \int d\mathbf{r}' \mathbf{H}_{\mathbf{r}\mathbf{r}'}^{\mu\nu\mu'}\left(\mathbf{v}^{\mu'}(\mathbf{r}') - \mathbf{V}^{\mu'}\right) = \boldsymbol{\nabla}_\mathbf{r}^\nu \int d\mathbf{r}' \delta(\mathbf{r}-\mathbf{r}')\frac{1}{4\pi a^2}\delta(|\mathbf{r}-\mathbf{R}|-a)\mathbf{H}^{\mu\nu\mu'}\left(\mathbf{v}^{\mu'}(\mathbf{r}') - \mathbf{V}^{\mu'}\right)$$

$$= \boldsymbol{\nabla}_\mathbf{r}^\nu \left(\delta_\mathbf{r}^S \mathbf{H}^{\mu\nu\mu'}\left(\mathbf{v}^{\mu'}(\mathbf{r}) - \mathbf{V}^{\mu'}\right)\right)$$

The third term is

$$-\int d\mathbf{r}' \gamma_{\mathbf{r}\mathbf{r}'}^{\mu\mu'}\left(\mathbf{v}^{\mu'}(\mathbf{r}') - \mathbf{V}^{\mu'}\right) = -\delta_\mathbf{r}^S \gamma^{\mu\mu'}\left(\mathbf{v}^{\mu'}(\mathbf{r}) - \mathbf{V}^{\mu'}\right)$$

Collecting the three terms we have

$$\phi^\mu(\mathbf{r}) = -\delta_\mathbf{r}^S \mathbf{G}^{\mu\mu'\nu'}\boldsymbol{\nabla}^{\nu'}\mathbf{v}^{\mu'}(\mathbf{r}) + \boldsymbol{\nabla}^\nu\left(\delta_\mathbf{r}^S \mathbf{H}^{\mu\nu\mu'}(\mathbf{v}^{\mu'}(\mathbf{r}) - \mathbf{V}^{\mu'})\right) - \delta_\mathbf{r}^S \gamma^{\mu\mu'}\left(\mathbf{v}^{\mu'}(\mathbf{r}) - \mathbf{V}^{\mu'}\right)$$

The different terms in this expression may be explicitly computed with Eq. (10.5.2)

$$
\begin{aligned}
\mathbf{H}_{\mu\nu\mu'}(\mathbf{v}^{\mu'}(\mathbf{r}) - \mathbf{V}^{\mu'}) &= \left[h_1(\mathbf{n}_\mu\boldsymbol{\delta}_{\nu\mu'} + \mathbf{n}_\nu\boldsymbol{\delta}_{\mu\mu'}) + h_2\boldsymbol{\delta}_{\mu\nu}\mathbf{n}_{\mu'} + h_3(\mathbf{n}_\mu\mathbf{n}^{(2)}_{\nu\mu'} + \mathbf{n}_\nu\mathbf{n}^{(2)}_{\mu'\nu'}) + h_4\mathbf{n}_\mu\mathbf{n}_\nu\mathbf{n}_{\mu'} \right] (\mathbf{v}^{\mu'}(\mathbf{r}) - \mathbf{V}^{\mu'}) \\
&= h_1(\mathbf{n}_\mu(\mathbf{v} - \mathbf{V})_\nu + (\mathbf{v} - \mathbf{V})_\mu\mathbf{n}_\nu) + h_2\boldsymbol{\delta}_{\mu\nu}\mathbf{n}\cdot(\mathbf{v} - \mathbf{V}) \\
&\quad + h_3(\mathbf{n}_\mu\mathbf{n}^{(2)}_{\nu\mu'} + \mathbf{n}_\nu\mathbf{n}^{(2)}_{\mu'\nu'})(\mathbf{v}^{\mu'}(\mathbf{r}) - \mathbf{V}^{\mu'}) + h_4\mathbf{n}_\mu\mathbf{n}_\nu(\mathbf{n}\cdot(\mathbf{v} - \mathbf{V})) \\
&= h_1(\mathbf{n}_\mu(\mathbf{v} - \mathbf{V})_\nu + (\mathbf{v} - \mathbf{V})_\mu\mathbf{n}_\nu) + h_3(\mathbf{n}_\mu\mathbf{n}^{(2)}_{\nu\mu'} + \mathbf{n}_\nu\mathbf{n}^{(2)}_{\mu'\nu'})(\mathbf{v}^{\mu'}(\mathbf{r}) - \mathbf{V}^{\mu'})
\end{aligned}
$$

$$
\begin{aligned}
\mathbf{G}_{\mu\mu'\nu'}\boldsymbol{\nabla}^{\nu'}\mathbf{v}^{\mu'}(\mathbf{r}) &= \left[h_1(\boldsymbol{\delta}_{\mu\mu'}\mathbf{n}_{\nu'} + \boldsymbol{\delta}_{\mu\nu'}\mathbf{n}_{\mu'}) + h_2\mathbf{n}_\mu\boldsymbol{\delta}_{\mu'\nu'} + h_3(\mathbf{n}^{(2)}_{\mu'\nu'}\mathbf{n}_{\nu'} + \mathbf{n}^{(2)}_{\mu\nu'}\mathbf{n}_{\mu'}) + h_4\mathbf{n}_\mu\mathbf{n}_{\mu'}\mathbf{n}_{\nu'} \right] \boldsymbol{\nabla}^{\nu'}\mathbf{v}^{\mu'}(\mathbf{r}) \\
&= h_1(\mathbf{n}\cdot\boldsymbol{\nabla}\mathbf{v}^\mu(\mathbf{r}) + (\boldsymbol{\nabla}^\mu\mathbf{v})\cdot\mathbf{n}) + h_2\mathbf{n}_\mu\boldsymbol{\nabla}\cdot\mathbf{v}(\mathbf{r}) \\
&\quad + h_3\mathbf{n}_\mu\mathbf{n}^{(2)}_{\mu'\nu'}\boldsymbol{\nabla}^{\nu'}\mathbf{v}^{\mu'}(\mathbf{r}) + h_3\mathbf{n}_{\mu'}\mathbf{n}^{(2)}_{\mu\nu'}\boldsymbol{\nabla}^{\nu'}\mathbf{v}^{\mu'}(\mathbf{r}) + h_4\mathbf{n}_\mu\mathbf{n}\cdot\boldsymbol{\nabla}\mathbf{v}(\mathbf{r})\mathbf{n}
\end{aligned}
$$

$$
\boldsymbol{\gamma}^{\mu\mu'}\left(\mathbf{v}^{\mu'}(\mathbf{r}) - \mathbf{V}^{\mu'}\right) = \gamma_{||}\left(\mathbf{v}^\mu(\mathbf{r}) - \mathbf{V}^\mu\right)
$$

we have used that $\mathbf{n}\cdot(\mathbf{v} - \mathbf{V}) = 0$, as will be discussed in the next section. By inserting (10.6.2) into Eq. (10.6.2) we obtain the explicit form for the boundary force in the singular boundary model. The forces on the fluid are concentrated (singular) in the region of contact with the solid.

One observation is in order. In the momentum equation for the sphere, there is a term due to the boundary force which is proportional to $\gamma_{||}$. This term is of the form

$$
\gamma_{||} \int d\mathbf{r}\delta^S_\mathbf{r}\left(\mathbf{v}^\mu(\mathbf{r}) - \mathbf{V}^\mu\right) = \gamma_{||}\left(\int d\mathbf{r}\delta^S_\mathbf{r}\mathbf{v}^\mu(\mathbf{r}) - \mathbf{V}^\mu\right)
$$

Therefore, there is a friction force on the particle, proportional to the difference between the average of the fluid velocity on the surface of the sphere and the particle's velocity. Note that the friction coefficient is $\gamma_{||}$ involving the tangential component of the microscopic force, and not γ that is the usual definition of the Kirkwood friction force. Of course, this is due to the fact that the average of the fluid velocity on the sphere is different from the simple "fluid velocity" that may appear in a theory where the solvent is completely eliminated.

10.6.3   All together

We collect now all the results in order to give the dynamic equations for a fluid and a solid sphere in the singular boundary model. They are given by

$$\partial_t \rho_{\mathbf{r}} = -\boldsymbol{\nabla} \cdot \mathbf{g_r}$$

$$\partial_t \mathbf{g_r} = -\boldsymbol{\nabla}\mathbf{g_r}\mathbf{v_r} - \boldsymbol{\nabla} P_0(\mathbf{r}) + \eta\boldsymbol{\nabla}^2\mathbf{v}^\mu + \left(\frac{\eta}{3} + \zeta\right)\boldsymbol{\nabla}^\mu(\boldsymbol{\nabla}{\cdot}\mathbf{v}) + V_0 n(\mathbf{r})\delta^S(\mathbf{r}) + \boldsymbol{\phi}(\mathbf{r})$$

$$\partial_t \mathbf{R} = \frac{\mathbf{P}}{M}$$

$$\partial_t \mathbf{P} = -V_0 \int d\mathbf{r}\, n(\mathbf{r})\delta^S(\mathbf{r})\mathbf{n} - \int d\mathbf{r}\boldsymbol{\phi}(\mathbf{r})$$

with the irreversible coupling force is given by Eqs. (10.6.2) with (10.6.2). These equations are just the Navier-Stokes equations for an isothermal compressible fluid, with an additional force density that is only different from zero at the solid sphere boundary. In the next section, we consider the situation in which the surface forces may be substituted with boundary conditions on the fluid.
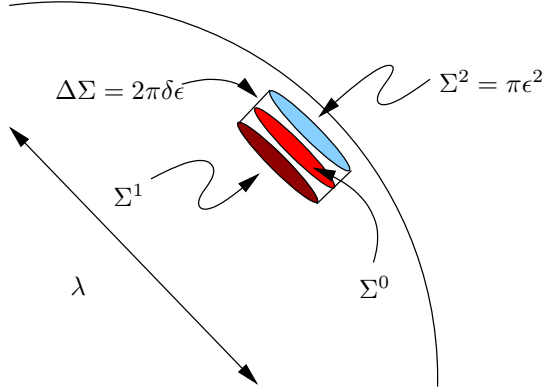
Figure 10.1: A pillbox of height δ, area $\pi\epsilon^2$, and lateral surface $\Delta\Sigma$ intersects the surface of the solid sphere at Σ_0. The "surface" Σ_0 has a molecular width σ_0. The length scale λ of the flow field is assumed to be of the order of the radius of the sphere. It is assumed that $\sigma_0 \ll \delta \ll \epsilon \ll \lambda$.

10.7   Boundary conditions

In this section we show how the singular boundary model introduced in the previous section can be reformulated in terms of boundary conditions. Because the irreversible boundary force $\boldsymbol{\phi}(\mathbf{r})$ contains Green-Kubo transport coefficients, *the resulting boundary conditions contain also these transport coefficients.* This provides, in particular, a statistical mechanics expression of the slip coefficient.

Consider the well-known theorem that relates the time derivative of the integral of a function $A(\mathbf{r})$ over a time-dependent volume $\Omega(t)$

$$\frac{d}{dt}\int_{\Omega(t)} A(\mathbf{r},t)d\mathbf{r} = \int_{\Omega(t)} \frac{\partial}{\partial t}A(\mathbf{r},t)d\mathbf{r}$$
$$+ \int_{\Sigma(t)} dS\mathbf{n}\cdot\mathbf{v}^{\Sigma}(\mathbf{r})A(\mathbf{r},t)$$

The first term exists even if the volume does not move, the second term is the variation on the amount of A that is inside the volume due to the sweeping of the surface as it moves. In this expression, $\Sigma(t)$ is the boundary of $\Omega(t)$, $\mathbf{n}$ is the normal of the surface pointing outwards and $\mathbf{v}^{\Sigma}(\mathbf{r})$ is the velocity of the surface at the point $\mathbf{r}$.

By taking the density as the function A in Eq. (10.7) and an infinitesimal "pillbox" volume as shown in Fig. 10.1, the theorem (10.7) becomes

$$\frac{d}{dt}\int_{\Omega(t)} \rho(\mathbf{r},t)d\mathbf{r} = \int_{\Omega(t)} \frac{\partial}{\partial t}\rho(\mathbf{r},t)d\mathbf{r}$$
$$+ \int_{\Sigma(t)} dS\mathbf{n}\cdot\mathbf{V}\rho(\mathbf{r},t)$$

where we have taken $\mathbf{v}^{\Sigma} = \mathbf{V}$ (the particle does not rotate). By using the continuity equation and use of Gauss theorem we may write the above as

$$\frac{d}{dt}\int_{\Omega(t)}\rho(\mathbf{r},t)d\mathbf{r} = \int_{\Sigma^1(t)}dS\mathbf{n}\cdot(\mathbf{v}(\mathbf{r},t)-\mathbf{V}(t))\rho(\mathbf{r},t)$$

$$+ \int_{\Sigma^2(t)}dS\mathbf{n}\cdot(\mathbf{v}(\mathbf{r},t)-\mathbf{V}(t))\rho(\mathbf{r},t)$$

$$+ \int_{\Delta\Sigma}dS\mathbf{n}\cdot(\mathbf{v}(\mathbf{r},t)-\mathbf{V}(t))\rho(\mathbf{r},t)$$

The pillbox is a cylinder limited by $\Sigma = \Sigma^1 + \Sigma^2 + \Delta\Sigma$. The area of Σ^1, Σ^2 is $\pi\epsilon^2$ while the area of $\Delta\Sigma$ is $2\pi\delta$, where ϵ is the radius of the cylinder and δ its height. We assume that $\delta \ll \epsilon$. We also assume that $\epsilon \ll \lambda$, where λ is the length scale of variation of the flow fields, typically of the order of the radius of the sphere. Therefore, the left hand side is approximately given by $\frac{d}{dt}\rho(\mathbf{r},t)\epsilon^2\delta$. This is of order δ, as well as the integral over the surface $\Delta\Sigma$ which is proportional to $\epsilon\delta$. The rest of the terms, on the right hand side of Eq. (10.7) are of order ϵ^2. We may neglect therefore the terms of order δ. In addition, as we have already discussed, there can be no fluid inside the solid sphere because otherwise infinite forces would develop. Therefore the density field evaluated on the surface Σ^1 vanishes. This implies

$$\int_{\Sigma^2(t)}dS\mathbf{n}\cdot(\mathbf{v}(\mathbf{r},t)-\mathbf{V}(t))\rho(\mathbf{r},t) = 0$$

Because the pillbox is arbitrary this implies that

$$\mathbf{n}\cdot(\mathbf{v}(\mathbf{r},t)-\mathbf{V}(t)) = 0$$

for $\mathbf{r} \in \Sigma^0(t)$ which is the usual impenetrability boundary condition.

When we use the momentum density in theorem (10.7), we have

$$\frac{d}{dt}\int_{\Omega(t)}\mathbf{g}(\mathbf{r},t)d\mathbf{r} = \int_{\Omega(t)}\frac{\partial}{\partial t}\mathbf{g}(\mathbf{r},t)d\mathbf{r} + \int_{\Sigma(t)}dS\mathbf{n}\cdot\mathbf{V}\mathbf{g}(\mathbf{r},t)$$

$$= \int_{\Omega(t)}d\mathbf{r}\left[-\boldsymbol{\nabla}\mathbf{g_r}\mathbf{v_r}-\rho(\mathbf{r})\boldsymbol{\nabla}\mu(\mathbf{r})+\boldsymbol{\nabla}\hat{\boldsymbol{\sigma}}_{\mathbf{r}}+\boldsymbol{\phi}_{\mathbf{r}}\right] + \int_{\Sigma(t)}dS\mathbf{n}\cdot\mathbf{V}\mathbf{g}(\mathbf{r},t)$$

$$= \int_{\Sigma(t)}dS\mathbf{n}\cdot(\mathbf{V}-\mathbf{v_r})\mathbf{g}(\mathbf{r},t) + \int_{\Omega(t)}d\mathbf{r}\left[-\rho(\mathbf{r})\boldsymbol{\nabla}\mu(\mathbf{r})+\boldsymbol{\nabla}\hat{\boldsymbol{\sigma}}_{\mathbf{r}}+\boldsymbol{\phi}_{\mathbf{r}}\right]$$

By using Eq. (10.7) and the scaling relations $\delta \ll \epsilon \ll \lambda$, we end up with

$$\int_{\Omega(t)}d\mathbf{r}\left[-\rho(\mathbf{r})\boldsymbol{\nabla}\mu(\mathbf{r})+\boldsymbol{\nabla}\hat{\boldsymbol{\sigma}}_{\mathbf{r}}+\boldsymbol{\phi}_{\mathbf{r}}\right] = 0$$

The reversible term is

$$\int_{\Omega(t)} d\mathbf{r} \rho(\mathbf{r}) \boldsymbol{\nabla} \mu(\mathbf{r}) = \int_{\Omega(t)} d\mathbf{r} \left[\boldsymbol{\nabla} P_0(\rho(\mathbf{r})) + \rho(\mathbf{r}) \mathbf{n} V_0 \delta^s(\mathbf{r}) \right]$$

$$= \underbrace{\int_{\Sigma^1(t)} dS\mathbf{n} P_0(\rho(\mathbf{r}))}_{=0} + \int_{\Sigma^2(t)} dS\mathbf{n} P_0(\rho(\mathbf{r})) + \underbrace{\int_{\Delta\Sigma(t)} dS\mathbf{n} P_0(\rho(\mathbf{r}))}_{=0} + \int_{\Sigma^0(t)} \rho(\mathbf{r}) \mathbf{n} V_0$$

The first integral vanishes because Σ^1 is inside the solid sphere for which the density and pressure vanish. The third integral is of order δ and negligible in front of the rest of terms.

Let us consider now the irreversible contribution

$$\int_{\Omega(t)} d\mathbf{r} \left[\boldsymbol{\nabla}^\nu \boldsymbol{\sigma}_\mathbf{r}^{\nu\mu} + \boldsymbol{\phi}_\mathbf{r}^\mu \right]$$

$$= \underbrace{\int_{\Sigma^1(t)} dS\mathbf{n}^\nu \boldsymbol{\sigma}_\mathbf{r}^{\nu\mu}}_{=0} + \int_{\Sigma^2(t)} dS\mathbf{n}^\nu \boldsymbol{\sigma}_\mathbf{r}^{\nu\mu} + \underbrace{\int_{\Delta\Sigma(t)} dS\mathbf{n}^\nu \boldsymbol{\sigma}_\mathbf{r}^{\nu\mu}}_{=0}$$

$$- \int_{\Sigma^0(t)} dS\mathbf{G}^{\mu\mu'\nu'} \boldsymbol{\nabla}^{\nu'} \mathbf{v}^{\mu'}(\mathbf{r}) + \underbrace{\int_{\Omega(t)} d\mathbf{r} \boldsymbol{\nabla}^\nu \left(\delta_\mathbf{r}^S \mathbf{H}^{\mu\nu\mu'} (\mathbf{v}^{\mu'}(\mathbf{r}) - \mathbf{V}^{\mu'}) \right)}_{(*)} - \int_{\Sigma^0(t)} dS\boldsymbol{\gamma}^{\mu\mu'} \left(\mathbf{v}^{\mu'}(\mathbf{r}) - \mathbf{V}^{\mu'} \right)$$

Let us consider the term (*) involving the gradient of the surface delta. This is a delicate term because of the derivative of a singularity. A naive treatment would be the following

$$\int_{\Omega(t)} d\mathbf{r} \boldsymbol{\nabla}^\nu \left(\delta_\mathbf{r}^S \mathbf{H}^{\mu\nu\mu'} (\mathbf{v}^{\mu'}(\mathbf{r}) - \mathbf{V}^{\mu'}) \right) = \int_{\Sigma(t)} dS\mathbf{n}^\nu \left(\delta_\mathbf{r}^S \mathbf{H}^{\mu\nu\mu'} (\mathbf{v}^{\mu'}(\mathbf{r}) - \mathbf{V}^{\mu'}) \right)$$

The surface delta is singular at the surface Σ_0, but Σ_0 does not coincide neither with Σ_1 nor Σ_2. Note that we have assumed that $\sigma_0 \ll \delta$ and the surface delta (which is non-zero only in the region of width σ_0 near the surface of the sphere) gives non contribution in the surfaces Σ^1, Σ^2. Therefore, this term (10.7) should vanish. We can provide a more convincing argument by using the expression for this term *before* assuming a local model. In this case, it takes the form

$$= \int_{\Omega(t)} d\mathbf{r} \boldsymbol{\nabla} \int d\mathbf{r}' \mathbf{H}_{\mathbf{rr}'} (\mathbf{v}_{\mathbf{r}'} - \mathbf{V})$$

$$= \int_{\Sigma(t)} dS\mathbf{n} \int d\mathbf{r}' \mathbf{H}_{\mathbf{rr}'} (\mathbf{v}_{\mathbf{r}'} - \mathbf{V})$$

$$= \int_{\Sigma(t)} dS\mathbf{n} \int d\mathbf{r}' \frac{1}{k_B T} \int_0^\infty dt \left\langle \delta\hat{\boldsymbol{\sigma}}_\mathbf{r}(t) \delta\hat{\mathbf{F}}_{\mathbf{r}'}^{s\to1} \right\rangle^\lambda (\mathbf{v}_{\mathbf{r}'} - \mathbf{V})$$

The correlation $\left\langle \delta \hat{\boldsymbol{\sigma}}_{\mathbf{r}}(t) \delta \hat{\mathbf{F}}^{\mathrm{s}, \rightarrow 1}_{\mathbf{r}'} \right\rangle^{\lambda}$ is assumed to decay in a molecular length scale of the order σ_0. At the same time, due to the force $\hat{\mathbf{F}}^{\mathrm{s}, \rightarrow 1}_{\mathbf{r}'}$, only for points $\mathbf{r}'$ within the range σ_0 of the solid-liquid interface, this correlation is different from zero. Therefore, because we are integrating over points $\mathbf{r}, \mathbf{r}'$ which are separated by $\delta/2$, typically, this correlation is always zero. Therefore, the above term (10.7) vanishes.

Let us return to Eq. (10.7). By continuity we have

$$\int_{\Sigma^2(t)} dS \mathbf{n}^{\nu} \boldsymbol{\sigma}^{\nu \mu}_{\mathbf{r}} \approx \int_{\Sigma^0(t)} dS \mathbf{n}^{\nu} \boldsymbol{\sigma}^{\nu \mu}_{\mathbf{r}}$$

and, therefore, we end up with the following condition

$$0 = \int_{\Sigma^0(t)} dS \mathbf{n} P_0(\rho(\mathbf{r})) + \int_{\Sigma^0(t)} \rho(\mathbf{r}) \mathbf{n} V_0 + \int_{\Sigma^0(t)} dS \mathbf{n}^{\nu} \boldsymbol{\sigma}^{\nu \mu}_{\mathbf{r}} - \int_{\Sigma^0(t)} dS \mathbf{G}^{\mu \mu' \nu'} \boldsymbol{\nabla}^{\nu'} \mathbf{v}^{\mu'}(\mathbf{r}) - \int_{\Sigma^0(t)} dS \gamma^{\mu \mu'} \left(\mathbf{v}^{\mu'}(\mathbf{r}) - \mathbf{V}^{\mu'} \right)$$

Because the pillbox volume is arbitrarily small, we have finally for those points at the surface of the sphere, $\mathbf{r} \in \Sigma^0(t)$

$$\boxed{0 = -\mathbf{n}^{\mu} P_0(\rho(\mathbf{r})) + \rho(\mathbf{r}) \mathbf{n}^{\mu} V_0 + \mathbf{n}^{\nu} \boldsymbol{\sigma}^{\nu \mu}_{\mathbf{r}} - \mathbf{G}^{\mu \mu' \nu'} \boldsymbol{\nabla}^{\nu'} \mathbf{v}^{\mu'}(\mathbf{r}) - \gamma^{\mu \mu'} \left(\mathbf{v}^{\mu'}(\mathbf{r}) - \mathbf{V}^{\mu'} \right)}$$

$$(10.7.\text{-}10)$$

This equation is the force balance at the surface of the sphere. Let us decompose this vector equation in normal and tangential components. By multiplying (10.7.-10) with $\mathbf{n}$ we obtain

$$-P_0(\rho) + \rho V_0 + \mathbf{n} \boldsymbol{\sigma} \mathbf{n} - \mathbf{n} \mathbf{G} \boldsymbol{\nabla} \mathbf{v} = 0$$

The following terms enter into this equation

$$\mathbf{n} \boldsymbol{\sigma} \mathbf{n} = \eta 2 \mathbf{n} \cdot \boldsymbol{\nabla} \mathbf{v} \cdot \mathbf{n} + \left(\zeta - \frac{2}{3} \eta \right) \boldsymbol{\nabla} \cdot \mathbf{v}$$

$$\mathbf{n} \mathbf{G} \boldsymbol{\nabla} \mathbf{v} = h_2 \boldsymbol{\nabla} \cdot \mathbf{v} + (2 h_1 + h_4) \mathbf{n} \cdot \boldsymbol{\nabla} \mathbf{v} \cdot \mathbf{n}$$

Therefore, we have finally

$$-P_0(\rho) + \rho V_0 + (2\eta - 2 h_1) \mathbf{n} \cdot \boldsymbol{\nabla} \mathbf{v} \cdot \mathbf{n} + \left(\zeta - \frac{2}{3} \eta - h_2 \right) \boldsymbol{\nabla} \cdot \mathbf{v} = 0$$

We next multiply (10.7.-10) with a vector $\mathbf{t}$ tangential to the surface with the result

$$0 = \mathbf{n}\boldsymbol{\sigma}\mathbf{t} - \mathbf{t}\mathbf{G}\boldsymbol{\nabla}\mathbf{v} - \gamma_{||}\mathbf{t}\cdot(\mathbf{v} - \mathbf{V})$$

$$\mathbf{n}\boldsymbol{\sigma}\mathbf{t} = \eta\left[\mathbf{n}\cdot\boldsymbol{\nabla}\mathbf{v}\cdot\mathbf{t} + \mathbf{t}\cdot\boldsymbol{\nabla}\mathbf{v}\cdot\mathbf{n}\right]$$

$$\mathbf{t}\mathbf{G}\boldsymbol{\nabla}\mathbf{v} = h_1\left[\mathbf{n}\cdot\boldsymbol{\nabla}\mathbf{v}\cdot\mathbf{t} + \mathbf{t}\cdot\boldsymbol{\nabla}\mathbf{v}\cdot\mathbf{n}\right] + h_3\mathbf{t}_\mu\epsilon_{\mu\mu'\sigma}\mathbf{n}_\sigma\mathbf{n}_{\nu'}\boldsymbol{\nabla}^{\nu'}\mathbf{v}^{\mu'} + h_3\mathbf{t}_\mu\epsilon_{\mu\nu'\sigma}\mathbf{n}_\sigma\mathbf{n}_{\mu'}\boldsymbol{\nabla}^{\nu'}\mathbf{v}^{\mu'}$$
$$= h_1\left[\mathbf{n}\cdot\boldsymbol{\nabla}\mathbf{v}\cdot\mathbf{t} + \mathbf{t}\cdot\boldsymbol{\nabla}\mathbf{v}\cdot\mathbf{n}\right] + h_3\mathbf{n}\cdot\boldsymbol{\nabla}\mathbf{v}\cdot(\mathbf{t}\times\mathbf{n}) - h_3(\mathbf{t}\times\mathbf{n})\cdot(\boldsymbol{\nabla}\mathbf{v})\cdot\mathbf{n}$$

where we have made use of the impenetrability condition (10.7). Note that we have two equations for each tangent vector $\mathbf{t}_1, \mathbf{t}_2$. We take the convention that $\mathbf{t}_1 \times \mathbf{t}_2 = \mathbf{n}$, $\mathbf{t}_2 \times \mathbf{n} = \mathbf{t}_1$, $\mathbf{n} \times \mathbf{t}_1 = \mathbf{t}_2$.

The final boundary conditions are

$$\mathbf{n}\cdot(\mathbf{v} - \mathbf{V}) = 0$$

$$-P_0(\rho) + \rho V_0 + (2\eta - 2h_1)\mathbf{n}\cdot\boldsymbol{\nabla}\mathbf{v}\cdot\mathbf{n} + \left(\zeta - \frac{2}{3}\eta - h_2\right)\boldsymbol{\nabla}\cdot\mathbf{v} = 0$$

$$(\eta - h_1)\left[\mathbf{n}\cdot\boldsymbol{\nabla}\mathbf{v}\cdot\mathbf{t}_1 + \mathbf{t}_1\cdot\boldsymbol{\nabla}\mathbf{v}\cdot\mathbf{n}\right] + h_3\left[\mathbf{t}_2\cdot\boldsymbol{\nabla}\mathbf{v}\cdot\mathbf{n} + \mathbf{n}\cdot\boldsymbol{\nabla}\mathbf{v}\cdot\mathbf{t}_2\right] - \gamma_{||}\mathbf{t}_1\cdot(\mathbf{v} - \mathbf{V}) = 0$$

$$(\eta - h_1)\left[\mathbf{n}\cdot\boldsymbol{\nabla}\mathbf{v}\cdot\mathbf{t}_2 + \mathbf{t}_2\cdot\boldsymbol{\nabla}\mathbf{v}\cdot\mathbf{n}\right] - h_3\left[\mathbf{t}_1\cdot\boldsymbol{\nabla}\mathbf{v}\cdot\mathbf{n} + \mathbf{n}\cdot\boldsymbol{\nabla}\mathbf{v}\cdot\mathbf{t}_1\right] - \gamma_{||}\mathbf{t}_2\cdot(\mathbf{v} - \mathbf{V}) = 0 \quad (10.7.\text{-}15)$$

If we take the transformation $\mathbf{t}_1 \to \mathbf{t}_2$ and $\mathbf{t}_2 \to -\mathbf{t}_1$ we are performing an anticlockwise rotation of 90 degrees around $\mathbf{n}$. In that case the equations remain invariant.

10.7.1 The force on the particle

The force on the solid sphere is given by

$$\dot{\mathbf{P}} = -\frac{\partial F}{\partial \mathbf{R}} - \int d\mathbf{r}\phi(\mathbf{r})$$

In the singular boundary model, we may use (10.5.1) and (10.6.2) in this expression, leading to

$$\dot{\mathbf{P}} = \int d\mathbf{r}\left[\delta_\mathbf{r}^S\frac{V_0}{m}\rho(\mathbf{r})\mathbf{n} + \delta_\mathbf{r}^S\mathbf{G}\boldsymbol{\nabla}\mathbf{v}(\mathbf{r}) - \boldsymbol{\nabla}\left(\delta_\mathbf{r}^S\mathbf{H}(\mathbf{v}(\mathbf{r}) - \mathbf{V})\right) + \delta_\mathbf{r}^S\boldsymbol{\gamma}\left(\mathbf{v}(\mathbf{r}) - \mathbf{V}\right)\right]$$

Note that the space integral is extended to all space (including the interior of the sphere). This implies that the term involving the tensor $\mathbf{H}$ is a pure divergence. In periodic boundary conditions or infinite systems, Gauss theorem allows to neglect this term. The resulting integral is

$$\dot{\mathbf{P}} = \int d\mathbf{r}\delta_\mathbf{r}^S\left[\frac{V_0}{m}\rho(\mathbf{r})\mathbf{n} + \mathbf{G}\boldsymbol{\nabla}\mathbf{v}(\mathbf{r}) + \boldsymbol{\gamma}\left(\mathbf{v}(\mathbf{r}) - \mathbf{V}\right)\right]$$
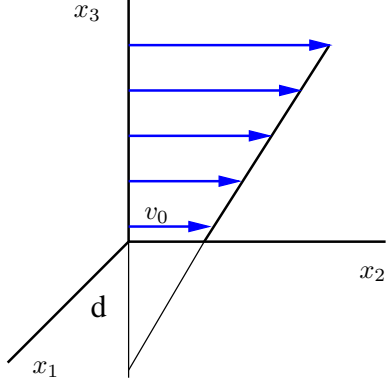
Figure 10.2: Linear shear flow of the form $\mathbf{v}(\mathbf{r}) = (0, v_0 + \dot{\gamma} x_3, 0)$.

This is just a surface integral and on that surface we may use the boundary conditions (10.7.-10), leading to

$$\dot{\mathbf{P}} = \int d\mathbf{r} \delta_{\mathbf{r}}^S \left[\frac{V_0}{m} \rho(\mathbf{r}) \mathbf{n} + \mathbf{G} \boldsymbol{\nabla} \mathbf{v}(\mathbf{r}) + \boldsymbol{\gamma} \left(\mathbf{v}(\mathbf{r}) - \mathbf{V} \right) \right]$$

$$= \int d\mathbf{r} \delta_{\mathbf{r}}^S \left[\mathbf{n} P_0(\rho(\mathbf{r})) - \mathbf{n} \hat{\boldsymbol{\sigma}}_{\mathbf{r}} \right]$$

$$= \int dS \mathbf{n} \left[P_0(\rho(\mathbf{r})) \boldsymbol{\delta} - \hat{\boldsymbol{\sigma}}_{\mathbf{r}} \right]$$

$$= \int d\mathbf{r} \boldsymbol{\nabla} \boldsymbol{\Pi}$$

where $\boldsymbol{\Pi}$ is the total bulk stress of the fluid. **repasar signos**. This is the usual expresion for computing the force on a sphere due to the interaction with the fluid. This gives strong confidence on the procedure used to formulate the boundary model and the boundary conditions.

10.8   Examples

10.8.1   Planar wall

Let us consider now a planar wall at rest, which can be understood here as a solid sphere of very large radius. Let us choose a reference frame x_1, x_2, x_3 where x_1, x_2 are tangent to the wall and x_3 is normal to the wall. In this way, $\mathbf{n} = (0, 0, 1)$ and $\mathbf{t}_1 = (1, 0, 0)$,

$\mathbf{t}_2 = (0, 1, 0)$.

$$\mathbf{n}\boldsymbol{\nabla}\mathbf{vn} = (0,0,1) \begin{pmatrix} \partial_1 v_1 & \partial_1 v_2 & \partial_1 v_3 \\ \partial_2 v_1 & \partial_2 v_2 & \partial_2 v_3 \\ \partial_3 v_1 & \partial_3 v_2 & \partial_3 v_3 \end{pmatrix} \begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix} = \partial_3 v_3$$

$$\mathbf{n}\cdot\boldsymbol{\nabla}\mathbf{v}\cdot\mathbf{t}_1 = (0,0,1) \begin{pmatrix} \partial_1 v_1 & \partial_1 v_2 & \partial_1 v_3 \\ \partial_2 v_1 & \partial_2 v_2 & \partial_2 v_3 \\ \partial_3 v_1 & \partial_3 v_2 & \partial_3 v_3 \end{pmatrix} \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix} = \partial_3 v_1$$

$$\mathbf{n}\boldsymbol{\nabla}\mathbf{vt}_2 = (0,0,1) \begin{pmatrix} \partial_1 v_1 & \partial_1 v_2 & \partial_1 v_3 \\ \partial_2 v_1 & \partial_2 v_2 & \partial_2 v_3 \\ \partial_3 v_1 & \partial_3 v_2 & \partial_3 v_3 \end{pmatrix} \begin{pmatrix} 0 \\ 1 \\ 0 \end{pmatrix} = \partial_3 v_2$$

$$\mathbf{t}_1\boldsymbol{\nabla}\mathbf{vn} = (1,0,0) \begin{pmatrix} \partial_1 v_1 & \partial_1 v_2 & \partial_1 v_3 \\ \partial_2 v_1 & \partial_2 v_2 & \partial_2 v_3 \\ \partial_3 v_1 & \partial_3 v_2 & \partial_3 v_3 \end{pmatrix} \begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix} = \partial_1 v_3$$

$$\mathbf{t}_2\boldsymbol{\nabla}\mathbf{vn} = (0,1,0) \begin{pmatrix} \partial_1 v_1 & \partial_1 v_2 & \partial_1 v_3 \\ \partial_2 v_1 & \partial_2 v_2 & \partial_2 v_3 \\ \partial_3 v_1 & \partial_3 v_2 & \partial_3 v_3 \end{pmatrix} \begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix} = \partial_2 v_3$$

By collecting all results we end up with

$$P_0(\rho) + \rho V_0 + (2\eta - 2h_1)\mathbf{n}\cdot\boldsymbol{\nabla}\mathbf{v}\cdot\mathbf{n} + \left(\zeta - \frac{2}{3}\eta - h_2\right)\boldsymbol{\nabla}\cdot\mathbf{v} = 0$$

$$(\eta - h_1)\left[\mathbf{n}\cdot\boldsymbol{\nabla}\mathbf{v}\cdot\mathbf{t}_2 + \mathbf{t}_2\cdot\boldsymbol{\nabla}\mathbf{v}\cdot\mathbf{n}\right] - h_3\left[\mathbf{t}_1\cdot\boldsymbol{\nabla}\mathbf{v}\cdot\mathbf{n} + \mathbf{n}\cdot\boldsymbol{\nabla}\mathbf{v}\cdot\mathbf{t}_1\right] - \gamma_{||}\mathbf{t}_2\cdot(\mathbf{v} - \mathbf{V}) = 0$$

$$(\eta - h_1)\left[\mathbf{n}\cdot\boldsymbol{\nabla}\mathbf{v}\cdot\mathbf{t}_1 + \mathbf{t}_1\cdot\boldsymbol{\nabla}\mathbf{v}\cdot\mathbf{n}\right] + h_3\left[\mathbf{t}_2\cdot\boldsymbol{\nabla}\mathbf{v}\cdot\mathbf{n} + \mathbf{n}\cdot\boldsymbol{\nabla}\mathbf{v}\cdot\mathbf{t}_2\right] - \gamma_{||}\mathbf{t}_1\cdot(\mathbf{v} - \mathbf{V}) = 0$$

$$P_0(\rho) + \rho V_0 + (2\eta - 2h_1)\partial_3 v_3 = 0$$

$$(\eta - h_1)(\partial_3 v_2 + \partial_2 v_3) - h_3(\partial_1 v_3 + \partial_2 v_1) - \gamma_{||}(v_2 - V_2) = 0$$

$$(\eta - h_1)(\partial_3 v_1 + \partial_1 v_3) + h_3(\partial_2 v_3 + \partial_3 v_2) - \gamma_{||}(v_1 - V_1) = 0$$

Let us assume that the flow field is of the form $\mathbf{v} = (v_1^0, v_2^0 + \dot{\gamma}x_3, 0)$ and the wall is not moving $\mathbf{V} = 0$. In this case, the above conditions translate into conditions to be satisfied among the tangent velocity at the surface $\mathbf{v}^0 = (v_1^0, v_2^0, 0)$ and the shear rate $\dot{\gamma}$, this is

$$P_0(\rho) + \rho V_0 = 0$$

$$(\eta - h_1)\partial_3 v_2 - \gamma_{||}v_2^0 = 0$$

$$h_3\partial_3 v_2 - \gamma_{||}v_1^0 = 0$$

The first equation is a mechanical equilibrium condition that fixes the density. The second equation has the form of the usual Navier boundary condition relating shear rate

with slip velocity. The slip length is defined as $\dot\gamma = \frac{1}{\delta_\text{slip}}(v_0 - V_2)$ and, in our case

$$\delta_\text{slip} = \frac{\eta - h_1}{\gamma_{||}}$$

This simple equation allows to compute, from Green-Kubo expressions obtained in MD, the slip length. An equation similar to this one was first obtained by Bocquet and Barrat. Eq. (10.8.1) is slightly different from the original formula given by Bocquet and Barrat [?]. The main difference is the presence of the coefficient h_1. BB defined $z_\text{wall} = h_1/\gamma_{||}$. Therefore our result implies

$$z_\text{wall} + \delta_\text{slip} = \frac{\eta}{\gamma_{||}}$$

Alternatively, we may understand $\eta - h_1$ as a modified viscosity due to the interaction of the solid on the liquid.

The third equation in Eq. (10.8.1) is new and says that whenever h_3 is not negligible, there will be a component *perpendicular* to the main shear. Recall that h_3 defined in Eq. (10.5.2) involves the correlation of the fluid stress tensor with the force $\mathbf{F}^{s\to l}_\times$. This force is, on average, in a tangent direction to the surface, as shown in Eq. (10.5.2) that takes the form

$$\hat{\mathbf{F}}^{s\to l}_\times = \sum_i^N \hat{\mathbf{F}}^{s\to l}_i \times \frac{\mathbf{q}_i - \mathbf{R}}{|\mathbf{q}_i - \mathbf{R}|}$$

where $\hat{\mathbf{F}}_i$ is the total force that the solid exerts on the fluid particle i. Typically, this microscopic foce will be in the normal direction and, therefore, $\hat{\mathbf{F}}^{s\to l}_\times$ will be typically small. However, if the solid surface presents "grooves", this will produce tangential effects on the fluid particles. Of course, as we are considering the *total* force, due to the contribution of all fluid particles, we expect a large cancelation of this component, which should lead to a very small value for the transport coefficient h_3.

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10.8.2   Cylinder with flow perpendicular to the axis

The boundary conditions (10.7.-15) have been obtained for a sphere. However, being formulated in a local way, we believe that they can be applied to a cylinder as well. The cylinder axis is along x_1. The normal vector is of the form $\mathbf{n} = (0, c, s)$ where $c = \cos(\theta)$ and $s = \sin(\theta)$, the first tangential vector is $\mathbf{t}_1 = (1, 0, 0)$ and the second is $\mathbf{t}_2 = (0, s, -c)$. The velocity gradient tensor is

$$\begin{pmatrix} \partial_1 v_1 & \partial_1 v_2 & \partial_1 v_3 \\ \partial_2 v_1 & \partial_2 v_2 & \partial_2 v_3 \\ \partial_3 v_1 & \partial_3 v_2 & \partial_3 v_3 \end{pmatrix}$$
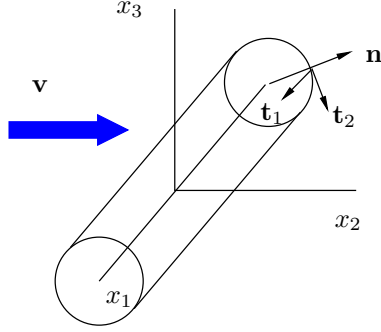
Figure 10.3: Infinite cylinder with a flow field of the form $\mathbf{v}(\mathbf{r}) = (0, v_2(x_2, x_3), v_3(x_2, x_3))$.

Therefore

$$
\mathbf{n}\boldsymbol{\nabla}\mathbf{v}\mathbf{n} = (0, c, s) \begin{pmatrix} \partial_1 v_1 & \partial_1 v_2 & \partial_1 v_3 \\ \partial_2 v_1 & \partial_2 v_2 & \partial_2 v_3 \\ \partial_3 v_1 & \partial_3 v_2 & \partial_3 v_3 \end{pmatrix} \begin{pmatrix} 0 \\ c \\ s \end{pmatrix}
$$

$$
= c^2 \partial_2 v_2 + cs \partial_2 v_3 + cs \partial_3 v_2 + s^2 \partial_3 v_3
$$

$$
\mathbf{n}\boldsymbol{\nabla}\mathbf{v}\mathbf{t}_1 = (0, c, s) \begin{pmatrix} \partial_1 v_1 & \partial_1 v_2 & \partial_1 v_3 \\ \partial_2 v_1 & \partial_2 v_2 & \partial_2 v_3 \\ \partial_3 v_1 & \partial_3 v_2 & \partial_3 v_3 \end{pmatrix} \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix}
$$

$$
= c \partial_2 v_1 + s \partial_3 v_1
$$

$$
\mathbf{n}\boldsymbol{\nabla}\mathbf{v}\mathbf{t}_2 = (0, c, s) \begin{pmatrix} \partial_1 v_1 & \partial_1 v_2 & \partial_1 v_3 \\ \partial_2 v_1 & \partial_2 v_2 & \partial_2 v_3 \\ \partial_3 v_1 & \partial_3 v_2 & \partial_3 v_3 \end{pmatrix} \begin{pmatrix} 0 \\ s \\ -c \end{pmatrix}
$$

$$
= cs \partial_2 v_2 - c^2 \partial_2 v_3 + s^2 \partial_3 v_2 - cs \partial_3 v_3
$$

$$
\mathbf{t}_1 \boldsymbol{\nabla}\mathbf{v}\mathbf{n} = (1, 0, 0) \begin{pmatrix} \partial_1 v_1 & \partial_1 v_2 & \partial_1 v_3 \\ \partial_2 v_1 & \partial_2 v_2 & \partial_2 v_3 \\ \partial_3 v_1 & \partial_3 v_2 & \partial_3 v_3 \end{pmatrix} \begin{pmatrix} 0 \\ c \\ s \end{pmatrix}
$$

$$
= c \partial_1 v_2 + s \partial_1 v_3
$$

$$
\mathbf{t}_2 \boldsymbol{\nabla}\mathbf{v}\mathbf{n} = (0, s, -c) \begin{pmatrix} \partial_1 v_1 & \partial_1 v_2 & \partial_1 v_3 \\ \partial_2 v_1 & \partial_2 v_2 & \partial_2 v_3 \\ \partial_3 v_1 & \partial_3 v_2 & \partial_3 v_3 \end{pmatrix} \begin{pmatrix} 0 \\ c \\ s \end{pmatrix}
$$

$$
= cs \partial_2 v_2 + s^2 \partial_2 v_3 - c^2 \partial_3 v_2 - cs \partial_3 v_3
$$

By collecting all results we end up with

$$P_0(\rho) + \rho V_0 + (2\eta - h_1 - h_2 - h_4)\mathbf{nn} : \boldsymbol{\nabla}\mathbf{v} + \left(\zeta - \frac{2}{3}\eta - h_1\right)\boldsymbol{\nabla}\cdot\mathbf{v} - h_3\mathbf{n}\cdot\boldsymbol{\nabla}\times\mathbf{v} = 0$$

$$P_0(\rho) + \rho V_0 + (2\eta - h_1 - h_2 - h_4)\left[c^2\partial_2 v_2 + cs\partial_2 v_3 + cs\partial_3 v_2 + s^2\partial_3 v_3\right] + \left(\zeta - \frac{2}{3}\eta - h_1\right)\boldsymbol{\nabla}\cdot\mathbf{v}$$
$$-h_3 c(\partial_3 v_1 - \partial_1 v_3) + s(\partial_1 v_2 - \partial_2 v_1) = 0$$

$$0 = \left[(\eta - h_1)\mathbf{nt}_1 + (\eta - h_2)\mathbf{t}_1\mathbf{n}\right] : \boldsymbol{\nabla}\mathbf{v} + h_3\mathbf{t}_2\mathbf{n} : \boldsymbol{\nabla}\mathbf{v} - \gamma_{||}\mathbf{t}_1\cdot(\mathbf{v} - \mathbf{V})$$
$$= (\eta - h_1)(c\partial_2 v_1 + s\partial_3 v_1) + (\eta - h_2)(c\partial_1 v_2 + s\partial_1 v_3)$$
$$+ h_3(cs\partial_2 v_2 + s^2\partial_2 v_3 - c^2\partial_3 v_2 - cs\partial_3 v_3) - \gamma_{||}\mathbf{t}_1\cdot(\mathbf{v} - \mathbf{V})$$

$$0 = \left[(\eta - h_1)\mathbf{nt}_2 + (\eta - h_2)\mathbf{t}_2\mathbf{n}\right] : \boldsymbol{\nabla}\mathbf{v} - h_3\mathbf{t}_1\mathbf{n} : \boldsymbol{\nabla}\mathbf{v} - \gamma_{||}\mathbf{t}_2\cdot(\mathbf{v} - \mathbf{V})$$
$$= (\eta - h_1)\left[cs\partial_2 v_2 - c^2\partial_2 v_3 + s^2\partial_3 v_2 - cs\partial_3 v_3\right]$$
$$+ (\eta - h_2)\left[cs\partial_2 v_2 + s^2\partial_2 v_3 - c^2\partial_3 v_2 - cs\partial_3 v_3\right] - h_3(c\partial_1 v_2 + s\partial_1 v_3) - \gamma_{||}\mathbf{t}_2\cdot(\mathbf{v} - \mathbf{V})$$
$$= (\eta - h_1)\left[cs\partial_2 v_2 - c^2\partial_2 v_3 + s^2\partial_3 v_2 - cs\partial_3 v_3\right] - \gamma_{||}\mathbf{t}_2\cdot(\mathbf{v} - \mathbf{V})$$

This is the general boundary conditions for the flow. If we now assume a flow field which is translationally invariant along the axis of the cylinder, this is $\mathbf{v}(\mathbf{r}) = (0, v_2(x_2, x_3), v_3(x_2, x_3))$, we will have

$$P_0(\rho) + \rho V_0 + (2\eta - h_1 - h_2 - h_4)\left[c^2\partial_2 v_2 + cs\partial_2 v_3 + cs\partial_3 v_2 + s^2\partial_3 v_3\right] + \left(\zeta - \frac{2}{3}\eta - h_1\right)\boldsymbol{\nabla}\cdot\mathbf{v} = 0$$
$$cs\partial_2 v_2 + s^2\partial_2 v_3 - c^2\partial_3 v_2 - cs\partial_3 v_3 = 0$$
$$(\eta - h_1)\left[\partial_3 v_2 - \partial_2 v_3\right] - \gamma_{||}\mathbf{t}_2\cdot(\mathbf{v} - \mathbf{V}) = 0$$

The second equation comes from the term proportional to the transport coefficient h_3. At the end, this boundary condition does not depend on h_3 anymore, but note that should $h_3 = 0$, we would not have this condition on the flow field. Therefore, this is a reflection of the effect of the forces that eventually produce h_3. The last equation is rather physical, it says that rotation of the flow field should be cancelled by the friction force. For example, if $\mathbf{v} = \frac{1}{2}\mathbf{r}\times\boldsymbol{\Omega}$, a rigid rotation with $\boldsymbol{\Omega} = \Omega\mathbf{t}_1$, then the rotational is ...

Note that because

$$\mathbf{v} = (0, v_2(x_2, x_3), v_3(x_2, x_3)$$
$$x_2 = a\cos\theta$$
$$x_3 = a\sin\theta$$

then

$$\frac{1}{a}\frac{\partial \mathbf{v}}{\partial \theta}\cdot \mathbf{n} = (0, -s\partial_2 v_2 + c\partial_3 v_2, -s\partial_2 v_3 + c\partial_3 v_3)\cdot(0, c, s) = -cs\partial_2 v_2 + c^2\partial_3 v_2 - s^2\partial_2 v_3 + cs\partial_3 v_3$$

10.8.3 Cylinder with flow paralell to the axis

The result is very much the same as for a planar wall. The shear conditions are

$$(\eta - h_1)(c\partial_2 v_1 + s\partial_3 v_1) - \gamma_{||}v_1 = 0$$

10.9   Other exotic models

We have considered the model in which all the fluid/solid interaction occurs at an idealized boundary on the solid surface. We explore in this section other possibilities that may be useful in a computational setting.

Reescribir

10.9.1   Point particle

We are now going to assume that the velocity field has space variations in a scale much larger than the size of the particle and any other molecular correlation. In that case, we may assume that the above kernels are local in space. This is, we will assume that

$$\boldsymbol{\eta_{rr'}} = \boldsymbol{\eta}\delta(\mathbf{r} - \mathbf{r}')$$
$$\boldsymbol{\gamma_{rr'}} = \boldsymbol{\gamma}\delta(\mathbf{r} - \mathbf{R})\delta(\mathbf{r}' - \mathbf{R})$$

In this way, the resulting final coupled equations are

$$\partial_t \rho_\mathbf{r} = -\boldsymbol{\nabla} \cdot \mathbf{g_r}$$
$$\partial_t \mathbf{g_r} = -\boldsymbol{\nabla}\mathbf{g_r}\mathbf{v_r} - \boldsymbol{\nabla}P_\mathbf{r} + \boldsymbol{\nabla}\boldsymbol{\nabla}\boldsymbol{\eta}\mathbf{v_r}$$
$$\qquad - \rho_\mathbf{r}\frac{\partial}{\partial\mathbf{r}}V^{\text{eff}}(\mathbf{r} - \mathbf{R}) - \boldsymbol{\gamma}\delta(\mathbf{r} - \mathbf{R})(\mathbf{v_r} - \mathbf{V})$$
$$\dot{\mathbf{R}} = \frac{\mathbf{P}}{M}$$
$$\dot{\mathbf{P}} = -\frac{\partial}{\partial\mathbf{R}}\int d\mathbf{r}\rho_\mathbf{r}V^{\text{eff}}(\mathbf{r} - \mathbf{R}) + \boldsymbol{\gamma}(\mathbf{v_R} - \mathbf{V})$$

In the same spirit of *point particle* approximation, we may assume that the effective potential is just a repulsive Dirac delta function, this is

$$V^{\text{eff}}(\mathbf{r} - \mathbf{R}) = \epsilon\delta(\mathbf{r} - \mathbf{R})$$

The resulting equations are then,

$$\partial_t \rho_\mathbf{r} = -\boldsymbol{\nabla} \cdot \mathbf{g_r}$$
$$\partial_t \mathbf{g_r} = -\boldsymbol{\nabla}\mathbf{g_r}\mathbf{v_r} - \boldsymbol{\nabla}P_\mathbf{r} + \boldsymbol{\nabla}\boldsymbol{\nabla}\boldsymbol{\eta}\mathbf{v_r}$$
$$\qquad - \rho_\mathbf{r}\epsilon\boldsymbol{\nabla}\delta(\mathbf{r} - \mathbf{R}) - \boldsymbol{\gamma}\delta(\mathbf{r} - \mathbf{R})(\mathbf{v_r} - \mathbf{V})$$
$$\dot{\mathbf{R}} = \frac{\mathbf{P}}{M}$$
$$\dot{\mathbf{P}} = -\epsilon\boldsymbol{\nabla}\rho_\mathbf{r} + \boldsymbol{\gamma}(\mathbf{v_R} - \mathbf{V})$$

In words, the liquid feels the presence of the particle through a highly peaked potential localized on top of the particle, and also through a friction force density where the particle happens to be. The particle, in turn, feels the reaction force of the fluid, which takes the form of a term proportional to the density gradients, and a friction proportional to the relative velocity with the surrounding fluid ($\mathbf{v_R}$ is the velocity field at the point where

the particle sits).

10.9.2   The blob particle

In this section we consider a model which is not very realistic but that will provide a useful example. We assume that at the microscopic level the system is made of N fluid molecules and one single point solid sphere particle that interacts with the fluid molecules with a potential of interaction whose range of interaction is much larger than the typical separation between solvent molecules, which is also of the order of the range of interaction between solvent molecules.

In this particular case, we can safely make the following approximations. The effective potential is given by the direct potential of interaction between the point solid sphere and the solvent molecules. The force density in Eq. (10.1) will take the simple form

$$\mathbf{F_r}(z) = n_\mathbf{r}(z)\mathbf{F}(\mathbf{r} - \mathbf{R})$$

The equations (10.6.1) take identical form except that the effective potential is replaced by the direct potential of interaction between the point solid sphere and a molecule of the solvent. Because the force (10.9.2) is a function of the microstate through a CG variable $n_\mathbf{r}(z)$, this implies that its projected part simply vanishes, i.e. $\delta\mathbf{F_r}(z) = \mathbf{F_r}(z) - \langle\mathbf{F_r}\rangle^{\rho,\mathbf{q},\mathbf{R},\mathbf{P}} = 0$. As a consequence, all transport coefficients, except those involving the stress-stress correlation will vanish. As a result, the motion of the point solid sphere particle is purely reversible, and the only irreversibility appears through the viscosity of the solvent. In this example where the solid sphere is structureless, the solid sphere particle is just a *reversible ghost*.

10.10   Questions

- **How to deduce the impenetrability condition (10.7) from the dynamic equations (10.6.1)** **understood.**

- **What happens to the non-local viscosity near the wall?** **understood, we neglect this effect**

- **How to infer what boundary conditions correspond to the obtained force terms in the dynamic equations? This is, what boundary conditions would reproduce the dynamics if we neglect the boundary terms in the equations of motion?** **OK! understood**

- **What happens with thermal fluctuations? Is it reasonable to use free energy functionals that give structured fluids (and therefore, probe molecular length scales) and not to include the diffusive motion of the Brownian particle?** **OK! understood, needs to be completed.**

- **Introduce the wall viscosity tensor**

10.11   Conclusion

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The present hydrodynamic theory expressed in Eq. (18.8) differs, however, from the "usual" Navier-Stokes equations in that now the full structure of the fluid is retained. These equations (18.8) have been previously obtained in Ref. [?] as a local equilibrium approximation of a more general kinetic Boltzmann density functional approach. It is re-assuring that the same hydrodynamic equations are obtained. The present theory reduces to the (isothermal) Navier-Stokes theory, when we approximate the density functional $\Omega[n]$ with a local functional of the form

$$\Omega[n] = \int d\mathbf{r}\, f(n(\mathbf{r}, t))$$

where $f(n)$ is the equilibrium free energy density, and uses the isotropic local version (5.7) for the friction matrix. As discussed in Ref. [?], the use of a local functional like (10.11) is justified when the scale of variation of the density field is large compared to molecular scales. The hydrodynamic equations (18.8) generalize Navier-Stokes equations to situations when the hydrodynamic fields vary on molecular scales, due to the presence of, for example, confinement or liquid-vapor phase transitions.

10.12   Appendix: Forces

In this appendix we summarize the different forces and force densities that appear in the system, and present some results concerning its averages with the relevant ensemble. The force densities that the fluid or de solid exert on a fluid molecule located at the point $\mathbf{r}$ are introduced in (10.1),

$$\hat{\mathbf{F}}_\mathbf{r}^{l \to l}(z) \equiv \sum_{ij}^{NN} \hat{\mathbf{F}}_{ij} \delta(\mathbf{r} - \mathbf{q}_i)$$

$$\hat{\mathbf{F}}_\mathbf{r}^{s \to l}(z) \equiv \sum_{ij'}^{NN'} \hat{\mathbf{F}}_{ij'} \delta(\mathbf{r} - \mathbf{q}_i)$$

where $\hat{\mathbf{F}}_{ij'}$ is the force that atom j' of the molecule exerts on atom i of the liquid. This is $\hat{\mathbf{F}}_\mathbf{r}^{l \to l}(z)$ is the force density that the liquid exerts on the liquid molecules that are around the point $\mathbf{r}$ and that force density $\hat{\mathbf{F}}_\mathbf{r}^{s \to l}(z)$ that the object exerts on the liquid at the point $\mathbf{r}$.

The total force density on the fluid is

$$\hat{\mathbf{F}}_\mathbf{r}^l = \hat{\mathbf{F}}_\mathbf{r}^{l \to l} + \hat{\mathbf{F}}_\mathbf{r}^{s \to l} = \sum_j^N -\frac{\partial U}{\partial \mathbf{r}_j} \delta(\mathbf{r} - \mathbf{q}_j)$$

The total force on the fluid and on the solid are

$$\hat{\mathbf{F}}^l = \int d\mathbf{r} \hat{\mathbf{F}}_{\mathbf{r}}^l$$

$$\hat{\mathbf{F}}^s = -\hat{\mathbf{F}}^l$$

where we have used that the total force

$$\hat{\mathbf{F}} = -\sum_i^N \frac{\partial U}{\partial \mathbf{q}_i} - \sum_{i'}^{N'} \frac{\partial U}{\partial \mathbf{r}_{i'}} = \hat{\mathbf{F}}^l + \hat{\mathbf{F}}^s$$

vanishes because the potentials are translational invariant (and therefore, Newton's third law holds).

Note that we have the result

$$\hat{\mathbf{F}}^s = -\int d\mathbf{r} \hat{\mathbf{F}}_{\mathbf{r}}^{\mathrm{s}\to\mathrm{l}}$$

Now, let us consider the average of the total force density on the liquid, Eq. (10.1)

$$\mathbf{F}_{\mathbf{r}}^l \equiv \mathrm{Tr}[\bar{\rho}_t \hat{\mathbf{F}}_{\mathbf{r}}^l] = \langle \hat{\mathbf{F}}_{\mathbf{r}}^l \rangle^{\mu, \boldsymbol{\lambda}_R}$$

$$= \frac{1}{\Xi[\mu, \boldsymbol{\lambda}_R]} \sum_{N=0}^{\infty} \frac{1}{N!} \int \frac{dq}{\Lambda^{3N}} \frac{dq'}{\Lambda^{3N'}} \left[\sum_j^N -\frac{\partial U}{\partial \mathbf{r}_j} \delta(\mathbf{r} - \mathbf{q}_j) \right] e^{-\beta U} \exp\left\{ -\beta \left(\boldsymbol{\lambda}_R \hat{\mathbf{R}} - \sum_{i=1}^N m\mu(\mathbf{q}_i) \right) \right\}$$

$$= \frac{1}{\Xi[\mu, \boldsymbol{\lambda}_R]} \sum_{N=0}^{\infty} \frac{1}{N!} \int \frac{dq}{\Lambda^{3N}} \frac{dq'}{\Lambda^{3N'}} \exp\left\{ -\beta \left(\boldsymbol{\lambda}_R \hat{\mathbf{R}} - \sum_{i=1}^N m\mu(\mathbf{q}_i) \right) \right\} k_B T \sum_j^N \delta(\mathbf{r} - \mathbf{q}_j) \frac{\partial}{\partial \mathbf{r}_j} e^{-\beta U}$$

$$= \frac{1}{\Xi[\mu, \boldsymbol{\lambda}_R]} \sum_{N=0}^{\infty} \frac{1}{N!} \int \frac{dq}{\Lambda^{3N}} \frac{dq'}{\Lambda^{3N'}} e^{-\beta U} k_B T \sum_j^N -\frac{\partial}{\partial \mathbf{r}_j} \left[\delta(\mathbf{r} - \mathbf{q}_j) \exp\left\{ -\beta \left(\boldsymbol{\lambda}_R \hat{\mathbf{R}} - \sum_{i=1}^N m\mu(\mathbf{q}_i) \right) \right\} \right]$$

$$= \frac{1}{\Xi[\mu, \boldsymbol{\lambda}_R]} \sum_{N=0}^{\infty} \frac{1}{N!} \int \frac{dq}{\Lambda^{3N}} \frac{dq'}{\Lambda^{3N'}} e^{-\beta U} \sum_j^N \exp\left\{ -\beta \left(\boldsymbol{\lambda}_R \hat{\mathbf{R}} - \sum_{i\neq j}^N m\mu(\mathbf{q}_j) \right) \right\}$$

$$\times k_B T \left[-\frac{\partial}{\partial \mathbf{r}_j} \delta(\mathbf{r} - \mathbf{q}_j) \exp\left\{ \beta m\mu(\mathbf{q}_j) \right\} \right]$$

$$= \frac{k_B T}{m} \boldsymbol{\nabla} \rho(\mathbf{r}) - \rho(\mathbf{r}) \boldsymbol{\nabla} \mu(\mathbf{r})$$

We may compute the average of the total force on the solid $\mathbf{F}^s$ and obtain

$$\mathbf{F}^s = \mathrm{Tr}[\overline{\rho}_t \hat{\mathbf{F}}^s] = \langle \hat{\mathbf{F}}^s \rangle^{\mu, \boldsymbol{\lambda}_R}$$

$$= \frac{1}{\Xi[\mu, \boldsymbol{\lambda}_R]} \sum_{N=0}^{\infty} \frac{1}{N!} \int \frac{dq}{\Lambda^{3N}} \frac{dq'}{\Lambda^{3N'}} \left[-\sum_{i'}^{N'} \frac{\partial U}{\partial \mathbf{r}_{i'}} \right] e^{-\beta U} \exp\left\{ -\beta \left(\sum_{i=1}^{N} m\mu(\mathbf{q}_i) + \boldsymbol{\lambda}_R \hat{\mathbf{R}} \right) \right\}$$

$$= \frac{1}{\Xi[\mu, \boldsymbol{\lambda}_R]} \sum_{N=0}^{\infty} \frac{1}{N!} \int \frac{dq}{\Lambda^{3N}} \frac{dq'}{\Lambda^{3N'}} \exp\left\{ -\beta \left(\sum_{i=1}^{N} m\mu(\mathbf{q}_i) + \boldsymbol{\lambda}_R \hat{\mathbf{R}} \right) \right\} k_B T \left[\sum_{i'}^{N'} \frac{\partial}{\partial \mathbf{r}_{i'}} \right] e^{-\beta U}$$

$$= \frac{1}{\Xi[\mu, \boldsymbol{\lambda}_R]} \sum_{N=0}^{\infty} \frac{1}{N!} \int \frac{dq}{\Lambda^{3N}} \frac{dq'}{\Lambda^{3N'}} e^{-\beta U} k_B T \left[-\sum_{i'}^{N'} \frac{\partial}{\partial \mathbf{r}_{i'}} \right] \exp\left\{ -\beta \left(\sum_{i=1}^{N} m\mu(\mathbf{q}_i) + \boldsymbol{\lambda}_R \hat{\mathbf{R}} \right) \right\}$$

$$= \frac{1}{\Xi[\mu, \boldsymbol{\lambda}_R]} \sum_{N=0}^{\infty} \frac{1}{N!} \int \frac{dq}{\Lambda^{3N}} \frac{dq'}{\Lambda^{3N'}} e^{-\beta U} \exp\left\{ -\beta \left(\sum_{i=1}^{N} m\mu(\mathbf{q}_i) + \boldsymbol{\lambda}_R \hat{\mathbf{R}} \right) \right\} \left[\sum_{i'}^{N'} \frac{\partial}{\partial \mathbf{r}_{i'}} \right] \boldsymbol{\lambda}_R \hat{\mathbf{R}}$$

$$= \boldsymbol{\lambda}_R$$

This allows to interprete physically the Lagrange multiplier $\boldsymbol{\lambda}_R$. By using (10) we obtain that the total force on the solid sphere is due to the gradient of the free energy functional

$$\mathbf{F}^s = -\frac{\partial F}{\partial \mathbf{R}}[\rho, \mathbf{R}]$$

10.13 Appendix: Invariant tensors under a rotation around a fixed axis

In this appendix we review what tensors of second, third and fourth order are invariant under a rotation $\mathscr{R}$ around a given axis $\mathbf{n}$. We know that the Kroenecker tensor $\boldsymbol{\delta}$ with components given by the Kroenecker symbol $\boldsymbol{\delta}_{\alpha\beta}$ and the permutation tensor $\boldsymbol{\epsilon}^n$ with components given by the Levi-Civita symbol $\underbrace{\boldsymbol{\epsilon}_{\alpha\cdots\gamma}}_{n}$ (of order n) are invariant under an arbitrary rotation. If $\mathscr{R}_{\alpha\alpha'}$ is the orthogonal matrix that represent the rotation around a fixed axis, we have

$$\mathscr{R}_{\alpha\alpha'}\mathbf{n}_{\alpha'} = \mathbf{n}_{\alpha}$$
$$\mathscr{R}_{\alpha\alpha'}\mathscr{R}_{\beta\beta'}\boldsymbol{\delta}_{\alpha'\beta'} = \boldsymbol{\delta}_{\alpha\beta}$$
$$\mathscr{R}_{\alpha\alpha'}\mathscr{R}_{\beta\beta'}\mathscr{R}_{\gamma\gamma'}\boldsymbol{\epsilon}_{\alpha'\beta'\gamma'} = \boldsymbol{\epsilon}_{\alpha\beta\gamma}$$
$$\vdots$$

Here, the first order tensor $\mathbf{n}$ (with components $\mathbf{n}_{\alpha}$) is the unit vector determining the axis of rotation of the rotation matrix $\mathscr{R}$, which is obviously left invariant under a rotation. Of course, any contraction of $\mathbf{n}, \boldsymbol{\delta}, \boldsymbol{\epsilon}^n$ will produce a tensor that is also invariant under the rotation $\mathscr{R}$. The only non-trivial contractions are the order m tensors $\mathbf{n}^{(m)}$ with components $n^{(m)}_{\alpha\cdots\beta} = \epsilon^{(m+1)}_{\alpha\cdots\beta\gamma}\mathbf{n}_{\gamma}$.

10.13.1 Second order tensors

In order to construct the most general *second* order tensor that is invariant around arbitrary rotations around a fixed axis $\mathbf{n}$ we have to construct all possible tensorial products of the following tensors (in increasing tensorial order) (1) $\mathbf{n}_{\alpha}$, (2) $\boldsymbol{\delta}_{\alpha\beta}$, $\mathbf{n}^{(2)}_{\alpha\beta}$ and (3) $\boldsymbol{\epsilon}_{\alpha\beta\gamma}$. The possible combinations that form a second order tensor are (in increasing order of the number of times the vector $\mathbf{n}$ appears)

$$\boldsymbol{\delta}_{\alpha\beta} \qquad\qquad\qquad (0n)$$
$$\mathbf{n}^{(2)}_{\alpha\beta} \qquad\qquad\qquad (1n)$$
$$\mathbf{n}_{\alpha}\mathbf{n}_{\beta} \qquad\qquad\qquad (2n)$$

In this way, the most general second order tensor which is invariant under rotation around the axis $\mathbf{n}$ is of the form

$$\mathbf{T} = t_1\boldsymbol{\delta} + t_2\mathbf{n}\mathbf{n} + t_3\mathbf{n}^{(2)}$$

where t_1, t_2, t_3 are arbitrary coefficients. Instead of the 9 independent components of a general second order tensor, the invariant tensor has only three independent components. If the tensor is fully isotropic, it means that it cannot depend on the actual axis $\mathbf{n}$, and this implies $t_2 = t_3 = 0$. If the tensor is symmetric, then we need to have $t_2 = 0$.

The coefficients t_1, t_2, t_3 can be obtained by fully contracting (10.13.1) with the tensors

(10.13.1), this is

$$\text{Tr}[\mathbf{T}\boldsymbol{\delta}] = T_{\alpha\beta}\boldsymbol{\delta}_{\alpha\beta} = 3t_1 + t_2$$
$$\text{Tr}[\mathbf{Tnn}] = T_{\alpha\beta}n_\alpha\mathbf{n}_\beta = t_1 + t_2$$
$$\text{Tr}[\mathbf{Tn}^{(2)}] = T_{\alpha\beta}\mathbf{n}^{(2)}_{\alpha\beta} = 2t_3$$

with solution

$$t_1 = \frac{1}{2}\left[\text{Tr}[\mathbf{T}\boldsymbol{\delta}] - \text{Tr}[\mathbf{Tnn}]\right]$$

$$t_2 = \frac{1}{2}\left[3\text{Tr}[\mathbf{Tnn}] - \text{Tr}[\mathbf{T}\boldsymbol{\delta}]\right]$$

$$t_3 = \frac{1}{2}\text{Tr}[\mathbf{Tn}^{(2)}]$$

Therefore, we may write the tensor $\mathbf{T}$ in the form

$$\begin{aligned}
\mathbf{T} &= \frac{1}{2}\left[\text{Tr}[\mathbf{T}\boldsymbol{\delta}] - \text{Tr}[\mathbf{Tnn}]\right]\boldsymbol{\delta} + \frac{1}{2}\left[3\text{Tr}[\mathbf{Tnn}] - \text{Tr}[\mathbf{T}\boldsymbol{\delta}]\right]\mathbf{nn} \\
&+ \frac{1}{2}\text{Tr}[\mathbf{Tn}^{(2)}]\mathbf{n}^{(2)} \\
&= \frac{1}{2}\text{Tr}[\mathbf{T}\boldsymbol{\delta}](\boldsymbol{\delta} - \mathbf{nn}) + \frac{1}{2}\text{Tr}[\mathbf{Tnn}](3\mathbf{nn} - \boldsymbol{\delta}) + \frac{1}{2}\text{Tr}[\mathbf{Tn}^{(2)}]\mathbf{n}^{(2)}
\end{aligned}$$

10.13.2   Third order tensors

In order to construct the most general third order tensor that is invariant around arbitrary rotations around a fixed axis $\mathbf{n}$ we have to construct all possible tensorial products of the following tensors (in increasing tensorial order) (1) $\mathbf{n}_\alpha$, (2) $\boldsymbol{\delta}_{\alpha\beta}$, $\mathbf{n}^{(2)}_{\alpha\beta}$ and (3) $\boldsymbol{\epsilon}_{\alpha\beta\gamma}$. The possible tensor product combinations that form a third order tensor are (in increasing order of the number of times the vector $\mathbf{n}$ appears)

$$\boldsymbol{\epsilon}_{\alpha\beta\gamma} \qquad\qquad\qquad\qquad\qquad\qquad (0n)$$
$$\boldsymbol{\delta}_{\alpha\beta}\mathbf{n}_\gamma \quad \boldsymbol{\delta}_{\alpha\gamma}\mathbf{n}_\beta \quad \boldsymbol{\delta}_{\beta\gamma}\mathbf{n}_\alpha \qquad\qquad (1n)$$
$$n^{(3)}_{\alpha\beta\gamma} \qquad\qquad\qquad\qquad\qquad\qquad (1n)$$
$$\mathbf{n}^{(2)}_{\alpha\beta}\mathbf{n}_\gamma \quad \mathbf{n}^{(2)}_{\alpha\gamma}\mathbf{n}_\beta \quad \mathbf{n}^{(2)}_{\beta\gamma}\mathbf{n}_\alpha \qquad (2n)$$
$$\mathbf{n}_\alpha\mathbf{n}_\beta\mathbf{n}_\gamma \qquad\qquad\qquad\qquad\qquad (3n)$$

Any linear combination of the above tensors will produce a third order tensor that is invariant under rotation around a fixed axis. In this way, such a tensor, instead of having 27 independent components, has only 9. All tensors above, except $\boldsymbol{\epsilon}^{(3)}$ depend on $\mathbf{n}$. For this reason, the only third order tensor that is invariant under an *arbitrary* rotation is $\boldsymbol{\epsilon}^{(3)}$, which is fully antisymmetric. There is no isotropic symmetric third order tensor.

Now consider a third order tensor $\mathbf{H}$ that is symmetric with respect its last two indices i.e. $\mathbf{H}_{\alpha\beta\gamma} = \mathbf{H}_{\alpha\gamma\beta}$. If this tensor is invariant with respect to rotations around $\mathbf{n}$, it should have the following form

$$\mathbf{H}_{\alpha\beta\gamma} = h_1(\boldsymbol{\delta}_{\alpha\beta}\mathbf{n}_\gamma + \boldsymbol{\delta}_{\alpha\gamma}\mathbf{n}_\beta) + h_2\mathbf{n}_\alpha\boldsymbol{\delta}_{\beta\gamma}$$
$$+ h_3(\mathbf{n}^{(2)}_{\alpha\beta}\mathbf{n}_\gamma + \mathbf{n}^{(2)}_{\alpha\gamma}\mathbf{n}_\beta) + h_4\mathbf{n}_\alpha\mathbf{n}_\beta\mathbf{n}_\gamma$$

The coeficients h_1, h_2, h_3, h_4 can be obtained from the traces of the full contractions of the third order tensor $\mathbf{H}$ with the tensors in (10.13.2). We have

$$\begin{aligned}
\mathrm{Tr}[\mathbf{n}\boldsymbol{\delta}\mathbf{H}] = \mathbf{n}_\alpha\boldsymbol{\delta}_{\beta\gamma}\mathbf{H}_{\alpha\beta\gamma} &= 2h_1 + 3h_2 + h_4 \\
\mathrm{Tr}[\boldsymbol{\delta}\mathbf{n}\mathbf{H}] = \boldsymbol{\delta}_{\alpha\beta}\mathbf{n}_\gamma\mathbf{H}_{\alpha\beta\gamma} &= 4h_1 + h_2 + h_4 \\
\mathrm{Tr}[\mathbf{n}\mathbf{n}\mathbf{n}\mathbf{H}] = \mathbf{n}_\alpha\mathbf{n}_\beta\mathbf{n}_\gamma\mathbf{H}_{\alpha\beta\gamma} &= 2h_1 + h_2 + h_4 \\
\mathrm{Tr}[\mathbf{n}^{(2)}\mathbf{n}\mathbf{H}] = \mathbf{n}^{(2)}_{\alpha\beta}\mathbf{n}_\gamma\mathbf{H}_{\alpha\beta\gamma} &= 2h_3
\end{aligned}$$

where in the last identity we have used the well-known property $\boldsymbol{\epsilon}_{\alpha\beta\mu}\boldsymbol{\epsilon}_{\alpha\beta\mu'} = 2\boldsymbol{\delta}_{\mu\mu'}$. We may solve for the coefficients, with the result

$$\frac{1}{2}\begin{pmatrix} 0 & 1 & -1 \\ 1 & 0 & -1 \\ -1 & -2 & 5 \end{pmatrix}$$

$$h_1 = \frac{1}{2}\left[\mathrm{Tr}[\boldsymbol{\delta}\mathbf{n}\mathbf{H}] - \mathrm{Tr}[\mathbf{n}\mathbf{n}\mathbf{n}\mathbf{H}]\right]$$

$$h_2 = \frac{1}{2}\left[\mathrm{Tr}[\mathbf{n}\boldsymbol{\delta}\mathbf{H}] - \mathrm{Tr}[\mathbf{n}\mathbf{n}\mathbf{n}\mathbf{H}]\right]$$

$$h_4 = \frac{1}{2}\left[5\mathrm{Tr}[\mathbf{n}\mathbf{n}\mathbf{n}\mathbf{H}] - 2\mathrm{Tr}[\boldsymbol{\delta}\mathbf{n}\mathbf{H}] - \mathrm{Tr}[\mathbf{n}\boldsymbol{\delta}\mathbf{H}]\right]$$

$$h_3 = \frac{1}{2}\mathrm{Tr}[\mathbf{n}^{(2)}\mathbf{n}\mathbf{H}]$$

Therefore, we may write

$$\mathbf{H}_{\alpha\beta\gamma} = \frac{1}{2}\left[\mathrm{Tr}[\boldsymbol{\delta}\mathbf{n}\mathbf{H}] - \mathrm{Tr}[\mathbf{n}\mathbf{n}\mathbf{n}\mathbf{H}]\right](\boldsymbol{\delta}_{\alpha\beta}\mathbf{n}_\gamma + \boldsymbol{\delta}_{\alpha\gamma}\mathbf{n}_\beta)$$

$$+ \frac{1}{2}\left[\mathrm{Tr}[\mathbf{n}\boldsymbol{\delta}\mathbf{H}] - \mathrm{Tr}[\mathbf{n}\mathbf{n}\mathbf{n}\mathbf{H}]\right]\mathbf{n}_\alpha\boldsymbol{\delta}_{\beta\gamma}$$

$$+ \frac{1}{2}\mathrm{Tr}[\mathbf{n}^{(2)}\mathbf{n}\mathbf{H}](\mathbf{n}^{(2)}_{\alpha\beta}\mathbf{n}_\gamma + \mathbf{n}^{(2)}_{\alpha\gamma}\mathbf{n}_\beta)$$

$$+ \frac{1}{2}\left[5\mathrm{Tr}[\mathbf{n}\mathbf{n}\mathbf{n}\mathbf{H}] - 2\mathrm{Tr}[\boldsymbol{\delta}\mathbf{n}\mathbf{H}] - \mathrm{Tr}[\mathbf{n}\boldsymbol{\delta}\mathbf{H}]\right]\mathbf{n}_\alpha\mathbf{n}_\beta\mathbf{n}_\gamma$$

Similarly, a third order tensor $\mathbf{G}$ that is symmetric with respect its first two indices i.e. $\mathbf{G}_{\alpha\beta\gamma} = \mathbf{G}_{\beta\alpha\gamma}$. If this tensor is invariant with respect to rotations around $\mathbf{n}$, it should have the following form

$$\mathbf{G}_{\alpha\beta\gamma} = g_1(\mathbf{n}_\alpha\boldsymbol{\delta}_{\beta\gamma} + \mathbf{n}_\beta\boldsymbol{\delta}_{\alpha\gamma}) + g_2\boldsymbol{\delta}_{\alpha\beta}\mathbf{n}_\gamma$$
$$+ g_3(\mathbf{n}_\alpha\mathbf{n}^{(2)}_{\beta\gamma} + \mathbf{n}_\beta\mathbf{n}^{(2)}_{\alpha\gamma}) + g_4\mathbf{n}_\alpha\mathbf{n}_\beta\mathbf{n}_\gamma$$

We may now construct the following traces

$$\begin{aligned}
\mathrm{Tr}[\mathbf{n}\boldsymbol{\delta}\mathbf{G}] = \mathbf{n}_\alpha\boldsymbol{\delta}_{\beta\gamma}\mathbf{G}_{\alpha\beta\gamma} && = 4g_1 + g_2 + g_4 \\
\mathrm{Tr}[\boldsymbol{\delta}\mathbf{n}\mathbf{G}] = \boldsymbol{\delta}_{\alpha\beta}\mathbf{n}_\gamma\mathbf{G}_{\alpha\beta\gamma} && = 2g_1 + 3g_2 + g_4 \\
\mathrm{Tr}[\mathbf{n}\mathbf{n}\mathbf{n}\mathbf{G}] = \mathbf{n}_\alpha\mathbf{n}_\beta\mathbf{n}_\gamma\mathbf{G}_{\alpha\beta\gamma} && = 2g_1 + g_2 + g_4 \\
\mathrm{Tr}[\mathbf{n}^{(2)}\mathbf{n}\mathbf{G}] = \mathbf{n}^{(2)}_{\alpha\gamma}\mathbf{n}_\beta\mathbf{G}_{\alpha\beta\gamma} && = 2g_3
\end{aligned}$$

The solution is

$$\frac{1}{2}\begin{pmatrix} 1 & 0 & -1 \\ 0 & 1 & -1 \\ -2 & -1 & 5 \end{pmatrix}$$

this is

$$g_1 = \frac{1}{2}\left[\mathrm{Tr}[\mathbf{n}\boldsymbol{\delta}\mathbf{G}] - \mathrm{Tr}[\mathbf{n}\mathbf{n}\mathbf{n}\mathbf{G}]\right]$$

$$g_2 = \frac{1}{2}\left[\mathrm{Tr}[\boldsymbol{\delta}\mathbf{n}\mathbf{G}] - \mathrm{Tr}[\mathbf{n}\mathbf{n}\mathbf{n}\mathbf{G}]\right]$$

$$g_4 = \frac{1}{2}\left[5\mathrm{Tr}[\mathbf{n}\mathbf{n}\mathbf{n}\mathbf{G}] - 2\mathrm{Tr}[\mathbf{n}\boldsymbol{\delta}\mathbf{G}] - \mathrm{Tr}[\boldsymbol{\delta}\mathbf{n}\mathbf{G}]\right]$$

$$g_3 = \frac{1}{2}\mathrm{Tr}[\mathbf{n}^{(2)}\mathbf{n}\mathbf{G}]$$

Therefore, we may write

$$\mathbf{G}_{\alpha\beta\gamma} = \frac{1}{2}\left[\mathrm{Tr}[\mathbf{n}\boldsymbol{\delta}\mathbf{G}] - \mathrm{Tr}[\mathbf{n}\mathbf{n}\mathbf{n}\mathbf{G}]\right](\mathbf{n}_\alpha\boldsymbol{\delta}_{\beta\gamma} + \mathbf{n}_\beta\boldsymbol{\delta}_{\alpha\gamma})$$
$$+ \frac{1}{2}\left[\mathrm{Tr}[\boldsymbol{\delta}\mathbf{n}\mathbf{G}] - \mathrm{Tr}[\mathbf{n}\mathbf{n}\mathbf{n}\mathbf{G}]\right]\boldsymbol{\delta}_{\alpha\beta}\mathbf{n}_\gamma$$
$$+ \frac{1}{2}\mathrm{Tr}[\mathbf{n}\mathbf{n}^{(2)}\mathbf{G}](\mathbf{n}_\alpha\mathbf{n}^{(2)}_{\beta\gamma} + \mathbf{n}_\beta\mathbf{n}^{(2)}_{\alpha\gamma})$$
$$+ \frac{1}{2}\left[5\mathrm{Tr}[\mathbf{n}\mathbf{n}\mathbf{n}\mathbf{G}] - 2\mathrm{Tr}[\mathbf{n}\boldsymbol{\delta}\mathbf{G}] - \mathrm{Tr}[\boldsymbol{\delta}\mathbf{n}\mathbf{G}]\right]\mathbf{n}_\alpha\mathbf{n}_\beta\mathbf{n}_\gamma$$

10.13.3 Fourth order tensors

The fourth order tensor which is invariant under rotations around a given vector $\mathbf{n}$ are linear combinations of the tensor products of $\mathbf{n}_\alpha, \boldsymbol{\delta}_{\alpha\beta}, \boldsymbol{\epsilon}_{\alpha\beta\gamma}, \boldsymbol{\epsilon}_{\alpha\beta\gamma\delta}$ and of any non-trivial tensor product of them, like $\hat{\mathbf{n}}^{(2)}_{\alpha\beta} = \boldsymbol{\epsilon}_{\alpha\beta\gamma}\mathbf{n}_\gamma$, and $\hat{\mathbf{n}}^{(3)}_{\alpha\beta\gamma} = \boldsymbol{\epsilon}_{\alpha\beta\gamma\delta}\mathbf{n}_\delta$.

Out of these tensors of different orders we may construct throught tensor products the following fourth order tensors (listed in order of decreasing number of times the vector $\mathbf{n}$ appears in it)

$$\mathbf{n}_\alpha\mathbf{n}_\beta\mathbf{n}_\gamma\mathbf{n}_\delta \tag{4n}$$

$$\mathbf{n}_\alpha\mathbf{n}_\beta\boldsymbol{\delta}_{\gamma\delta} \quad \mathbf{n}_\alpha\mathbf{n}_\gamma\boldsymbol{\delta}_{\beta\delta} \quad \mathbf{n}_\alpha\mathbf{n}_\delta\boldsymbol{\delta}_{\beta\gamma} \quad \mathbf{n}_\beta\mathbf{n}_\gamma\boldsymbol{\delta}_{\alpha\delta} \quad \mathbf{n}_\beta\mathbf{n}_\delta\boldsymbol{\delta}_{\alpha\gamma} \quad \mathbf{n}_\gamma\mathbf{n}_\delta\boldsymbol{\delta}_{\alpha\beta} \tag{2n}$$

$$\boldsymbol{\epsilon}_{\alpha\beta\gamma}\mathbf{n}_\delta \quad \boldsymbol{\epsilon}_{\beta\gamma\delta}\mathbf{n}_\alpha \quad \boldsymbol{\epsilon}_{\gamma\delta\alpha}\mathbf{n}_\beta \quad \boldsymbol{\epsilon}_{\delta\alpha\beta}\mathbf{n}_\gamma \tag{1n}$$

$$\mathbf{n}^{(2)}_{\alpha\beta}\boldsymbol{\delta}_{\gamma\delta} \quad \mathbf{n}^{(2)}_{\alpha\gamma}\boldsymbol{\delta}_{\beta\delta} \quad \mathbf{n}^{(2)}_{\alpha\delta}\boldsymbol{\delta}_{\beta\gamma} \quad \mathbf{n}^{(2)}_{\beta\gamma}\boldsymbol{\delta}_{\alpha\delta} \quad \mathbf{n}^{(2)}_{\beta\delta}\boldsymbol{\delta}_{\alpha\gamma} \quad \mathbf{n}^{(2)}_{\gamma\delta}\boldsymbol{\delta}_{\alpha\beta} \tag{1n}$$

$$\mathbf{n}^{(2)}_{\alpha\beta\gamma}\mathbf{n}_\delta \quad \mathbf{n}^{(2)}_{\beta\gamma\delta}\mathbf{n}_\alpha \quad \mathbf{n}^{(2)}_{\gamma\delta\alpha}\mathbf{n}_\beta \tag{1n}$$

$$\boldsymbol{\delta}_{\alpha\beta}\boldsymbol{\delta}_{\gamma\delta} \quad \boldsymbol{\delta}_{\alpha\gamma}\boldsymbol{\delta}_{\beta\delta} \quad \boldsymbol{\delta}_{\alpha\delta}\boldsymbol{\delta}_{\beta\gamma} \tag{0n}$$

Now, with this tensors we need to construct the most general fourth order tensor that is symmetric with respect its first two indices and symmetric with respect its last two indices. The only allowed linear combinations of the tensors that give this property is

$$s_1\mathbf{n}_\alpha\mathbf{n}_\beta\mathbf{n}_\gamma\mathbf{n}_\delta + s_2\mathbf{n}_\alpha\mathbf{n}_\beta\boldsymbol{\delta}_{\gamma\delta} + s_2\boldsymbol{\delta}_{\alpha\beta}\mathbf{n}_\gamma\mathbf{n}_\delta + s_4(\mathbf{n}_\alpha\mathbf{n}_\gamma\boldsymbol{\delta}_{\beta\delta} + \mathbf{n}_\beta\mathbf{n}_\gamma\boldsymbol{\delta}_{\alpha\delta} + \mathbf{n}_\alpha\mathbf{n}_\delta\boldsymbol{\delta}_{\beta\gamma} + \mathbf{n}_\beta\mathbf{n}_\delta\boldsymbol{\delta}_{\alpha\gamma})$$
$$+ s_5(\mathbf{n}^{(2)}_{\alpha\gamma}\boldsymbol{\delta}_{\beta\delta} + \mathbf{n}^{(2)}_{\alpha\delta}\boldsymbol{\delta}_{\beta\gamma} + \mathbf{n}^{(2)}_{\beta\gamma}\boldsymbol{\delta}_{\alpha\delta} + \mathbf{n}^{(2)}_{\beta\delta}\boldsymbol{\delta}_{\alpha\gamma}) + s_6\boldsymbol{\delta}_{\alpha\beta}\boldsymbol{\delta}_{\gamma\delta} + s_7(\boldsymbol{\delta}_{\alpha\gamma}\boldsymbol{\delta}_{\beta\delta} + \boldsymbol{\delta}_{\alpha\delta}\boldsymbol{\delta}_{\beta\gamma})$$

10.14 The dissipative matrix is positive semidefinite

We know from the structure of the dissipative matrix (**??**) that it is a positive, semidefinite operator. This implies that for any vector $(a_\mathbf{r}, \mathbf{b_r}, \mathbf{c}, \mathbf{d})$ we have

$$q = (a_\mathbf{r}, \mathbf{b_r}, \mathbf{c}, \mathbf{d}) \begin{pmatrix} 0 & 0 & 0 & 0 \\ 0 & M^{gg}_{\mathbf{rr'}} & 0 & M^{gP}_{\mathbf{r}} \\ 0 & 0 & 0 & 0 \\ 0 & M^{Pg}_{\mathbf{r'}} & 0 & M^{PP} \end{pmatrix} \begin{pmatrix} a_{\mathbf{r'}} \\ \mathbf{b_{r'}} \\ \mathbf{c} \\ \mathbf{d} \end{pmatrix} = \int d\mathbf{r}\int d\mathbf{r'}\mathbf{b_r}M^{gg}_{\mathbf{rr'}}\mathbf{b_{r'}} + \int d\mathbf{r}M^{gP}_{\mathbf{r}}\mathbf{b_r}\mathbf{d} + \int d\mathbf{r'}\mathbf{d}M^{Pg}_{\mathbf{r'}}\mathbf{b_{r'}} + \mathbf{d}M^{PP}\mathbf{d} \geq$$

where we understand that repeated continuum "indices" $\mathbf{r}, \mathbf{r}'$ are integrated over. By using

$$M_{\mathbf{rr}'}^{gg} = \boldsymbol{\nabla}\boldsymbol{\nabla}'\boldsymbol{\eta}_{\mathbf{rr}'} - \boldsymbol{\nabla}'\mathbf{G}_{\mathbf{rr}'} - \boldsymbol{\nabla}\mathbf{H}_{\mathbf{rr}'} + \boldsymbol{\gamma}_{\mathbf{rr}'}$$

$$M_{\mathbf{r}}^{gP} = \int d\mathbf{r}' \boldsymbol{\nabla}\mathbf{H}_{\mathbf{rr}'} - \int d\mathbf{r}'\boldsymbol{\gamma}_{\mathbf{rr}'}$$

$$M_{\mathbf{r}'}^{Pg} = \int d\mathbf{r}\,\boldsymbol{\nabla}'\mathbf{G}_{\mathbf{rr}'} - \int d\mathbf{r}\boldsymbol{\gamma}_{\mathbf{rr}'}$$

$$M^{PP} = \int d\mathbf{r} \int d\mathbf{r}'\boldsymbol{\gamma}_{\mathbf{rr}'}$$

we have

$$q = \int d\mathbf{r} \int d\mathbf{r}'\mathbf{b_r} \left[\boldsymbol{\nabla}\boldsymbol{\nabla}'\boldsymbol{\eta}_{\mathbf{rr}'} - \boldsymbol{\nabla}'\mathbf{G}_{\mathbf{rr}'} - \boldsymbol{\nabla}\mathbf{H}_{\mathbf{rr}'} + \boldsymbol{\gamma}_{\mathbf{rr}'}\right]\mathbf{b}_{\mathbf{r}'} + \int d\mathbf{r}\mathbf{b_r} \left[\int d\mathbf{r}'\boldsymbol{\nabla}\mathbf{H}_{\mathbf{rr}'} - \int d\mathbf{r}'\boldsymbol{\gamma}_{\mathbf{rr}'}\right]\mathbf{d}$$

$$+ \int d\mathbf{r}'\mathbf{d} \left[\int d\mathbf{r}\,\boldsymbol{\nabla}'\mathbf{G}_{\mathbf{rr}'} - \int d\mathbf{r}\boldsymbol{\gamma}_{\mathbf{rr}'}\right]\mathbf{b}_{\mathbf{r}'} + \int d\mathbf{r} \int d\mathbf{r}'\mathbf{d}\boldsymbol{\gamma}_{\mathbf{rr}'}\mathbf{d}$$

$$= \int d\mathbf{r} \int d\mathbf{r}'\boldsymbol{\nabla}\mathbf{b_r}\boldsymbol{\eta}_{\mathbf{rr}'}\boldsymbol{\nabla}'\mathbf{b}_{\mathbf{r}'} + \int d\mathbf{r} \int d\mathbf{r}'\mathbf{b_r}\mathbf{G}_{\mathbf{rr}'}\boldsymbol{\nabla}'\mathbf{b}_{\mathbf{r}'} + \int d\mathbf{r} \int d\mathbf{r}'\boldsymbol{\nabla}\mathbf{b_r}\mathbf{H}_{\mathbf{rr}'}\mathbf{b}_{\mathbf{r}'} + \int d\mathbf{r} \int d\mathbf{r}'\mathbf{b_r}\boldsymbol{\gamma}_{\mathbf{rr}'}\mathbf{b}_{\mathbf{r}'}$$

$$- \int d\mathbf{r} \int d\mathbf{r}'\boldsymbol{\nabla}\mathbf{b_r}\mathbf{H}_{\mathbf{rr}'}\mathbf{d} - \int d\mathbf{r} \int d\mathbf{r}'\mathbf{b_r}\boldsymbol{\gamma}_{\mathbf{rr}'}\mathbf{d} - \int d\mathbf{r}' \int d\mathbf{r}\mathbf{d}\mathbf{G}_{\mathbf{rr}'}\boldsymbol{\nabla}'\mathbf{b}_{\mathbf{r}'} - \int d\mathbf{r}' \int d\mathbf{r}\mathbf{d}\boldsymbol{\gamma}_{\mathbf{rr}'}\mathbf{b}_{\mathbf{r}'} + \int d\mathbf{r} \int d\mathbf{r}'\mathbf{d}\boldsymbol{\gamma}_{\mathbf{rr}'}\mathbf{d}$$

Next, we use the local approximation

$$q = \int d\mathbf{r}\boldsymbol{\nabla}\mathbf{b_r}\boldsymbol{\eta}\boldsymbol{\nabla}\mathbf{b_r} + \int d\mathbf{r}\delta_{\mathbf{r}}^{\Sigma}\mathbf{b_r}\mathbf{G}\boldsymbol{\nabla}\mathbf{b_r} + \int d\mathbf{r}\delta_{\mathbf{r}}^{\Sigma}\boldsymbol{\nabla}\mathbf{b_r}\mathbf{H}\mathbf{b_r} + \int d\mathbf{r}\delta_{\mathbf{r}}^{\Sigma}\mathbf{b_r}\boldsymbol{\gamma}\mathbf{b_r} - \int d\mathbf{r}\delta_{\mathbf{r}}^{\Sigma}\boldsymbol{\nabla}\mathbf{b_r}\mathbf{H}\mathbf{d}$$

$$- \int d\mathbf{r}\delta_{\mathbf{r}}^{\Sigma}\mathbf{b_r}\boldsymbol{\gamma}\mathbf{d} - \int d\mathbf{r}\delta_{\mathbf{r}}^{\Sigma}\mathbf{d}\mathbf{G}\boldsymbol{\nabla}\mathbf{b_r} - \int d\mathbf{r}\delta_{\mathbf{r}}^{\Sigma}\mathbf{d}\boldsymbol{\gamma}\mathbf{b_r} + \int d\mathbf{r}\delta_{\mathbf{r}}^{\Sigma}\mathbf{d}\boldsymbol{\gamma}\mathbf{d}$$

Regrouping terms

$$q = \int d\mathbf{r}\boldsymbol{\eta}\boldsymbol{\nabla}\mathbf{b_r}\boldsymbol{\nabla}\mathbf{b_r} + \int d\mathbf{r}\delta_{\mathbf{r}}^{\Sigma}(\mathbf{b_r} - \mathbf{d})\mathbf{G}\boldsymbol{\nabla}\mathbf{b_r} + \int d\mathbf{r}\delta_{\mathbf{r}}^{\Sigma}\boldsymbol{\nabla}\mathbf{b_r}\mathbf{H}(\mathbf{b_r} - \mathbf{d}) + \int d\mathbf{r}\delta_{\mathbf{r}}^{\Sigma}(\mathbf{b_r} - \mathbf{d})\boldsymbol{\gamma}(\mathbf{b_r} - \mathbf{d})$$

Now we use the explicit forms (**??**) for the transport coefficients. For example

$$\int d\mathbf{r}\boldsymbol{\eta}\boldsymbol{\nabla}\mathbf{b_r}\boldsymbol{\nabla}\mathbf{b_r} =$$

and

$$(\mathbf{b_r} - \mathbf{d})\mathbf{G}\boldsymbol{\nabla}\mathbf{b_r} = (\mathbf{b_r} - \mathbf{d})_\alpha \left[g_1(\mathbf{n}_\alpha\boldsymbol{\delta}_{\beta\gamma} + \mathbf{n}_\beta\boldsymbol{\delta}_{\alpha\gamma}) + g_2\boldsymbol{\delta}_{\alpha\beta}\mathbf{n}_\gamma + g_3(\mathbf{n}_\alpha\mathbf{n}_{\beta\gamma}^{(2)} + \mathbf{n}_\beta\mathbf{n}_{\alpha\gamma}^{(2)}) + g_4\mathbf{n}_\alpha\mathbf{n}_\beta\mathbf{n}_\gamma\right]\boldsymbol{\nabla}^\beta\mathbf{b}_{\mathbf{r}}^\gamma$$

$$\boldsymbol{\nabla}\mathbf{b_r}\mathbf{H}(\mathbf{b_r} - \mathbf{d}) = \boldsymbol{\nabla}^\alpha\mathbf{b}_{\mathbf{r}}^\beta \left[h_1(\boldsymbol{\delta}_{\alpha\beta}\mathbf{n}_\gamma + \boldsymbol{\delta}_{\alpha\gamma}\mathbf{n}_\beta) + h_2\mathbf{n}_\alpha\boldsymbol{\delta}_{\beta\gamma} + h_3(\mathbf{n}_{\alpha\beta}^{(2)}\mathbf{n}_\gamma + \mathbf{n}_{\alpha\gamma}^{(2)}\mathbf{n}_\beta) + h_4\mathbf{n}_\alpha\mathbf{n}_\beta\mathbf{n}_\gamma\right](\mathbf{b}_{\mathbf{r}}^\gamma - \mathbf{d}^\gamma)$$

Because $g_i = h_i$, these two terms are identical.

Including a surface viscosity tensor we have that

$$
\begin{aligned}
q =& \boldsymbol{\nabla}^\alpha \mathbf{b}^\beta \left[s_1 \mathbf{n}_\alpha \mathbf{n}_\beta \mathbf{n}_\gamma \mathbf{n}_\delta + s_2 \mathbf{n}_\alpha \mathbf{n}_\beta \boldsymbol{\delta}_{\gamma\delta} + s_2 \boldsymbol{\delta}_{\alpha\beta} \mathbf{n}_\gamma \mathbf{n}_\delta + s_4 (\mathbf{n}_\alpha \mathbf{n}_\gamma \boldsymbol{\delta}_{\beta\delta} + \mathbf{n}_\beta \mathbf{n}_\gamma \boldsymbol{\delta}_{\alpha\delta} + \mathbf{n}_\alpha \mathbf{n}_\delta \boldsymbol{\delta}_{\beta\gamma} + \mathbf{n}_\beta \mathbf{n}_\delta \boldsymbol{\delta}_{\alpha\gamma}) \right. \\
& \left. + s_5 (\mathbf{n}^{(2)}_{\alpha\gamma} \boldsymbol{\delta}_{\beta\delta} + \mathbf{n}^{(2)}_{\alpha\delta} \boldsymbol{\delta}_{\beta\gamma} + \mathbf{n}^{(2)}_{\beta\gamma} \boldsymbol{\delta}_{\alpha\delta} + \mathbf{n}^{(2)}_{\beta\delta} \boldsymbol{\delta}_{\alpha\gamma}) + s_6 \boldsymbol{\delta}_{\alpha\beta} \boldsymbol{\delta}_{\gamma\delta} + s_7 (\boldsymbol{\delta}_{\alpha\gamma} \boldsymbol{\delta}_{\beta\delta} + \boldsymbol{\delta}_{\alpha\delta} \boldsymbol{\delta}_{\beta\gamma}) \right] \boldsymbol{\nabla}^\gamma \mathbf{b}^\delta \\
& + 2 \boldsymbol{\nabla}^\alpha \mathbf{b}^\beta \left[h_1 (\boldsymbol{\delta}_{\alpha\beta} \mathbf{n}_\gamma + \boldsymbol{\delta}_{\alpha\gamma} \mathbf{n}_\beta) + h_2 \mathbf{n}_\alpha \boldsymbol{\delta}_{\beta\gamma} + h_3 (\mathbf{n}^{(2)}_{\alpha\beta} \mathbf{n}_\gamma + \mathbf{n}^{(2)}_{\alpha\gamma} \mathbf{n}_\beta) + h_4 \mathbf{n}_\alpha \mathbf{n}_\beta \mathbf{n}_\gamma \right] \mathbf{c}^\gamma \\
& + \mathbf{c}^\alpha \left[f_1 \boldsymbol{\delta}_{\alpha\beta} + f_2 \mathbf{n}_\alpha \mathbf{n}_\beta \right] \mathbf{c}^\beta
\end{aligned}
$$

Contract $\boldsymbol{\nabla}^\alpha \mathbf{b}^\beta \boldsymbol{\nabla}^\gamma \mathbf{b}^\delta$

$$
\begin{aligned}
q =& s_1 (\mathbf{n}\!\cdot\!\boldsymbol{\nabla}\mathbf{b}\!\cdot\!\mathbf{n})^2 + 2 s_2 (\mathbf{n}\!\cdot\!\boldsymbol{\nabla}\mathbf{b}\!\cdot\!\mathbf{n})\boldsymbol{\nabla}\!\cdot\!\mathbf{b} + s_4 (\mathbf{n}\!\cdot\!\boldsymbol{\nabla}\mathbf{b}^\beta \mathbf{n}\!\cdot\!\boldsymbol{\nabla}\mathbf{b}^\beta + \mathbf{n}\!\cdot\!\boldsymbol{\nabla}\mathbf{b}\!\cdot\!\boldsymbol{\nabla}\mathbf{b}\!\cdot\!\mathbf{n} + \mathbf{n}\!\cdot\!\boldsymbol{\nabla}\mathbf{b}\!\cdot\!\boldsymbol{\nabla}\mathbf{b}\!\cdot\!\mathbf{n} + (\boldsymbol{\nabla}^\alpha \mathbf{b}\!\cdot\!\mathbf{n})\boldsymbol{\nabla}^\alpha \mathbf{b}\!\cdot\!\mathbf{n}) \\
& \left. + s_5 (\mathbf{n}^{(2)}_{\alpha\gamma} \boldsymbol{\delta}_{\beta\delta} + \mathbf{n}^{(2)}_{\alpha\delta} \boldsymbol{\delta}_{\beta\gamma} + \mathbf{n}^{(2)}_{\beta\gamma} \boldsymbol{\delta}_{\alpha\delta} + \mathbf{n}^{(2)}_{\beta\delta} \boldsymbol{\delta}_{\alpha\gamma}) + s_6 (\boldsymbol{\nabla}\!\cdot\!\mathbf{b})^2 + s_7 (\boldsymbol{\nabla}^\alpha \mathbf{b}^\beta \boldsymbol{\nabla}^\alpha \mathbf{b}^\beta + \boldsymbol{\nabla}^\alpha \mathbf{b}^\beta \boldsymbol{\nabla}^\beta \mathbf{b}^\alpha) \right] \\
& + 2 \boldsymbol{\nabla}^\alpha \mathbf{b}^\beta \left[h_1 (\boldsymbol{\delta}_{\alpha\beta} \mathbf{n}_\gamma + \boldsymbol{\delta}_{\alpha\gamma} \mathbf{n}_\beta) + h_2 \mathbf{n}_\alpha \boldsymbol{\delta}_{\beta\gamma} + h_3 (\mathbf{n}^{(2)}_{\alpha\beta} \mathbf{n}_\gamma + \mathbf{n}^{(2)}_{\alpha\gamma} \mathbf{n}_\beta) + h_4 \mathbf{n}_\alpha \mathbf{n}_\beta \mathbf{n}_\gamma \right] \mathbf{c}^\gamma \\
& + \left[f_1 \mathbf{c}\!\cdot\!\mathbf{c} + f_2 (\mathbf{n}\!\cdot\!\mathbf{c})^2 \right]
\end{aligned}
$$

Extract the antisymmetric bits

$$
\begin{aligned}
& \boldsymbol{\nabla}^\alpha \mathbf{b}^\beta \left[s_5 (\mathbf{n}^{(2)}_{\alpha\gamma} \boldsymbol{\delta}_{\beta\delta} + \mathbf{n}^{(2)}_{\alpha\delta} \boldsymbol{\delta}_{\beta\gamma} + \mathbf{n}^{(2)}_{\beta\gamma} \boldsymbol{\delta}_{\alpha\delta} + \mathbf{n}^{(2)}_{\beta\delta} \boldsymbol{\delta}_{\alpha\gamma}) \right] \boldsymbol{\nabla}^\gamma \mathbf{b}^\delta \\
& + 2 \boldsymbol{\nabla}^\alpha \mathbf{b}^\beta \left[h_3 (\mathbf{n}^{(2)}_{\alpha\beta} \mathbf{n}_\gamma + \mathbf{n}^{(2)}_{\alpha\gamma} \mathbf{n}_\beta) \right] \mathbf{c}^\gamma
\end{aligned}
$$

11

Fluid-solid interaction: $n_{\mathbf{r}}, \mathbf{g_r}, e_{\mathbf{r}}, \mathbf{R}, \mathbf{P}, E$

11.1 The system and the relevant variables

We have in mind the molecular dynamics set up discussed in Sec. in which a fluid is in contact with to massive walls. However, in order to account for momentum conservation, in the formulation of the theory we consider a different set up, depicted in Fig. **??**. A large massive but in principle mobile spherical solid particle immersed in a fluid. In the limit of very large radius, the surface of the solid particle will be assimilated to a planar wall.

We consider a fluid system of N particles (atoms or molecules) of mass m described with the position and momenta of their center of mass. The particles are allowed to move through space unrestrictedly. To avoid the issues of an infinite number of particles required in the thermodynamic limit, and to make closer contact with molecular dynamics simulations, we simply assume that the system is within periodic boundary conditions. Interacting with that sea of fluid particles there is a group of N' bonded particles of mass m' forming what we would understand at a macroscopic level as a solid object of spherical shape.

At the *microscopic level* the system is described by the set of all positions $\mathbf{q}_i$ and momenta $\mathbf{p}_i = m\mathbf{v}_i$ $(i = 1, \cdots, N)$ of the fluid particles plus the positions $\mathbf{q}_{i'}$ and momenta $\mathbf{p}_{i'} = m'\mathbf{v}_{i'}$ $(i' = 1, \cdots, N')$ of the particles of the solid sphere. For compactness we will denote the microstate in either of the following forms z or q, p, q', p'. We will distinguish with a prime the labels of the particles of the solid sphere from the unprimed labels of the fluid particles. The microstate of the system evolves according to Hamilton's equations with a Hamiltonian given by

$$\hat{H}(z) \;\; = \;\; \sum_i^N \frac{p_i^2}{2m} + \sum_{i'}^{N'} \frac{p_{i'}^2}{2m'} + U(z) \tag{11.1.1}$$

where the potential energy $U(z)$ is given by

$$U(z) = V^{\text{f}}(q) + V^{\text{fs}}(q, q') + V^{\text{s}}(q')$$

We assume, for simplicity, a pair-wise potential energy, where $V^{\text{f}}(q) = \frac{1}{2} \sum_{ij}^{N} \phi_{ij}^{\text{ff}}$ is the potential of interaction between fluid particles, $V^{\text{fs}}(q, q') = \sum_{ii'}^{NN'} \phi_{ii'}^{\text{fs}}$ is the potential of interaction between fluid particles and solid particles, while $V^{\text{s}}(q') = \frac{1}{2} \sum_{i'j'}^{N'} \phi_{i'j'}^{\text{ss}}$ is the potential of interaction between the particles of the solid object. Self interaction of the particles is not considered, so $\phi_{ii} = 0$, etc. There are no external conservative potentials acting on the system, although they can be easily introduced. We do not consider such external potentials in order to transparently discuss the issues of momentum conservation. However, in some of the arguments to be presented below it turns out necessary to include also a *tethering potential* that keeps the center of mass of the solid sphere confined in a particular position of space, and hinders the full rotations of the sphere. This tethering potential may be a (stiff spring) potential acting on any three non-colinear particles of the sphere and will be denoted generically as $V^{\text{ext}}(q')$. This external potential breaks translational symmetry.

Note that at a microscopic level *we do not have boundaries of any kind*, we only have particles interacting with each other in free space. In lab situations, typically, fluids are contained in flasks and other type of solid objects that prevent the fluid from leaking. We could model a spherical flask containing a fluid in very much the same way as we are going to treat the solid spherical particle surrounded by the (possibly infinite in extension) fluid. Also, solidness is not easy to define at the microscopic level. All what we have is a collection of bounded particles (that is, their relative distances do not increase without bound) that are moving and vibrating. The spherical shape of the particle should be understood, of course, in a statistical sense.

11.1.1   The relevant variables

We describe the system at a *coarse grained level* by selecting as relevant variables the mass, momentum, and energy density fields of the fluid plus the center of mass position, momentum, and energy of the solid sphere. These are given by the following set of phase functions (phase functions are denoted with a hat, while its ensemble averages will be unhatted)

$$\hat{\rho}_{\mathbf{r}}(z) = \sum_{i}^{N} m\delta(\mathbf{r} - \mathbf{q}_i), \qquad\qquad \hat{\mathbf{R}}(z) = \frac{1}{N'} \sum_{i'}^{N'} \mathbf{q}_{i'}$$

$$\hat{\mathbf{g}}_{\mathbf{r}}(z) = \sum_{i}^{N} \mathbf{p}_i \delta(\mathbf{r} - \mathbf{q}_i), \qquad\qquad \hat{\mathbf{P}}(z) = \sum_{i'}^{N'} \mathbf{p}_{i'}$$

$$\hat{e}_{\mathbf{r}}(z) = \sum_{i}^{N} e_i \delta(\mathbf{r} - \mathbf{q}_i) \qquad\qquad \hat{E}(z) = \sum_{i'}^{N'} e_{i'}$$

where

$$e_i = \frac{\mathbf{p}_i^2}{2m} + \frac{1}{2} \sum_{j}^{N} \phi_{ij} + \frac{1}{2} \sum_{j'}^{N'} \phi_{ij'},$$

$$e_{i'} = \frac{\mathbf{p}_{i'}^2}{2m'} + \frac{1}{2} \sum_{j}^{N} \phi_{i'j} + \frac{1}{2} \sum_{j'}^{N'} \phi_{i'j'}$$

are the energies of a particle of fluid and of solid, respectively. In the phase functions (11.1.1), the position $\mathbf{r}$ plays the role of a continuous index labeling the phase function. The position $\mathbf{r}$ may take any value in $\mathbb{R}^3$ as we do not have any restriction to the possible motion of the particles. The domain of any integral of the form $\int d\mathbf{r} \cdots$ is understood to be $\mathbb{R}^3$. For the sake of simplicity, we do not include orientational degrees of freedom of the solid for the time being.

We expect that this selection of variables will be appropriate when the dynamics of solid is much faster than the hydrodynamic variables of the fluid. Note that by selecting the center of mass variables of the solid as the only ones necessary to describe the state of the solid we are implicitly assuming that the remaining solid degrees of freedom are much faster than the hydrodynamic fields. In particular, we assume that any elastic behaviour of the solid is so rapidly decaying towards its equilibrium state that elastic variables do not need to be included in the description. Should this assumption be violated, the resulting dynamic equations (not including these elastic variables for the solid) would not be Markovian. Also, by using the internal energy of the solid, and not the energy density field, we are assuming that in the time scale of evolution of the selected variables, the solid is already fully equilibrated with a constant temperature field. As an example, consider the thermal diffusivity of gold, copper, alumnium, silicon, and carbon, which is around $10^{-4}m^2/s$. The thermal diffusivity of liquids like water and alcohol is around $10^{-6}m^2/s$. This means that thermally, we expect that the temperature within the metal will relax much faster than the temperature in the liquid, within comparable length

scales. In this case, it seems appropriate to assume that the solid is fully equilibrated, and the only relevant variable of the solid is the total energy E. On the other hand, if the solid is PVC, which has a comparable thermal diffusivity as water, we will need to include the dynamics of the temperature field within the solid.

Observe that the energy of a fluid particle contains contributions from its interaction with the solid particles, and viceversa. The rationale for this particular definition of the relevant variables is that we would like to obtain a set of dynamic equations that satisfy total energy conservation. Therefore, we need to be able to express the total energy (12.3) of the system in terms of the relevant variables selected. In the case of the variables (11.1.1) the total energy can be obtained from the identity

$$\hat{H}(z) = \int d\mathbf{r}\,\hat{e}_{\mathbf{r}}(z) + \hat{E}(z)$$

11.1.2   The time derivatives of the relevant variables

The time derivatives of the coarse variables play a fundamental role in the final structure of the dynamic equations (12.2). The time derivative $i\mathcal{L}A$ is the result of applying the Liouville operator (12.2) to the relevant variables. In this section, we discuss the particular form of $i\mathcal{L}A$ for the case of selected CG variables (11.1.1). By separating the different types of forces (that the solid and fluid particles exert on fluid or solid particles) and using the standard trick [?, ?]

$$\delta(\mathbf{r} - \mathbf{q}_i) - \delta(\mathbf{r} - \mathbf{q}_j) = \int_0^1 d\epsilon \frac{d}{d\epsilon}\delta(\mathbf{r} - \mathbf{q}_j - \epsilon\mathbf{q}_{ij}) = -\boldsymbol{\nabla}\cdot\int_0^1 d\epsilon\mathbf{q}_{ij}\delta(\mathbf{r} - \mathbf{q}_j - \epsilon\mathbf{q}_{ij}) \quad (11.1.-1)$$

to write down differences of Dirac delta functions in terms of divergences, we arrive at the following time derivatives for the particular case of the microscopic densities introduced in Eq. (11.1.1)

$$i\mathcal{L}\hat{\rho}_{\mathbf{r}}(z) = -\boldsymbol{\nabla}\cdot\hat{\mathbf{g}}_{\mathbf{r}}(z), \quad i\mathcal{L}\hat{\mathbf{g}}_{\mathbf{r}}(z) = -\boldsymbol{\nabla}\cdot\hat{\boldsymbol{\sigma}}_{\mathbf{r}} + \hat{\mathbf{F}}_{\mathbf{r}}, \quad i\mathcal{L}\hat{e}_{\mathbf{r}} = -\nabla\cdot\hat{\mathbf{Q}}_{\mathbf{r}} + \hat{\pi}_{\mathbf{r}},$$

We have introduced in these expressions the following quantities. The total micro-

scopic stress tensor of the fluid $\hat{\boldsymbol{\sigma}}_{\mathbf{r}}$ is

$$\hat{\boldsymbol{\sigma}}_{\mathbf{r}} \equiv \hat{\mathbf{K}}_{\mathbf{r}} + \hat{\boldsymbol{\Pi}}_{\mathbf{r}}$$

$$\hat{\mathbf{K}}_{\mathbf{r}} \equiv \sum_i^N \mathbf{p}_i \mathbf{v}_i \delta(\mathbf{r} - \mathbf{q}_i)$$

$$\hat{\boldsymbol{\Pi}}_{\mathbf{r}} \equiv \frac{1}{2} \sum_{ij}^N \mathbf{q}_{ij} \hat{\mathbf{F}}_{ij} \int_0^1 d\epsilon \delta(\mathbf{r} - \mathbf{q}_j - \epsilon \mathbf{q}_{ij})$$

$$\hat{\mathbf{F}}_{\mathbf{r}}(z) \equiv \sum_{ij'}^{NN'} \hat{\mathbf{F}}_{ij'} \delta(\mathbf{r} - \mathbf{q}_i)$$

$$\hat{\mathbf{Q}}_{\mathbf{r}} \equiv \sum_i^N \mathbf{v}_i e_i \delta(\mathbf{r} - \mathbf{r}_i) + \frac{1}{2} \sum_{ij}^{NN} \frac{(\mathbf{v}_i + \mathbf{v}_j)}{2} \cdot \mathbf{F}_{ij} \mathbf{q}_{ij} \int_0^1 d\epsilon \delta(\mathbf{r} - \mathbf{q}_j - \epsilon \mathbf{q}_{ij})$$

$$\hat{\pi}_{\mathbf{r}} \equiv \sum_{ij'}^{NN'} \mathbf{F}_{ij'} \cdot \frac{(\mathbf{v}_i + \mathbf{v}_{j'})}{2} \delta(\mathbf{r} - \mathbf{q}_i)$$

where $\hat{\mathbf{F}}_{ij}$ is the force that particle j of the fluid exerts on particle i of the fluid and $\hat{\mathbf{F}}_{ij'}$ is the force that particle j' of the solid exerts on particle i of the fluid. The force density that the solid exerts on the fluid is $\hat{\mathbf{F}}_{\mathbf{r}}(z)$.

We observe that the force density on the fluid $i\mathcal{L}\hat{\mathbf{g}}_{\mathbf{r}}$ has two components, one which is the force done by the fluid itself and that has the form of a divergence of the stress tensor $\hat{\boldsymbol{\sigma}}_{\mathbf{r}}$ (which depends only on fluid particle coordinates), and another one due to the solid $\hat{\mathbf{F}}_{\mathbf{r}}$ that cannot be expressed as the divergence of a stress.

The time derivatives of the solid variables are

$$i\mathcal{L}\hat{\mathbf{R}} = \frac{\hat{\mathbf{P}}}{M}$$

$$i\mathcal{L}\hat{\mathbf{P}} = - \int d\mathbf{r} \hat{\mathbf{F}}_{\mathbf{r}}(z)$$

$$i\mathcal{L}\hat{E} = - \int d\mathbf{r} \hat{\pi}_{\mathbf{r}}(z)$$

Note that the total momentum and total energy, which are defined in terms of the coarse-grained variables as

$$\hat{\mathbf{P}}_T = \int \hat{\mathbf{g}}_{\mathbf{r}}(z) d\mathbf{r} + \hat{\mathbf{P}}(z)$$

$$\hat{E}_T = \int \hat{e}_{\mathbf{r}}(z) d\mathbf{r} + \hat{E}(z)$$

satisfy $i\mathcal{L}\hat{\mathbf{P}}_T = 0, i\mathcal{L}\hat{E}_T = 0$ and are, therefore, conserved quantity of the microscopic dynamics. We have used that $\int d\mathbf{r}\hat{\boldsymbol{\sigma}} = 0$ due to Gauss theorem and the fact that at the infinite we assume there are no fluid particles. A similar argument holds when the

domain of integration is periodic.

$$
i\mathcal{L}\hat{e}_{\mathbf{r}}(z) = -\boldsymbol{\nabla}\sum_i^N \mathbf{v}_i e_i \delta(\mathbf{r} - \mathbf{q}_i) + \sum_i^N i\mathcal{L}\left(\frac{\mathbf{p}_i^2}{2m} + \frac{1}{2}\sum_j^N \phi_{ij} + \frac{1}{2}\sum_{j'}^{N'} \phi_{ij'},\right)\delta(\mathbf{r} - \mathbf{q}_i)
$$

$$
= -\boldsymbol{\nabla}\sum_i^N \mathbf{v}_i e_i \delta(\mathbf{r} - \mathbf{q}_i) + \sum_i^N \left(\mathbf{v}_i\cdot\mathbf{F}_i - \frac{1}{2}\sum_j^N \mathbf{F}_{ij}\cdot\mathbf{v}_{ij} - \frac{1}{2}\sum_{j'}^{N'} \mathbf{F}_{ij'}\cdot\mathbf{v}_{ij'}\right)\delta(\mathbf{r} - \mathbf{q}_i)
$$

$$
= -\boldsymbol{\nabla}\sum_i^N \mathbf{v}_i e_i \delta(\mathbf{r} - \mathbf{q}_i) + \sum_{ij}^N \frac{\mathbf{v}_i + \mathbf{v}_j}{2}\cdot\mathbf{F}_{ij}\delta(\mathbf{r} - \mathbf{q}_i) + \sum_{ij'}^N \frac{\mathbf{v}_i + \mathbf{v}_{j'}}{2}\cdot\mathbf{F}_{ij'}\delta(\mathbf{r} - \mathbf{q}_i)
$$

$$
= -\boldsymbol{\nabla}\sum_i^N \mathbf{v}_i e_i \delta(\mathbf{r} - \mathbf{q}_i) + \frac{1}{2}\sum_{ij}^{NN} \frac{\mathbf{v}_i + \mathbf{v}_j}{2}\cdot\mathbf{F}_{ij}\left(\delta(\mathbf{r} - \mathbf{q}_i) - \delta(\mathbf{r} - \mathbf{q}_j)\right) + \sum_{ij'}^{NN'} \frac{\mathbf{v}_i + \mathbf{v}_{j'}}{2}\cdot\mathbf{F}_{ij'}\delta(\mathbf{r} - \mathbf{q}_i)
$$

$$
= -\boldsymbol{\nabla}\cdot\left[\sum_i^N \mathbf{v}_i e_i \delta(\mathbf{r} - \mathbf{q}_i) + \frac{1}{2}\sum_{ij}^{NN} \frac{\mathbf{v}_i + \mathbf{v}_j}{2}\cdot\mathbf{F}_{ij}\mathbf{q}_{ij}\int_0^1 d\epsilon\,\delta(\mathbf{r} - \mathbf{q}_j - \epsilon\mathbf{q}_{ij})\right] + \sum_{ij'}^{NN'} \frac{\mathbf{v}_i + \mathbf{v}_{j'}}{2}\cdot\mathbf{F}_{ij'}\delta(\mathbf{r} - \mathbf{q}_i)
$$

$$
= -\boldsymbol{\nabla}\cdot\hat{\mathbf{Q}}_{\mathbf{r}} + \hat{\pi}_{\mathbf{r}}
$$

11.1.3   The Galilean operator

The Galilean operator $\mathscr{G}$ is defined through its action on a phase function, which is to change the velocity arguments from $\mathbf{v}_i \to \mathbf{v}_i - \mathbf{v}(\mathbf{q}_i)$ for i a fluid particle and $\mathbf{v}_{i'} \to \mathbf{v}_{i'} - \mathbf{V}$ for i' a solid particle. The intuitive meaning of the action of the Galilean operator is that when applied to a phase function gives how it is seen in a reference frame that moves with the flow field. For a product of phase functions we have $\mathscr{G}(AB) = (\mathscr{G}A)(\mathscr{G}B)$. The effect of this change of variables within a phase space integral (denoted by a trace) implies the following properties

$$
\text{Tr}[\mathscr{G}\hat{F}] = \text{Tr}[\hat{F}]
$$

$$
\text{Tr}[\overline{\rho}_t\hat{F}] = \text{Tr}[(\mathscr{G}\overline{\rho}_t)(\mathscr{G}\hat{F})]
$$

$$
\text{Tr}[\overline{\rho}_t\mathscr{G}\hat{F}] = \text{Tr}[\hat{F}\mathscr{G}^{-1}\overline{\rho}_t]
$$

where the inverse operator $\mathscr{G}^{-1}$ is obtained by reversing the sign of the velocities $\mathbf{v}(\mathbf{r}), \mathbf{V}$.

The action of the Galilean operator on the relevant variables (11.1.1) is

$$\mathscr{G}\hat{\rho}_{\mathbf{r}} = \hat{\rho}_{\mathbf{r}}$$

$$\mathscr{G}\hat{\mathbf{g}}_{\mathbf{r}} = \hat{\mathbf{g}}_{\mathbf{r}} - \mathbf{v}(\mathbf{r})\hat{\rho}_{\mathbf{r}}$$

$$\mathscr{G}\hat{e}_{\mathbf{r}} = \hat{e}_{\mathbf{r}} - \mathbf{v}(\mathbf{r}){\cdot}\hat{\mathbf{g}}_{\mathbf{r}} + \frac{\mathbf{v}^2(\mathbf{r})}{2}\hat{\rho}_{\mathbf{r}}$$

$$\mathscr{G}\hat{\mathbf{R}} = \hat{\mathbf{R}}$$

$$\mathscr{G}\hat{\mathbf{P}} = \hat{\mathbf{P}} - M'\mathbf{V}$$

$$\mathscr{G}\hat{E} = \hat{E} - \hat{\mathbf{P}}{\cdot}\mathbf{V} + \frac{M_s V^2}{2}$$

We will also need the action of the Galilean operator on the time derivatives of the relevant variables, which require the action on the stress tensor and heat flux, as well as on the power source

$$\mathscr{G}\hat{\boldsymbol{\sigma}}_{\mathbf{r}} = \hat{\boldsymbol{\sigma}}_{\mathbf{r}} - \mathbf{v}(\mathbf{r})\hat{\mathbf{g}}_{\mathbf{r}} - \hat{\mathbf{g}}_{\mathbf{r}}\mathbf{v}(\mathbf{r}) + \mathbf{v}(\mathbf{r})\mathbf{v}(\mathbf{r})\hat{\rho}_{\mathbf{r}}$$

$$\mathscr{G}\hat{\mathbf{F}}_{\mathbf{r}} = \hat{\mathbf{F}}_{\mathbf{r}}$$

$$\mathscr{G}\hat{\mathbf{Q}}_{\mathbf{r}} = \hat{\mathbf{Q}}_{\mathbf{r}} - \hat{\boldsymbol{\sigma}}_{\mathbf{r}}{\cdot}\mathbf{v}(\mathbf{r}) - \Delta\hat{\boldsymbol{\sigma}}_{\mathbf{r}} + \frac{1}{2}\mathbf{v}^2(\mathbf{r})\hat{\mathbf{g}}_{\mathbf{r}} - \mathbf{v}(\mathbf{r})\mathscr{G}\hat{e}_{\mathbf{r}}$$

$$\mathscr{G}\hat{\pi}_{\mathbf{r}} = \hat{\pi}_{\mathbf{r}} - \frac{\mathbf{v}(\mathbf{r}) + \mathbf{V}}{2}\hat{\mathbf{F}}_{\mathbf{r}}$$

where

$$\Delta\hat{\boldsymbol{\sigma}}_{\mathbf{r}} = \frac{1}{2}\sum_{ij}^{NN} \frac{(\mathbf{v}(\mathbf{q}_i) - \mathbf{v}(\mathbf{r}) + \mathbf{v}(\mathbf{q}_j) - \mathbf{v}(\mathbf{r})))}{2}{\cdot}\mathbf{F}_{ij}\mathbf{q}_{ij}\int_0^1 d\epsilon\delta(\mathbf{r} - \mathbf{q}_j + \epsilon\mathbf{q}_{ij})$$

Note that, given $\mathbf{r}$ the Dirac delta functions multiplying the force $\mathbf{F}_{ij}$ says that only pairs i, j of particles near $\mathbf{r}$ will contribute to this function. Therefore, it makes sense to Taylor expand the velocity field around $\mathbf{r}$ and keep only the first order term, which gives

$$\Delta\hat{\boldsymbol{\sigma}}_{\mathbf{r}} \simeq \frac{1}{2}\sum_{ij}^{NN} \mathbf{q}_{ij}{\cdot}\mathbf{F}_{ij}\mathbf{q}_{ij}\int_0^1 d\epsilon\delta(\mathbf{r} - \mathbf{q}_j + \epsilon\mathbf{q}_{ij}){\cdot}\boldsymbol{\nabla}\mathbf{v}(\mathbf{r}) - \mathbf{v}(r){\cdot}\frac{1}{2}\sum_{ij}^{NN} \mathbf{F}_{ij}\mathbf{q}_{ij}\int_0^1 d\epsilon\delta(\mathbf{r} - \mathbf{q}_j + \epsilon\mathbf{q}_{ij})$$

This shows that this term is proportional to the velocity gradient to a first approximation. In addition, note that the structure of the proportionality factor is the same as the virial contribution to the stress tensor, with a further term $\mathbf{q}_{ij}$. This means that, typically, this factor is of the order of the virial times a distance of the order of the range of interactions. Under the assumption that the velocity gradient is very small in the length scale of the forces, the term (11.1.3) is negligible.

$$\mathscr{G}\hat{\mathbf{Q}}_{\mathbf{r}} = \sum_i^N (\mathbf{v}_i - \mathbf{v}(\mathbf{q}_i)) \left[\frac{m}{2}(\mathbf{v}_i - \mathbf{v}(\mathbf{q}_i))^2 + \phi_i\right] \delta(\mathbf{r} - \mathbf{q}_i) + \frac{1}{2}\sum_{ij}^{NN} \frac{(\mathbf{v}_i + \mathbf{v}_j - \mathbf{v}(\mathbf{q}_i) - \mathbf{v}(\mathbf{q}_j))}{2} \cdot \mathbf{F}_{ij}\mathbf{q}_{ij} \int_0^1 d\epsilon\,\delta(\mathbf{r} - \mathbf{q}_j + \epsilon\mathbf{q}_{ij})$$

$$= \sum_i^N (\mathbf{v}_i - \mathbf{v}(\mathbf{q}_i)) \left[\frac{m}{2}(\mathbf{v}_i^2 - 2\mathbf{v}_i\cdot\mathbf{v}(\mathbf{q}_i) + \mathbf{v}^2(\mathbf{q}_i)) + \phi_i\right] \delta(\mathbf{r} - \mathbf{q}_i)$$

$$+ \frac{1}{2}\sum_{ij}^{NN} \frac{(\mathbf{v}_i + \mathbf{v}_j - \mathbf{v}(\mathbf{q}_i) - \mathbf{v}(\mathbf{q}_j))}{2} \cdot \mathbf{F}_{ij}\mathbf{q}_{ij} \int_0^1 d\epsilon\,\delta(\mathbf{r} - \mathbf{q}_j + \epsilon\mathbf{q}_{ij})$$

$$= \sum_i^N \mathbf{v}_i \left[\frac{m}{2}(\mathbf{v}_i^2 - 2\mathbf{v}_i\cdot\mathbf{v}(\mathbf{r}) + \mathbf{v}^2(\mathbf{r})) + \phi_i\right] \delta(\mathbf{r} - \mathbf{q}_i)$$

$$- \mathbf{v}(\mathbf{r})\sum_i^N \left[\frac{m}{2}(\mathbf{v}_i^2 - 2\mathbf{v}_i\cdot\mathbf{v}(\mathbf{r}) + \mathbf{v}^2(\mathbf{r})) + \phi_i\right] \delta(\mathbf{r} - \mathbf{q}_i) + \frac{1}{2}\sum_{ij}^{NN} \frac{(\mathbf{v}_i + \mathbf{v}_j - \mathbf{v}(\mathbf{q}_i) - \mathbf{v}(\mathbf{q}_j))}{2} \cdot \mathbf{F}_{ij}\mathbf{q}_{ij} \int_0^1 d\epsilon\,\delta(\mathbf{r} - \mathbf{q}_j + \epsilon\mathbf{q}_{ij})$$

$$= \hat{\mathbf{Q}}_{\mathbf{r}} - \sum_i^N m\mathbf{v}_i\mathbf{v}_i\delta(\mathbf{r} - \mathbf{q}_i)\cdot\mathbf{v}(\mathbf{r}) - \frac{1}{2}\sum_{ij}^{NN} \frac{(\mathbf{v}(\mathbf{q}_i) + \mathbf{v}(\mathbf{q}_j))}{2} \cdot \mathbf{F}_{ij}\mathbf{q}_{ij} \int_0^1 d\epsilon\,\delta(\mathbf{r} - \mathbf{q}_j + \epsilon\mathbf{q}_{ij})$$

$$+ \frac{1}{2}\mathbf{v}^2(\mathbf{r})\hat{\mathbf{g}}_{\mathbf{r}} - \mathbf{v}(\mathbf{r})\hat{e}_{\mathbf{r}} + \hat{\mathbf{g}}_{\mathbf{r}}\cdot\mathbf{v}(\mathbf{r})\mathbf{v}(\mathbf{r}) - \frac{\mathbf{v}^2(\mathbf{r})}{2}\hat{\rho}_{\mathbf{r}}\mathbf{v}(\mathbf{r})$$

$$= \hat{\mathbf{Q}}_{\mathbf{r}} - \Delta\hat{\boldsymbol{\sigma}}_{\mathbf{r}} + \frac{1}{2}\mathbf{v}^2(\mathbf{r})\hat{\mathbf{g}}_{\mathbf{r}} - \mathbf{v}(\mathbf{r})\mathscr{G}\hat{e}_{\mathbf{r}}$$

We have introduced the term

$$\Delta\hat{\boldsymbol{\sigma}}_{\mathbf{r}} = \sum_i^N m\mathbf{v}_i\mathbf{v}_i\delta(\mathbf{r} - \mathbf{q}_i)\cdot\mathbf{v}(\mathbf{r}) + \frac{1}{2}\sum_{ij}^{NN} \frac{(\mathbf{v}(\mathbf{q}_i) + \mathbf{v}(\mathbf{q}_j))}{2} \cdot \mathbf{F}_{ij}\mathbf{q}_{ij} \int_0^1 d\epsilon\,\delta(\mathbf{r} - \mathbf{q}_j + \epsilon\mathbf{q}_{ij})$$

We now consider the action of the Galilean operator on the source terms (12.5)

$$\mathscr{G}\hat{\boldsymbol{\pi}}_{\mathbf{r}} = \sum_{ij'}^{NN'} \mathbf{F}_{ij'}\cdot\frac{(\mathbf{v}_i - \mathbf{v}(\mathbf{q}_i) + \mathbf{v}_{j'} - \mathbf{V})}{2}\delta(\mathbf{r} - \mathbf{q}_i) = \hat{\boldsymbol{\pi}}_{\mathbf{r}} - \frac{\mathbf{v}(\mathbf{r}) + \mathbf{V}}{2}\cdot\sum_{ij'}^{NN'} \mathbf{F}_{ij'}\delta(\mathbf{r} - \mathbf{q}_i)$$

11.2   The relevant ensemble and the entropy

The relevant ensemble (**??**) becomes, for the present level of description,

$$\overline{\rho}(z) = \frac{\rho_0}{\Xi[\lambda]} \exp\left\{ -\int d\mathbf{r}\, (\lambda_\rho(\mathbf{r})\hat{\rho}_\mathbf{r}(z) + \boldsymbol{\lambda}_g(\mathbf{r})\hat{\mathbf{g}}_\mathbf{r}(z) + \beta(\mathbf{r})\hat{e}_\mathbf{r}(z)) - \boldsymbol{\lambda}_R\cdot\hat{\mathbf{R}}(z) - \boldsymbol{\lambda}_P\cdot\hat{\mathbf{P}}(z) - \beta_\mathrm{s}\hat{E}(z) \right\}$$

Here $\rho_0 = \frac{1}{N!h^{3(N+N')}}$ where only the fluid particles are assumed to be indistinguishable (and hence the presence of the factor $N!$). The Lagrange multipliers λ are now the set $\lambda = \{\lambda_\rho(\mathbf{r}), \boldsymbol{\lambda}_g(\mathbf{r}), \beta_\mathrm{f}(\mathbf{r}), \boldsymbol{\lambda}_R, \boldsymbol{\lambda}_P, \beta_\mathrm{s}\}$. The dimensionless generalized partition function $\Xi[\lambda]$ normalizes the relevant ensemble and is given by

$$\Xi[\lambda] \equiv \sum_{N=0}^{\infty} \frac{1}{N!} \int \frac{dz}{h^{3N}} \exp\left\{ -\sum_i^N (\beta(\mathbf{q}_i)e_i - \lambda_\rho(\mathbf{q}_i)m - \boldsymbol{\lambda}_g(\mathbf{q}_i)\cdot\mathbf{p}_i) - \sum_{i'}^{N'} \left(\beta_\mathrm{s}e_{i'} + \boldsymbol{\lambda}_R\cdot\frac{m'}{M'}\hat{\mathbf{q}}_{i'} + \boldsymbol{\lambda}_P\cdot\hat{\mathbf{p}}_{i'} \right) \right\}$$

This partition function is a functional of the set of Lagrange multipliers λ. These conjugate variables of the relevant variables (11.1.1) are fixed by the condition that the averages of the relevant variables (11.1.1) with the relevant ensemble coincide with the averages $a = \{\rho(\mathbf{r}), \mathbf{g}(\mathbf{r}), e(\mathbf{r}), \mathbf{R}, \mathbf{P}, E\}$ computed with the actual ensemble, solution of the Liouville equation. This condition can be expressed, as in Eqs. (**??**), as

$$\rho(\mathbf{r}) = \frac{\delta\Phi[\lambda]}{\delta\lambda_\rho(\mathbf{r})} \qquad\qquad \mathbf{R} = \frac{\partial\Phi[\lambda]}{\partial\boldsymbol{\lambda}_R}$$

$$\mathbf{g}(\mathbf{r}) = \frac{\delta\Phi[\lambda]}{\delta\boldsymbol{\lambda}_g(\mathbf{r})} \qquad\qquad \mathbf{P} = \frac{\partial\Phi[\lambda]}{\partial\boldsymbol{\lambda}_P}$$

$$e(\mathbf{r}) = \frac{\delta\Phi[\lambda]}{\delta\beta(\mathbf{r})} \qquad\qquad E = \frac{\partial\Phi[\lambda]}{\partial\beta_\mathrm{s}}$$

where we have introduced the dimensionless generalized thermodynamic potential

$$\Phi[\lambda] \quad\equiv\quad -\ln\Xi[\lambda] \qquad\qquad (11.2.\text{-}1)$$

Because the functional $\Phi[\lambda]$ is convex the conjugate variables $\lambda = \{\lambda_\rho, \boldsymbol{\lambda}_g, \beta, \boldsymbol{\lambda}_R, \boldsymbol{\lambda}_P, \beta_\mathrm{s}\}$ are in one to one connection with the averages $a = \{\rho, \mathbf{g}, e, \mathbf{R}, \mathbf{P}, E\}$ of the relevant variables.

The entropy is defined as the result of evaluating the entropy functional (22.4) at the relevant ensemble (12.4). By inserting the relevant ensemble Eq. (12.4) in (22.4), we obtain the *entropy functional* of the present level of description

$$S[a] = -\Phi[\lambda[a]] + \int d\mathbf{r}\, [\rho(\mathbf{r})\lambda_\rho(\mathbf{r}) + \mathbf{g}(\mathbf{r})\boldsymbol{\lambda}_g(\mathbf{r}) + \beta(\mathbf{r})e(\mathbf{r})] + \boldsymbol{\lambda}_R\cdot\mathbf{R} + \boldsymbol{\lambda}_P\cdot\mathbf{P} + \beta_\mathrm{s}E$$

where here the conjugate fields λ are to be understood as functionals of the average fields.

The functional derivatives of the entropy functional are given by

$$\frac{\delta S[a]}{\delta \rho(\mathbf{r})} = \lambda_\rho(\mathbf{r}) \qquad\qquad \frac{\partial S[a]}{\partial \mathbf{R}} = \boldsymbol{\lambda}_R$$

$$\frac{\delta S[a]}{\delta \mathbf{g}(\mathbf{r})} = \boldsymbol{\lambda}_g(\mathbf{r}) \qquad\qquad \frac{\partial S[a]}{\partial \mathbf{P}} = \boldsymbol{\lambda}_P$$

$$\frac{\delta S[a]}{\delta e(\mathbf{r})} = \beta(\mathbf{r}) \qquad\qquad \frac{\partial S[a]}{\partial E} = \beta_\mathrm{s}$$

which are conjugate of those in Eq. (22.4).

For future convenience, it is convenient to redefine the Lagrange multipliers by introducing the combinations

$$\nu(\mathbf{r}) = -\frac{\lambda_\rho(\mathbf{r})}{\beta(\mathbf{r})}$$

$$\mathbf{v}(\mathbf{r}) = -\frac{\boldsymbol{\lambda}_\mathbf{g}(\mathbf{r})}{\beta(\mathbf{r})}$$

and also the chemical potential per unit mass defined in terms of these new conjugate variables as

$$\mu(\mathbf{r}) = \nu(\mathbf{r}) + \frac{\mathbf{v}^2(\mathbf{r})}{2}$$

In terms of the new conjugate variables (11.2) the relevant ensemble takes the form

$$\overline{\rho}(z) = \frac{\rho_0}{\Xi[\lambda]} \exp\left\{ -\int d\mathbf{r}\beta(\mathbf{r}) \left(\hat{e}_\mathbf{r} - \nu(\mathbf{r})\hat{\rho}_\mathbf{r} - \mathbf{v}(\mathbf{r})\cdot\hat{\mathbf{g}}_\mathbf{r}\right) - \boldsymbol{\lambda}_R\cdot\hat{\mathbf{R}} - \boldsymbol{\lambda}_P\cdot\hat{\mathbf{P}} - \beta_\mathrm{s}\hat{E} \right\}$$

where dimensionless generalized partition function is

$$\Xi[\lambda] \equiv \sum_{N=0}^{\infty} \frac{1}{N!} \int \frac{dz}{h^{3N}} \exp\left\{ -\sum_{i}^{N} \beta(\mathbf{q}_i)(e_i - \nu(\mathbf{q}_i)m - \mathbf{v}(\mathbf{q}_i)\cdot\mathbf{p}_i) - \sum_{i'}^{N'} \left(\beta_\mathrm{s}e_{i'} + \boldsymbol{\lambda}_R\cdot\frac{m'}{M'}\hat{\mathbf{q}}_{i'} + \boldsymbol{\lambda}_P\cdot\hat{\mathbf{p}}_{i'}\right) \right\}$$

The Gaussian momentum integrals in this generalized partition function (recall that $e_i, e_{i'}$ in (11.1.1) has quadratic momenta) are easily performed with the result

$$\Xi[\lambda] \equiv \sum_{N=0}^{\infty} \frac{1}{N!} \int \prod_{i}^{N} \frac{d\mathbf{q}_i}{\Lambda_\mathrm{f}^3(\mathbf{q}_i)} \int \prod_{i'}^{N'} \frac{d\mathbf{q}_{i'}}{\Lambda_\mathrm{s}^3} \exp\left\{ -\sum_{j}^{N} \beta(\mathbf{q}_j)\phi_j + \sum_{i}^{N} m\beta(\mathbf{q}_i)\mu(\mathbf{q}_i) - \boldsymbol{\lambda}_R\cdot\hat{\mathbf{R}} + \frac{M'}{2\beta_\mathrm{s}}\boldsymbol{\lambda}_P^2 - \sum_{j'}^{N'} \beta_\mathrm{s}\phi_{j'} \right\}$$

where the *thermal wavelengths* are defined as

$$\Lambda_{\mathrm{f}}(\mathbf{r}) \equiv \left(\frac{h^2 \beta(\mathbf{r})}{2\pi m} \right)^{\frac{1}{2}}$$

$$\Lambda_{\mathrm{s}} \equiv \left(\frac{h^2 \beta_{\mathrm{s}}}{2\pi m'} \right)^{\frac{1}{2}}$$

11.2.1   Physical interpretation of the conjugate variables

We may take the derivative with respect to $\boldsymbol{\lambda_P}$ and the functional derivative with respect to $\mathbf{v}(\mathbf{r})$ of the thermodynamic potential (11.2.-1). By using (22.4), (11.2.-1) and (18.4) we obtain

$$\mathbf{v}(\mathbf{r}) = \frac{\mathbf{g}(\mathbf{r})}{\rho(\mathbf{r})}$$

$$\boldsymbol{\lambda_P} = -\beta_{\mathrm{s}} \mathbf{V}$$

These equations allow one to interprete the conjugate variables $\mathbf{v}(\mathbf{r}), \boldsymbol{\lambda_P}$ in terms of the fluid and solid velocities respectively.

We may also obtain a physical interpretation for the Lagrange multiplier $\beta(\mathbf{r})$. The functional derivative in (22.4) becomes

$$e(\mathbf{r}) = \frac{3n(\mathbf{r})}{2\beta(\mathbf{r})} + \phi(\mathbf{r})$$

where we have introduced the average number density field and average potential energy field as

$$n(\mathbf{r}) = \mathrm{Tr} \left[\overline{\rho} \sum_i^N \delta(\mathbf{r} - \mathbf{q}_i) \right]$$

$$\phi(\mathbf{r}) = \mathrm{Tr} \left[\overline{\rho} \sum_i^N \phi_i \delta(\mathbf{r} - \mathbf{q}_i) \right]$$

It is natural to define the average kinetic energy field as $k(\mathbf{r}) = e(\mathbf{r}) - \phi(\mathbf{r})$, in such a way that the physical meaning of the Lagrange multiplier $\beta(\mathbf{r})$ becomes transparent as proportional to the inverse of the kinetic energy field. Note that we may introduce the microscopic kinetic density field as

$$\hat{k}_{\mathbf{r}}(z) = \sum_i^N \frac{\mathbf{p}_i^2}{2m} \delta(\mathbf{r} - \mathbf{q}_i)$$

and, therefore,

$$k(\mathbf{r}) = \langle \hat{k}_{\mathbf{r}} \rangle^\lambda = \frac{3n(\mathbf{r})}{2\beta(\mathbf{r})}$$

While this expression illuminates the physical meaning of the conjugate variable $\beta(\mathbf{r})$ as an inverse temperature, the utility of this expression to calculate $\beta(\mathbf{r})$ in MD simulations is hampered by the fact that one needs to perform an average of the kinetic energy density with the relevant ensemble.

Finally, note that, as shown in Eq. (11.10) in the Appendix, it is also possible to give a physical interpretation to the conjugate variable $\boldsymbol{\lambda}_R$ in terms of the force that the fluid exerts on the solid

$$-\int d\mathbf{r} \left[\frac{\beta(\mathbf{r}) + \beta_{\mathrm{s}}}{2} \right] \mathbf{F}(\mathbf{r}) = \boldsymbol{\lambda}_R$$

that shows the close connection of the conjugate variable $\boldsymbol{\lambda}_R$ with the force that the solid exerts on the fluid. The functional derivatives (22.4) of the entropy functional when we use the redefinitions (11.2), (11.2), and (11.2.1) are

$$\frac{\delta S[a]}{\delta\rho(\mathbf{r})} = -\beta(\mathbf{r}) \left(\mu(\mathbf{r}) - \frac{\mathbf{v}^2(\mathbf{r})}{2} \right) \qquad\qquad \frac{\partial S[a]}{\partial\mathbf{R}} = \boldsymbol{\lambda}_R$$

$$\frac{\delta S[a]}{\delta\mathbf{g}(\mathbf{r})} = -\beta(\mathbf{r})\mathbf{v}(\mathbf{r}) \qquad\qquad\qquad \frac{\partial S[a]}{\partial\mathbf{P}} = -\beta_{\mathrm{s}}\mathbf{V}$$

$$\frac{\delta S[a]}{\delta e(\mathbf{r})} = \beta(\mathbf{r}) \qquad\qquad\qquad\qquad \frac{\partial S[a]}{\delta E} = \beta_{\mathrm{s}}$$

11.2.2   The rest thermodynamic potential and entropy

The relevant ensemble (11.2) is Gaussian in momenta, as the energy density contains a quadratic kinetic energy but it does not give zero average momenta, because of the linear terms in the momentum density variable. For this reason it is convenient to use the Galilean operator that transforms the relevant ensemble into a Gaussian centered around zero momenta. The action of the Galilean operator on the relevant ensemble is obtained from its action (11.1.3) on the relevant variables. We will denote

$$\overline{\rho}^{\,\mathrm{rest}}(z) = \mathscr{G}^{-1}\overline{\rho}(z)$$

and refer to $\overline{\rho}^{\,\mathrm{rest}}(z)$ as the comoving ensemble or ensemble at rest. Its explicit form is

$$\overline{\rho}^{\,\mathrm{rest}}(z) = \frac{\rho_0}{\Xi_{\mathrm{rest}}[\lambda]} \exp\left\{ -\int d\mathbf{r}\beta(\mathbf{r}) \left(\hat{e}_{\mathbf{r}} - \mu(\mathbf{r})\hat{\rho}_{\mathbf{r}} \right) - \boldsymbol{\lambda}_R \cdot \hat{\mathbf{R}} - \beta_{\mathrm{s}}\hat{E} \right\}$$

The ensemble (11.2.2) is quadratic, with no linear terms, in the microscopic momenta $\mathbf{p}_i, \mathbf{p}_{i'}$. This fact makes convenient the use of the rest ensemble when computing averages of phase functions involving momentum variables.

We may express the averages of the relvant variables in terms of averages over the

rest ensemble

$$\rho(\mathbf{r}) = \text{Tr}\left[\overline{\rho}\hat{\rho}_{\mathbf{r}}\right] = \text{Tr}\left[\overline{\rho}_{\text{rest}}\mathscr{G}^{-1}\hat{\rho}_{\mathbf{r}}\right] = \text{Tr}\left[\overline{\rho}_{\text{rest}}\hat{\rho}_{\mathbf{r}}\right]$$

$$e(\mathbf{r}) = \text{Tr}\left[\overline{\rho}\hat{e}_{\mathbf{r}}\right] = \text{Tr}\left[\overline{\rho}_{\text{rest}}\mathscr{G}^{-1}\hat{e}_{\mathbf{r}}\right] = \text{Tr}\left[\overline{\rho}_{\text{rest}}\hat{e}_{\mathbf{r}}\right] + \frac{\mathbf{v}^2(\mathbf{r})}{2}\rho(\mathbf{r})$$

$$\mathbf{R} = \text{Tr}\left[\overline{\rho}\hat{\mathbf{R}}\right] = \text{Tr}\left[\overline{\rho}_{\text{rest}}\mathscr{G}^{-1}\hat{\mathbf{R}}\right] = \text{Tr}\left[\overline{\rho}_{\text{rest}}\hat{\mathbf{R}}\right]$$

$$E = \text{Tr}\left[\overline{\rho}\hat{E}\right] = \text{Tr}\left[\overline{\rho}_{\text{rest}}\mathscr{G}^{-1}\hat{E}\right] = \text{Tr}\left[\overline{\rho}_{\text{rest}}\hat{E}\right] + \frac{M\mathbf{V}^2}{2}$$

These equations can be written in the form

$$\rho(\mathbf{r}) = \text{Tr}\left[\overline{\rho}_{\text{rest}}\hat{\rho}_{\mathbf{r}}\right] \qquad\qquad \mathbf{R} = \text{Tr}\left[\overline{\rho}_{\text{rest}}\hat{\mathbf{R}}\right]$$

$$\epsilon(\mathbf{r}) = \text{Tr}\left[\overline{\rho}_{\text{rest}}\hat{e}_{\mathbf{r}}\right] \qquad\qquad U = \text{Tr}\left[\overline{\rho}_{\text{rest}}\hat{E}\right]$$

where we have introduced the internal energy of the fluid and solid as

$$\epsilon(\mathbf{r}) = e(\mathbf{r}) - \frac{\mathbf{g}^2(\mathbf{r})}{2\rho(\mathbf{r})}$$

$$U = E - \frac{\mathbf{P}^2}{2M}$$

Because the relevant ensemble at rest $\overline{\rho}_{\text{rest}}$ depends on the conjugate variables $\mu(\mathbf{r}), \beta(\mathbf{r}), \boldsymbol{\lambda}_R, \beta_{\text{s}}$, Eqs (11.10) show that there is a one to one connection between these conjugate variables and the variables $\rho(\mathbf{r}), \epsilon(\mathbf{r}), \mathbf{R}, U$. This suggests to work with the internal energy variables $\epsilon(\mathbf{r}), U$ instead of the energy variables $e(\mathbf{r}), E$, because the conjugate variables depend directly on such internal energies.

The normalization of (11.2.2) is given, after momentum integration, by

$$\Xi_{\text{rest}}[\mu, \beta, \boldsymbol{\lambda}_R, \beta_{\text{s}}] = \sum_{N=0}^{\infty} \frac{1}{N!} \int \prod_i^N \frac{d\mathbf{q}_i}{\Lambda_{\text{f}}^3(\mathbf{q}_i)} \int \prod_{i'}^{N'} \frac{d\mathbf{q}_{i'}}{\Lambda_{\text{s}}^3} \exp\left\{ -\sum_j^N \beta(\mathbf{q}_j)\phi_j + \sum_i^N m\beta(\mathbf{q}_i)\mu(\mathbf{q}_i) - \boldsymbol{\lambda}_R\cdot\hat{\mathbf{R}} - \sum_{j'}^{N'} \beta_{\text{s}}\phi_{j'} \right\}$$

The corresponding thermodynamic potential is given by

$$\Phi_{\text{rest}}[\mu, \beta, \boldsymbol{\lambda}_R, \beta_{\text{s}}] = -\ln\Xi_{\text{rest}}[\mu, \beta, \boldsymbol{\lambda}_R, \beta_{\text{s}}]$$

Eqs (11.10) can be written as the derivatives of the rest thermodynamic potential

$$\rho(\mathbf{r}) = -\frac{\delta\Phi_{\text{rest}}}{\delta\beta\mu(\mathbf{r})} \qquad\qquad \mathbf{R} = \frac{\partial\Phi_{\text{rest}}}{\partial\boldsymbol{\lambda}_R}$$

$$\epsilon(\mathbf{r}) = \frac{\delta\Phi_{\text{rest}}}{\delta\beta(\mathbf{r})} \qquad\qquad U = \frac{\partial\Phi_{\text{rest}}}{\partial\beta_{\text{s}}}$$

to be compared with (22.4).

The Legendre transform of the grand potential for a simple liquid gives the classic (free energy) density functional and we may pursue now the same route in order to define the (non-isothermal) free energy density functional for a fluid in the presence of a solid sphere. The dimensionless free energy functional is

$$F_{\text{rest}}[\rho, \beta, \mathbf{R}, \beta_{\text{s}}] = \Phi_{\text{rest}}[\mu, \beta, \boldsymbol{\lambda}_R, \beta_{\text{s}}] + \int d\mathbf{r}\beta(\mathbf{r})\mu(\mathbf{r})\rho(\mathbf{r}) - \boldsymbol{\lambda}_R \mathbf{R}$$

In the completely isothermal case, where the inverse temperature field $\beta(\mathbf{r}) = \beta_{\text{s}}$ is constant in space, the thermodynamic potential $\Phi^{\text{rest}}[\lambda]$ becomes the usual canonical thermodynamic potential of a fluid, except for the presence of the solid degrees of freedom and the corresponding conjugate variable $\boldsymbol{\lambda}_R$. The free energy functional (11.2.2), when the system is isothermal (the temperature fields are constant and equal to each other), coincides with the free energy functional of a structured fluid familiar from Density Functional Theory. The rest entropy, which is defined as the corresponding Legendre transform with respect to the energy variables is

$$S_{\text{rest}}[\rho, \epsilon, \mathbf{R}, U] = -F_{\text{rest}}[\rho, \beta, \mathbf{R}, \beta_{\text{s}}] + \int d\mathbf{r}\beta(\mathbf{r})\epsilon(\mathbf{r}) + \beta_{\text{s}}U$$

Recall that here, $\beta(\mathbf{r}), \beta_{\text{s}}$ are understood as functions of $\rho(\mathbf{r}), \epsilon(\mathbf{r}), \mathbf{R}, U$ and, therefore, the entropy depends also on this set of four variables (and not on velocity variables). The derivatives of the entropy are given by

$$\frac{\delta S_{\text{rest}}}{\delta\rho(\mathbf{r})} = -\beta(\mathbf{r})\mu(\mathbf{r}) \qquad\qquad \frac{\partial S_{\text{rest}}}{\partial\mathbf{R}} = \boldsymbol{\lambda}_R(\mathbf{r})$$

$$\frac{\delta S_{\text{rest}}}{\delta\epsilon(\mathbf{r})} = \beta(\mathbf{r}) \qquad\qquad \frac{\partial S_{\text{rest}}}{\partial U} = \beta_{\text{s}}$$

to be compared with (22.4).

By comparing the partition functions (18.4) with (11.2.2) we conclude that the corresponding thermodynamic potentials are related by

$$\Phi[\lambda] = \Phi_{\text{rest}}[\lambda] - \beta_{\text{s}}\frac{M'}{2}\mathbf{V}^2$$

The entropy (22.4) and (11.2) is easily computed with the result

$$S[\rho, e, \mathbf{R}, E] = S_{\text{rest}}[\rho, \epsilon, \mathbf{R}, U] - \int d\mathbf{r}\beta(\mathbf{r})\frac{\mathbf{g}^2(\mathbf{r})}{2\rho(\mathbf{r})} - \beta_{\text{s}}\frac{M'}{2}\mathbf{V}^2$$

where the total entropy is separated into velocity dependent, kinetic energy terms, and the entropy at rest. Note that if we take the deriatives of the entropy (11.2.2) and use (11.2.2) we recover (11.2.1) as we should.

11.3   The reversible part of the dynamics

We consider in this subsection the reversible part $v_i(t)$ in Eq. (12.2) for the case that the CG variables are (11.1.1). The reversible part of the dynamics has the form

$$\partial_t \rho(\mathbf{r})\big|_{\text{rev}} = \text{Tr}[\overline{\rho}_t i\mathcal{L}\hat{\rho}_{\mathbf{r}}] \qquad\qquad \partial_t\,\mathbf{R}\big|_{\text{rev}} = \text{Tr}[\overline{\rho}_t i\mathcal{L}\hat{\mathbf{R}}]$$

$$\partial_t\mathbf{g}(\mathbf{r})\big|_{\text{rev}} = \text{Tr}[\overline{\rho}_t i\mathcal{L}\hat{\mathbf{g}}_{\mathbf{r}}] \qquad\qquad \partial_t\,\mathbf{P}\big|_{\text{rev}} = \text{Tr}[\overline{\rho}_t i\mathcal{L}\hat{\mathbf{P}}]$$

$$\partial_t e(\mathbf{r})\big|_{\text{rev}} = \text{Tr}[\overline{\rho}_t i\mathcal{L}\hat{e}_{\mathbf{r}}] \qquad\qquad \partial_t E\big|_{\text{rev}} = \text{Tr}[\overline{\rho}_t i\mathcal{L}\hat{E}]$$

For the mass density we have

$$\partial_t \rho(\mathbf{r}, t)\big|_{\text{rev}} = \text{Tr}[\overline{\rho}_t i\mathcal{L}\hat{\rho}_{\mathbf{r}}] = -\boldsymbol{\nabla}\!\cdot\!\mathbf{g}(\mathbf{r}, t)$$

where we have used Eq. (11.1.2) and the fact that the relevant ensemble average of $\hat{\mathbf{g}}_{\mathbf{r}}$ is precisely the momentum density field $\mathbf{g}(\mathbf{r}, t)$.

In order to compute the right hand side of the rest of equations, we consider the Galilean change of variables

$$\text{Tr}[\overline{\rho}_t i\mathcal{L}A] = \text{Tr}\left[\overline{\rho}^{\text{rest}}\left(\mathscr{G}^{-1}i\mathcal{L}A\right)\right]$$

because, as we know, the ensemble $\overline{\rho}^{\text{rest}}$ is Gaussian in momenta with zero momentum averages.

The reversible part of the momentum density evolution equation is

$$\partial_t\mathbf{g}(\mathbf{r})\big|_{\text{rev}} = \text{Tr}[\overline{\rho}_t i\mathcal{L}\hat{\mathbf{g}}_{\mathbf{r}}] = -\boldsymbol{\nabla}\text{Tr}\left[\overline{\rho}_t^{\text{rest}}\left(\mathscr{G}^{-1}\hat{\boldsymbol{\sigma}}_{\mathbf{r}}\right)\right] + \text{Tr}\left[\overline{\rho}_t\hat{\mathbf{F}}_{\mathbf{r}}\right]$$

$$= -\boldsymbol{\nabla}\!\cdot\!\mathbf{v}(\mathbf{r})\mathbf{g}(\mathbf{r}) - \boldsymbol{\nabla}\text{Tr}\left[\overline{\rho}_t^{\text{rest}}\hat{\boldsymbol{\sigma}}_{\mathbf{r}}\right] + \text{Tr}\left[\overline{\rho}_t^{\text{rest}}\hat{\mathbf{F}}_{\mathbf{r}}\right]$$

$$= -\boldsymbol{\nabla}\!\cdot\!\mathbf{v}(\mathbf{r})\mathbf{g}(\mathbf{r}) - \boldsymbol{\nabla}\!\cdot\!\boldsymbol{\sigma}(\mathbf{r}) + \mathbf{F}(\mathbf{r})$$

where we have introduced the rest average of the stress tensor (that shortly will be seen to be the local pressure)

$$\boldsymbol{\sigma}(\mathbf{r}) \equiv \text{Tr}\left[\overline{\rho}_t^{\text{rest}}\hat{\boldsymbol{\sigma}}_{\mathbf{r}}\right]$$

$$\mathbf{F}(\mathbf{r}) \equiv \text{Tr}\left[\overline{\rho}_t^{\text{rest}}\hat{\mathbf{F}}_{\mathbf{r}}\right]$$

The fluid energy equation has the reversible part

$$\partial_t e(\mathbf{r})\big|_{\text{rev}} = \text{Tr}\left[\overline{\rho}_t^{\text{rest}}\mathscr{G}^{-1}\left(-\nabla\hat{\mathbf{Q}}_{\mathbf{r}} + \hat{\pi}_{\mathbf{r}}\right)\right] = -\boldsymbol{\nabla}\!\cdot\!\text{Tr}\left[\overline{\rho}_t^{\text{rest}}\mathscr{G}^{-1}\hat{\mathbf{Q}}_{\mathbf{r}}\right] + \text{Tr}\left[\overline{\rho}_t^{\text{rest}}\mathscr{G}^{-1}\hat{\pi}_{\mathbf{r}}\right]$$

$$= -\boldsymbol{\nabla}\!\cdot\!\text{Tr}\left[\overline{\rho}_t^{\text{rest}}\left(\hat{\mathbf{Q}}_{\mathbf{r}} + \Delta\hat{\boldsymbol{\sigma}}_{\mathbf{r}} + \mathbf{v}(\mathbf{r})\mathscr{G}^{-1}\hat{e}_{\mathbf{r}} + \frac{\mathbf{v}^2(\mathbf{r})}{2}\hat{\mathbf{g}}_{\mathbf{r}}\right)\right] + \text{Tr}\left[\overline{\rho}_t^{\text{rest}}\left(\hat{\pi}_{\mathbf{r}} + \frac{\mathbf{v}(\mathbf{r})+\mathbf{V}}{2}\hat{\mathbf{F}}_{\mathbf{r}}\right)\right]$$

$$= -\boldsymbol{\nabla}\!\cdot\!\mathbf{v}(\mathbf{r})e(\mathbf{r}) - \boldsymbol{\nabla}\!\cdot\!\Delta\boldsymbol{\sigma}(\mathbf{r}) + \frac{\mathbf{v}(\mathbf{r})+\mathbf{V}}{2}\mathbf{F}(\mathbf{r})$$

where we have used that $\mathscr{G}^{-1}\hat{\mathbf{Q}}_{\mathbf{r}}, \mathscr{G}^{-1}\hat{\pi}_{\mathbf{r}}$ are odd functions of momenta, while the rest

ensemble is Gaussian with zero mean. We have introduced

$$\Delta\boldsymbol{\sigma}(\mathbf{r}) \equiv \mathrm{Tr}\left[\overline{\rho}_t^{\mathrm{rest}}\Delta\hat{\boldsymbol{\sigma}}_{\mathbf{r}}\right]$$

In summary, the exact reversible part of the dynamics is given by the set of equations

$$\partial_t \rho(\mathbf{r})\big|_{\mathrm{rev}} = -\boldsymbol{\nabla}\cdot\mathbf{g}(\mathbf{r})$$
$$\partial_t \mathbf{g}(\mathbf{r})\big|_{\mathrm{rev}} = -\boldsymbol{\nabla}\cdot\mathbf{v}(\mathbf{r})\mathbf{g}(\mathbf{r}) - \boldsymbol{\nabla}\cdot\boldsymbol{\sigma}(\mathbf{r}) + \mathbf{F}(\mathbf{r})$$
$$\partial_t e(\mathbf{r})\big|_{\mathrm{rev}} = -\boldsymbol{\nabla}\cdot\mathbf{v}(\mathbf{r})e(\mathbf{r}) - \boldsymbol{\nabla}\cdot\boldsymbol{\sigma}(\mathbf{r})\cdot\mathbf{v}(\mathbf{r}) - \boldsymbol{\nabla}\cdot\Delta\boldsymbol{\sigma}(\mathbf{r}) + \left(\frac{\mathbf{v}(\mathbf{r})+\mathbf{V}}{2}\right)\cdot\mathbf{F}(\mathbf{r})$$
$$\partial_t \left.\mathbf{R}\right|_{\mathrm{rev}} = \mathbf{V}$$
$$\partial_t \left.\mathbf{P}\right|_{\mathrm{rev}} = -\int d\mathbf{r}\mathbf{F}(\mathbf{r})$$
$$\partial_t E\big|_{\mathrm{rev}} = -\int d\mathbf{r}\left(\frac{\mathbf{v}(\mathbf{r})+\mathbf{V}}{2}\right)\cdot\mathbf{F}(\mathbf{r})$$

The internal energy variables (11.2.2) evolve according to the following equations

$$\partial_t \epsilon(\mathbf{r})\big|_{\mathrm{rev}} = \partial_t e(\mathbf{r}) - \mathbf{v}(\mathbf{r})\cdot\partial_t \mathbf{g}(\mathbf{r}) + \frac{\mathbf{v}^2(\mathbf{r})}{2}\partial_t\rho(\mathbf{r})$$
$$= -\boldsymbol{\nabla}\cdot(\mathbf{v}(\mathbf{r})e(\mathbf{r})) - \boldsymbol{\nabla}\cdot\boldsymbol{\sigma}(\mathbf{r})\cdot\mathbf{v}(\mathbf{r}) - \boldsymbol{\nabla}\cdot\Delta\boldsymbol{\sigma}(\mathbf{r}) + \left(\frac{\mathbf{v}(\mathbf{r})+\mathbf{V}}{2}\right)\mathbf{F}(\mathbf{r})$$
$$- \mathbf{v}(\mathbf{r})\cdot[-\boldsymbol{\nabla}\cdot(\mathbf{v}(\mathbf{r})\mathbf{g}(\mathbf{r})) - \boldsymbol{\nabla}\cdot\boldsymbol{\sigma}(\mathbf{r}) + \mathbf{F}(\mathbf{r})] - \frac{\mathbf{v}^2(\mathbf{r})}{2}\boldsymbol{\nabla}\cdot\mathbf{g}(\mathbf{r})$$
$$= -\boldsymbol{\nabla}\cdot\mathbf{v}(\mathbf{r})\left(\epsilon(\mathbf{r}) + \frac{\mathbf{g}^2(\mathbf{r})}{2\rho(\mathbf{r})}\right) - \boldsymbol{\sigma}(\mathbf{r}):\boldsymbol{\nabla}\mathbf{v}(\mathbf{r}) - \boldsymbol{\nabla}\cdot\Delta\boldsymbol{\sigma}(\mathbf{r}) + \left(\frac{\mathbf{V}-\mathbf{v}(\mathbf{r})}{2}\right)\mathbf{F}(\mathbf{r})$$
$$- \mathbf{v}(\mathbf{r})\cdot[-\boldsymbol{\nabla}\cdot(\mathbf{v}(\mathbf{r})\mathbf{g}(\mathbf{r}))] - \frac{\mathbf{v}^2(\mathbf{r})}{2}\boldsymbol{\nabla}\cdot\mathbf{g}(\mathbf{r})$$
$$= -\boldsymbol{\nabla}\cdot\mathbf{v}(\mathbf{r})\epsilon(\mathbf{r}) - \boldsymbol{\sigma}(\mathbf{r}):\boldsymbol{\nabla}\mathbf{v}(\mathbf{r}) - \boldsymbol{\nabla}\cdot\Delta\boldsymbol{\sigma}(\mathbf{r}) + \left(\frac{\mathbf{V}-\mathbf{v}(\mathbf{r})}{2}\right)\mathbf{F}(\mathbf{r})$$

and

$$\partial_t U\big|_{\mathrm{rev}} = \int d\mathbf{r}\left(\frac{\mathbf{v}(\mathbf{r})-\mathbf{V}}{2}\right)\mathbf{F}(\mathbf{r})$$

which have the virtue of being manifestly Galilean invariant.

11.3.1   Entropy conservation under the reversible dynamics

[Finish to see whether the term $\Delta\boldsymbol{\sigma}_{\mathbf{r}}$ can be neglected or not!]

We now show that the entropy is conserved by the reversible dynamics. The time

derivative of the entropy function is given by the chain rule

$$\frac{dS}{dt}[a] = \frac{\partial S}{\partial a}\dot{a} = \lambda\dot{a}$$

which in the present level of description becomes, by using (11.2.1) and (11.3)

$$\frac{dS}{dt} = \int d\mathbf{r}\beta(\mathbf{r})\left(\mu(\mathbf{r}) - \frac{\mathbf{v}^2(\mathbf{r})}{2}\right)\boldsymbol{\nabla}\rho(\mathbf{r})\mathbf{v}(\mathbf{r}) + \int d\mathbf{r}\beta(\mathbf{r})\mathbf{v}(\mathbf{r})\left[\boldsymbol{\nabla}\mathbf{v}(\mathbf{r})\mathbf{g}(\mathbf{r}) + \boldsymbol{\nabla}\boldsymbol{\sigma}(\mathbf{r}) - \mathbf{F}(\mathbf{r})\right]$$
$$+ \int d\mathbf{r}\beta(\mathbf{r})\left[-\boldsymbol{\nabla}\cdot\mathbf{v}(\mathbf{r})e(\mathbf{r}) - \textcolor{red}{\boldsymbol{\nabla}\cdot\Delta\boldsymbol{\sigma}(\mathbf{r})} + \frac{\mathbf{v}(\mathbf{r}) + \mathbf{V}}{2}\mathbf{F}(\mathbf{r})\right]$$
$$+ \boldsymbol{\lambda}_R\mathbf{V} + \int d\mathbf{r}\mathbf{F}(\mathbf{r})\beta_s\mathbf{V} - \beta_s\int d\mathbf{r}\frac{\mathbf{v}(\mathbf{r}) + \mathbf{V}}{2}\mathbf{F}(\mathbf{r})$$

This is

$$\frac{dS}{dt} = \int d\mathbf{r}\mathbf{v}(\mathbf{r})\cdot\left[-\rho(\mathbf{r})\boldsymbol{\nabla}\left(\beta(\mathbf{r})\mu(\mathbf{r})\right) + e(\mathbf{r})\boldsymbol{\nabla}\beta(\mathbf{r})\right] + \int d\mathbf{r}\beta(\mathbf{r})\left[\mathbf{v}(\mathbf{r})\cdot\boldsymbol{\nabla}\cdot\boldsymbol{\sigma}(\mathbf{r}) - \boldsymbol{\nabla}\cdot\Delta\boldsymbol{\sigma}(\mathbf{r})\right]$$
$$+ \int d\mathbf{r}\beta(\mathbf{r})\left[\frac{\mathbf{v}(\mathbf{r}) + \mathbf{V}}{2}\mathbf{F}(\mathbf{r}) - \mathbf{v}(\mathbf{r})\mathbf{F}(\mathbf{r})\right]$$
$$+ \boldsymbol{\lambda}_R\mathbf{V} + \int d\mathbf{r}\mathbf{F}(\mathbf{r})\beta_s\mathbf{V} - \beta_s\int d\mathbf{r}\frac{\mathbf{v}(\mathbf{r}) + \mathbf{V}}{2}\mathbf{F}(\mathbf{r})$$

i.e.

$$\frac{dS}{dt} = \int d\mathbf{r}\mathbf{v}(\mathbf{r})\cdot\left[-\rho(\mathbf{r})\boldsymbol{\nabla}\left(\beta(\mathbf{r})\mu(\mathbf{r})\right) + e(\mathbf{r})\boldsymbol{\nabla}\beta(\mathbf{r})\right] + \int d\mathbf{r}\beta(\mathbf{r})\left[\mathbf{v}(\mathbf{r})\cdot\boldsymbol{\nabla}\cdot\boldsymbol{\sigma}(\mathbf{r}) - \boldsymbol{\nabla}\cdot\Delta\boldsymbol{\sigma}(\mathbf{r})\right]$$
$$+ \int d\mathbf{r}\frac{\beta(\mathbf{r}) + \beta_s}{2}\left(\mathbf{V} - \mathbf{v}(\mathbf{r})\right)\cdot\mathbf{F}(\mathbf{r}) + \boldsymbol{\lambda}_R\mathbf{V}$$

Now, we introduce in this expression the exact translation invariance identity (11.10)

$$\frac{dS}{dt} = -\int d\mathbf{r}\left(\mathbf{V} - \mathbf{v}(\mathbf{r})\right)\cdot\left[-\rho(\mathbf{r})\boldsymbol{\nabla}\left(\beta(\mathbf{r})\mu(\mathbf{r})\right) + e(\mathbf{r})\boldsymbol{\nabla}\beta(\mathbf{r}) - \frac{\beta(\mathbf{r}) + \beta_s}{2}\mathbf{F}(\mathbf{r})\right] + \int d\mathbf{r}\beta(\mathbf{r})\left[\mathbf{v}(\mathbf{r})\cdot\boldsymbol{\nabla}\cdot\boldsymbol{\sigma}(\mathbf{r}) - \boldsymbol{\nabla}\cdot\Delta\boldsymbol{\sigma}(\mathbf{r})\right]$$

Then, by using the exact Gibbs-Duhem identity (11.9.1) we obtain

$$\frac{dS}{dt} = \int d\mathbf{r}\left(\mathbf{V} - \mathbf{v}(\mathbf{r})\right)\cdot\boldsymbol{\nabla}\beta(\mathbf{r})\tilde{\boldsymbol{\sigma}}(\mathbf{r}) + \int d\mathbf{r}\beta(\mathbf{r})\left[\mathbf{v}(\mathbf{r})\cdot\boldsymbol{\nabla}\cdot\boldsymbol{\sigma}(\mathbf{r}) - \boldsymbol{\nabla}\cdot\Delta\boldsymbol{\sigma}(\mathbf{r})\right]$$
$$= -\int d\mathbf{r}\mathbf{v}(\mathbf{r})\cdot\boldsymbol{\nabla}\beta(\mathbf{r})\tilde{\boldsymbol{\sigma}}(\mathbf{r}) + \int d\mathbf{r}\beta(\mathbf{r})\left[\mathbf{v}(\mathbf{r})\cdot\boldsymbol{\nabla}\cdot\boldsymbol{\sigma}(\mathbf{r}) - \boldsymbol{\nabla}\cdot\Delta\boldsymbol{\sigma}(\mathbf{r})\right]$$

Note that in the smooth approximation (11.10), this becomes

$$\frac{dS}{dt} = -\int d\mathbf{r}\mathbf{v}(\mathbf{r})\cdot\boldsymbol{\nabla}\beta(\mathbf{r})\boldsymbol{\sigma}(\mathbf{r}) + \int d\mathbf{r}\beta(\mathbf{r})\left[\mathbf{v}(\mathbf{r})\cdot\boldsymbol{\nabla}\cdot\boldsymbol{\sigma}(\mathbf{r}) - \boldsymbol{\nabla}\cdot\boldsymbol{\sigma}(\mathbf{r})\cdot\mathbf{v}(\mathbf{r})\right] = 0$$

We can show that even in the case that we do not use the smooth approximation, the entropy is conserved by the dynamics. We have to focus only on the virial part, because for the kinetic part of the different tensor the smooth approximation is actually exact. **[Finish]**

11.4   Irreversible part of the dynamics

While the reversible part of the dynamics (11.3) is exact, the irreversible part that we consider in this paper is approximate because we assume that the system is governed by Markovian dynamics. Under the Markovian approximation in which the memory kernel is assumed to decay in a time scale short as compared to the time scales of the hydrodynamic variables, the irreversible dynamics is given by the term $\sum_j D_{ij}\lambda_j$ in Eq. (12.2). Because the time derivatives of $\rho(\mathbf{r})$ and $\mathbf{R}$ are given in terms of momenta, which are relevant variables themselves, the effect of the projection operator in (20.2.1) is simply $\mathscr{Q}i\mathcal{L}\rho_{\mathbf{r}} = 0$ and $\mathscr{Q}i\mathcal{L}\mathbf{R}_\mu = 0$ resulting in a large simplification of the friction matrix. Note that the elements of the friction matrix are given in terms of Green-Kubo expressions which are time integrals of correlation functions. Because the number of elements is quite large, it proves convenient to introduce the following notation for the Green-Kubo formula

$$\langle \hat{A} \,\|\, \hat{B}\rangle = \int_0^\infty dt' \langle \mathscr{Q}\hat{A}(t')\mathscr{Q}\hat{B}\rangle^\lambda$$

In this way, we may write, for example

$$\langle \hat{\boldsymbol{\sigma}}_{\mathbf{r}}^{\mu\nu} \,\|\, \hat{\boldsymbol{\sigma}}_{\mathbf{r}'}^{\mu'\nu'}\rangle = \int_0^\infty dt' \langle \mathscr{Q}\hat{\boldsymbol{\sigma}}_{\mathbf{r}}^{\mu\nu}(t')\mathscr{Q}\hat{\boldsymbol{\sigma}}_{\mathbf{r}'}^{\mu'\nu'}\rangle^\lambda$$

We will also introduce the Green-Kubo expression *at rest* as

$$\langle \hat{A} \,\|\, \hat{B}\rangle^0 = \int_0^\infty dt' \left\langle \left(\mathscr{Q}\mathscr{G}\hat{A}(t')\right)\left(\mathscr{Q}\mathscr{G}\hat{B}\right)\right\rangle^\lambda$$

where the phase functions are acted upon with the Galilean operator. By using the properties (11.1.3) of the Galilean operator and the definition (11.2.2) of the comoving relevant ensemble, we note that

$$\langle \hat{A} \,\|\, \hat{B}\rangle^0 = \int_0^\infty dt' \text{Tr}\left[\overline{\rho}_{\text{rest}}\left(\mathscr{Q}\hat{A}(t')\right)\left(\mathscr{Q}\hat{B}\right)\right]$$

While the Green-Kubo coefficients (11.4) depend, in general on the full set of conjugate variables $\lambda_\rho, \mathbf{v}, \beta, \boldsymbol{\lambda}_R, \mathbf{V}, \beta_s$, the rest Green-Kubo coefficient (11.4) only depends on the conjugate variables $\mu, \beta, \boldsymbol{\lambda}_R, \beta_s$ implicit in the comoving ensemble $\overline{\rho}_{\text{rest}}$ and does not explicitly depend on velocity variables. Therefore, we will express the dynamics in terms of the transport coefficients at rest (11.4).

The irreversible part of the dynamics $\sum_j D_{ij}\lambda_j$ in Eq. (12.2) now takes the form

$$
\partial_t
\left.
\begin{pmatrix}
\rho(\mathbf{r}) \\[4pt]
\mathbf{g}(\mathbf{r}) \\[4pt]
e(\mathbf{r}) \\[4pt]
\mathbf{R} \\[4pt]
\mathbf{P} \\[4pt]
E
\end{pmatrix}
\right|_{\mathrm{irr}}
=
\begin{pmatrix}
0 & 0 & 0 & 0 & 0 & 0 \\[4pt]
0 & \int d\mathbf{r}'\langle \dot{\mathbf{g}}_{\mathbf{r}}\,\|\,\dot{\mathbf{g}}_{\mathbf{r}'}\rangle & \int d\mathbf{r}'\langle \dot{\mathbf{g}}_{\mathbf{r}}\,\|\,\dot{e}_{\mathbf{r}'}\rangle & 0 & \langle \dot{\mathbf{g}}_{\mathbf{r}}\,\|\,\dot{\mathbf{P}}\rangle & \langle \dot{\mathbf{g}}_{\mathbf{r}}\,\|\,\dot{E}\rangle \\[4pt]
0 & \int d\mathbf{r}'\langle \dot{e}_{\mathbf{r}}\,\|\,\dot{\mathbf{g}}_{\mathbf{r}'}\rangle & \int d\mathbf{r}'\langle \dot{e}_{\mathbf{r}}\,\|\,\dot{e}_{\mathbf{r}'}\rangle & 0 & \langle \dot{e}_{\mathbf{r}}\,\|\,\dot{\mathbf{P}}\rangle & \langle \dot{e}_{\mathbf{r}}\,\|\,\dot{E}\rangle \\[4pt]
0 & 0 & 0 & 0 & 0 & 0 \\[4pt]
0 & \int d\mathbf{r}'\langle \dot{\mathbf{P}}\,\|\,\dot{\mathbf{g}}_{\mathbf{r}'}\rangle & \int d\mathbf{r}'\langle \dot{\mathbf{P}}\,\|\,\dot{e}_{\mathbf{r}'}\rangle & 0 & \langle \dot{\mathbf{P}}\,\|\,\dot{\mathbf{P}}\rangle & \langle \dot{\mathbf{P}}\,\|\,\dot{E}\rangle \\[4pt]
0 & \int d\mathbf{r}'\langle \dot{E}\,\|\,\dot{\mathbf{g}}_{\mathbf{r}'}\rangle & \int d\mathbf{r}'\langle \dot{E}\,\|\,\dot{e}_{\mathbf{r}'}\rangle & 0 & \langle \dot{E}\,\|\,\dot{\mathbf{P}}\rangle & \langle \dot{E}\,\|\,\dot{E}\rangle
\end{pmatrix}
\begin{pmatrix}
\frac{\delta S}{\delta \rho_{\mathbf{r}'}} \\[4pt]
-\beta(\mathbf{r}')\mathbf{v}(\mathbf{r}') \\[4pt]
\beta(\mathbf{r}') \\[4pt]
\frac{\partial S}{\partial \mathbf{R}} \\[4pt]
-\beta_{\mathrm{s}}\mathbf{V} \\[4pt]
\beta_{\mathrm{s}}
\end{pmatrix}
$$

where we have used (11.2.1) for the derivatives of the entropy. The sum over the continuum "index" $\mathbf{r}$ becomes an integral. The domain of integration of this integral is $\mathbb{R}^3$, including the interior of the solid sphere. We have introduced the dot notation $\dot{\mathbf{g}}_{\mathbf{r}} = i\mathcal{L}\hat{\mathbf{g}}_{\mathbf{r}}$ to denote the action of the Liouville operator on the phase functions. By performing the matrix multiplication in (11.4) we arrive at the following set of equations

$$
\partial_t \mathbf{g}(\mathbf{r})|_{\mathrm{irr}} = -\int d\mathbf{r}'\langle \dot{\mathbf{g}}_{\mathbf{r}}\,\|\,\dot{\mathbf{g}}_{\mathbf{r}'}\rangle\beta(\mathbf{r}')\mathbf{v}(\mathbf{r}') + \int d\mathbf{r}'\langle \dot{\mathbf{g}}_{\mathbf{r}}\,\|\,\dot{e}_{\mathbf{r}'}\rangle\beta(\mathbf{r}') - \langle \dot{\mathbf{g}}_{\mathbf{r}}\,\|\,\dot{\mathbf{P}}\rangle\beta_{\mathrm{s}}\mathbf{V} + \langle \dot{\mathbf{g}}_{\mathbf{r}}\,\|\,\dot{E}\rangle\beta_{\mathrm{s}}
$$

$$
\partial_t e(\mathbf{r})|_{\mathrm{irr}} = -\int d\mathbf{r}'\langle \dot{e}_{\mathbf{r}}\,\|\,\dot{\mathbf{g}}_{\mathbf{r}'}\rangle\beta(\mathbf{r}')\mathbf{v}(\mathbf{r}') + \int d\mathbf{r}'\langle \dot{e}_{\mathbf{r}}\,\|\,\dot{e}_{\mathbf{r}'}\rangle\beta(\mathbf{r}') - \langle \dot{e}_{\mathbf{r}}\,\|\,\dot{\mathbf{P}}\rangle\beta_{\mathrm{s}}\mathbf{V} + \langle \dot{e}_{\mathbf{r}}\,\|\,\dot{E}\rangle\beta_{\mathrm{s}}
$$

$$
\left.\frac{d}{dt}\mathbf{P}\right|_{\mathrm{irr}} = -\int d\mathbf{r}'\langle \dot{\mathbf{P}}\,\|\,\dot{\mathbf{g}}_{\mathbf{r}'}\rangle\beta(\mathbf{r}')\mathbf{v}(\mathbf{r}') + \int d\mathbf{r}'\langle \dot{\mathbf{P}}\,\|\,\dot{e}_{\mathbf{r}'}\rangle\beta(\mathbf{r}') - \langle \dot{\mathbf{P}}\,\|\,\dot{\mathbf{P}}\rangle\beta_{\mathrm{s}}\mathbf{V} + \langle \dot{\mathbf{P}}\,\|\,\dot{E}\rangle\beta_{\mathrm{s}}
$$

$$
\left.\frac{d}{dt}E\right|_{\mathrm{irr}} = -\int d\mathbf{r}'\langle \dot{E}\,\|\,\dot{\mathbf{g}}_{\mathbf{r}'}\rangle\beta(\mathbf{r}')\mathbf{v}(\mathbf{r}') + \int d\mathbf{r}'\langle \dot{E}\,\|\,\dot{e}_{\mathbf{r}'}\rangle\beta(\mathbf{r}') - \langle \dot{E}\,\|\,\dot{\mathbf{P}}\rangle\beta_{\mathrm{s}}\mathbf{V} + \langle \dot{E}\,\|\,\dot{E}\rangle\beta_{\mathrm{s}}
$$

By using that, due to momentum and energy conservation, the time derivatives of the solid variables are related to those of the fluid as shown in Eq. (11.1.2), these equations can be written as

$$
\partial_t \mathbf{g}(\mathbf{r})|_{\mathrm{irr}} = -\int d\mathbf{r}'\langle \dot{\mathbf{g}}_{\mathbf{r}}\,\|\,\dot{\mathbf{g}}_{\mathbf{r}'}\rangle(\beta(\mathbf{r}')\mathbf{v}(\mathbf{r}') - \beta_{\mathrm{s}}\mathbf{V}) + \int d\mathbf{r}'\langle \dot{\mathbf{g}}_{\mathbf{r}}\,\|\,\dot{e}_{\mathbf{r}'}\rangle(\beta(\mathbf{r}') - \beta_{\mathrm{s}})
$$

$$
\partial_t e(\mathbf{r})|_{\mathrm{irr}} = -\int d\mathbf{r}'\langle \dot{e}_{\mathbf{r}}\,\|\,\dot{\mathbf{g}}_{\mathbf{r}'}\rangle(\beta(\mathbf{r}')\mathbf{v}(\mathbf{r}') - \beta_{\mathrm{s}}\mathbf{V}) + \int d\mathbf{r}'\langle \dot{e}_{\mathbf{r}}\,\|\,\dot{e}_{\mathbf{r}'}\rangle(\beta(\mathbf{r}') - \beta_{\mathrm{s}})
$$

$$
\left.\frac{d}{dt}\mathbf{P}\right|_{\mathrm{irr}} = -\int d\mathbf{r}\,\partial_t \mathbf{g}(\mathbf{r})|_{\mathrm{irr}}
$$

$$
\left.\frac{d}{dt}E\right|_{\mathrm{irr}} = -\int d\mathbf{r}\,\partial_t e(\mathbf{r})|_{\mathrm{irr}}
$$

Note that the evolution of the solid variables is fixed by conservation of momentum and

energy and we may omit them in the following.

The four Green-Kubo kernels entering (11.4) can in turn be decomposed by using (11.1.2) in different terms with different orders of space derivatives

$$\langle \dot{\mathbf{g}}_{\mathbf{r}} \,\|\, \dot{\mathbf{g}}_{\mathbf{r}'} \rangle = \boldsymbol{\nabla}\boldsymbol{\nabla}' \langle \hat{\boldsymbol{\sigma}}_{\mathbf{r}} \,\|\, \hat{\boldsymbol{\sigma}}_{\mathbf{r}'} \rangle - \boldsymbol{\nabla} \langle \hat{\boldsymbol{\sigma}}_{\mathbf{r}} \,\|\, \hat{\mathbf{F}}_{\mathbf{r}'} \rangle - \boldsymbol{\nabla}' \langle \hat{\mathbf{F}}_{\mathbf{r}} \,\|\, \hat{\boldsymbol{\sigma}}_{\mathbf{r}'} \rangle + \langle \hat{\mathbf{F}}_{\mathbf{r}} \,\|\, \hat{\mathbf{F}}_{\mathbf{r}'} \rangle$$

$$\langle \dot{\mathbf{g}}_{\mathbf{r}} \,\|\, \dot{e}_{\mathbf{r}'} \rangle = \boldsymbol{\nabla}\boldsymbol{\nabla}' \langle \hat{\boldsymbol{\sigma}}_{\mathbf{r}} \,\|\, \hat{\mathbf{Q}}_{\mathbf{r}'} \rangle - \boldsymbol{\nabla} \langle \hat{\boldsymbol{\sigma}}_{\mathbf{r}} \,\|\, \hat{\pi}_{\mathbf{r}'} \rangle - \boldsymbol{\nabla}' \langle \hat{\mathbf{F}}_{\mathbf{r}} \,\|\, \hat{\mathbf{Q}}_{\mathbf{r}'} \rangle + \langle \hat{\mathbf{F}}_{\mathbf{r}} \,\|\, \hat{\pi}_{\mathbf{r}'} \rangle$$

$$\langle \dot{e}_{\mathbf{r}} \,\|\, \dot{\mathbf{g}}_{\mathbf{r}'} \rangle = \boldsymbol{\nabla}\boldsymbol{\nabla}' \langle \hat{\mathbf{Q}}_{\mathbf{r}} \,\|\, \hat{\boldsymbol{\sigma}}_{\mathbf{r}'} \rangle - \boldsymbol{\nabla} \langle \hat{\mathbf{Q}}_{\mathbf{r}} \,\|\, \hat{\mathbf{F}}_{\mathbf{r}'} \rangle - \boldsymbol{\nabla}' \langle \hat{\pi}_{\mathbf{r}} \,\|\, \hat{\boldsymbol{\sigma}}_{\mathbf{r}'} \rangle + \langle \hat{\pi}_{\mathbf{r}} \,\|\, \hat{\mathbf{F}}_{\mathbf{r}'} \rangle$$

$$\langle \dot{e}_{\mathbf{r}} \,\|\, \dot{e}_{\mathbf{r}'} \rangle = \boldsymbol{\nabla}\boldsymbol{\nabla}' \langle \hat{\mathbf{Q}}_{\mathbf{r}} \,\|\, \hat{\mathbf{Q}}_{\mathbf{r}'} \rangle - \boldsymbol{\nabla} \langle \hat{\mathbf{Q}}_{\mathbf{r}} \,\|\, \hat{\pi}_{\mathbf{r}'} \rangle - \boldsymbol{\nabla}' \langle \hat{\pi}_{\mathbf{r}} \,\|\, \hat{\mathbf{Q}}_{\mathbf{r}'} \rangle + \langle \hat{\pi}_{\mathbf{r}} \,\|\, \hat{\pi}_{\mathbf{r}'} \rangle$$

Next, we insert (24.8.1) into the first two equations in (11.4) and perform an integration by parts over $\boldsymbol{\nabla}'$. The result of these operations allows to write the first two equations in (11.4) as

$$\partial_t \mathbf{g}(\mathbf{r})\big|_{\mathrm{irr}} = \boldsymbol{\nabla} \int d\mathbf{r}' \langle \hat{\boldsymbol{\sigma}}_{\mathbf{r}} \,\|\, \hat{\boldsymbol{\sigma}}_{\mathbf{r}'} \rangle \boldsymbol{\nabla}' \beta(\mathbf{r}') \mathbf{v}(\mathbf{r}') \qquad - \boldsymbol{\nabla} \int d\mathbf{r}' \langle \hat{\boldsymbol{\sigma}}_{\mathbf{r}} \,\|\, \hat{\mathbf{Q}}_{\mathbf{r}'} \rangle \boldsymbol{\nabla}' \beta(\mathbf{r}')$$

$$+ \boldsymbol{\nabla} \int d\mathbf{r}' \langle \hat{\boldsymbol{\sigma}}_{\mathbf{r}} \,\|\, \hat{\mathbf{F}}_{\mathbf{r}'} \rangle (\beta(\mathbf{r}')\mathbf{v}(\mathbf{r}') - \beta_{\mathrm{s}}\mathbf{V}) \quad - \boldsymbol{\nabla} \int d\mathbf{r}' \langle \hat{\boldsymbol{\sigma}}_{\mathbf{r}} \,\|\, \hat{\pi}_{\mathbf{r}'} \rangle (\beta(\mathbf{r}') - \beta_{\mathrm{s}})$$

$$- \int d\mathbf{r}' \langle \hat{\mathbf{F}}_{\mathbf{r}} \,\|\, \hat{\boldsymbol{\sigma}}_{\mathbf{r}'} \rangle \boldsymbol{\nabla}' \beta(\mathbf{r}') \mathbf{v}(\mathbf{r}') \qquad + \int d\mathbf{r}' \langle \hat{\mathbf{F}}_{\mathbf{r}} \,\|\, \hat{\mathbf{Q}}_{\mathbf{r}'} \rangle \boldsymbol{\nabla}' \beta(\mathbf{r}')$$

$$- \int d\mathbf{r}' \langle \hat{\mathbf{F}}_{\mathbf{r}} \,\|\, \hat{\mathbf{F}}_{\mathbf{r}'} \rangle (\beta(\mathbf{r}')\mathbf{v}(\mathbf{r}') - \beta_{\mathrm{s}}\mathbf{V}) \quad + \int d\mathbf{r}' \langle \hat{\mathbf{F}}_{\mathbf{r}} \,\|\, \hat{\pi}_{\mathbf{r}'} \rangle (\beta(\mathbf{r}') - \beta_{\mathrm{s}})$$

$$\partial_t e(\mathbf{r})\big|_{\mathrm{irr}} = \boldsymbol{\nabla} \int d\mathbf{r}' \langle \hat{\mathbf{Q}}_{\mathbf{r}} \,\|\, \hat{\boldsymbol{\sigma}}_{\mathbf{r}'} \rangle \boldsymbol{\nabla}' \beta(\mathbf{r}') \mathbf{v}(\mathbf{r}') \qquad - \boldsymbol{\nabla} \int d\mathbf{r}' \langle \hat{\mathbf{Q}}_{\mathbf{r}} \,\|\, \hat{\mathbf{Q}}_{\mathbf{r}'} \rangle \boldsymbol{\nabla}' \beta(\mathbf{r}')$$

$$+ \boldsymbol{\nabla} \int d\mathbf{r}' \langle \hat{\mathbf{Q}}_{\mathbf{r}} \,\|\, \hat{\mathbf{F}}_{\mathbf{r}'} \rangle (\beta(\mathbf{r}')\mathbf{v}(\mathbf{r}') - \beta_{\mathrm{s}}\mathbf{V}) \quad + \boldsymbol{\nabla} \int d\mathbf{r}' \langle \hat{\mathbf{Q}}_{\mathbf{r}} \,\|\, \hat{\pi}_{\mathbf{r}'} \rangle (\beta(\mathbf{r}') - \beta_{\mathrm{s}})$$

$$- \int d\mathbf{r}' \langle \hat{\pi}_{\mathbf{r}} \,\|\, \hat{\boldsymbol{\sigma}}_{\mathbf{r}'} \rangle \boldsymbol{\nabla}' \beta(\mathbf{r}') \mathbf{v}(\mathbf{r}') \qquad + \int d\mathbf{r}' \langle \hat{\pi}_{\mathbf{r}} \,\|\, \hat{\mathbf{Q}}_{\mathbf{r}'} \rangle \boldsymbol{\nabla}' \beta(\mathbf{r}')$$

$$- \int d\mathbf{r}' \langle \hat{\pi}_{\mathbf{r}} \,\|\, \hat{\mathbf{F}}_{\mathbf{r}'} \rangle (\beta(\mathbf{r}')\mathbf{v}(\mathbf{r}') - \beta_{\mathrm{s}}\mathbf{V}) \quad + \int d\mathbf{r}' \langle \hat{\pi}_{\mathbf{r}} \,\|\, \hat{\pi}_{\mathbf{r}'} \rangle (\beta(\mathbf{r}') - \beta_{\mathrm{s}})$$

We now consider the effect of the Galilean transformation on the Green-Kubo expression. We may think of it as a change of variables

$$\langle \hat{A} \,\|\, \hat{B} \rangle = \int_0^\infty dt' \mathrm{Tr}\left[\overline{\rho} \mathcal{Q} \hat{A}(t') \mathcal{Q} \hat{B} \right] = \int_0^\infty dt' \mathrm{Tr}\left[\overline{\rho}_{\mathrm{rest}} \left(\mathcal{Q}\mathcal{G}^{-1}\hat{A}(t') \right) \left(\mathcal{Q}\mathcal{G}^{-1}\hat{B} \right) \right]$$

We note that the projector operator $\mathcal{Q}$ acting on the relevant variables vanishes, and

therefore, from Eq. (11.1.3) we infer

$$\mathscr{Q}\mathscr{G}\hat{\boldsymbol{\sigma}}_{\mathbf{r}} = \mathscr{Q}\hat{\boldsymbol{\sigma}}_{\mathbf{r}}$$

$$\mathscr{Q}\mathscr{G}\hat{\mathbf{F}}_{\mathbf{r}} = \mathscr{Q}\hat{\mathbf{F}}_{\mathbf{r}}$$

$$\mathscr{Q}\mathscr{G}\hat{\mathbf{Q}}_{\mathbf{r}} = \mathscr{Q}\hat{\mathbf{Q}}_{\mathbf{r}} - \mathscr{Q}\hat{\boldsymbol{\sigma}}_{\mathbf{r}}\cdot\mathbf{v}(\mathbf{r}) - \mathscr{Q}\Delta\hat{\boldsymbol{\sigma}}_{\mathbf{r}}$$

$$\mathscr{Q}\mathscr{G}\hat{\pi}_{\mathbf{r}} = \mathscr{Q}\hat{\pi}_{\mathbf{r}} - \frac{\mathbf{v}(\mathbf{r}) + \mathbf{V}}{2}\mathscr{Q}\hat{\mathbf{F}}_{\mathbf{r}}$$

Because this implies a duplication or quatriplication of terms, we need to proceed with some order. We will consider the different lines by expanding the terms $\mathscr{Q}\mathscr{G}\hat{\mathbf{Q}}_{\mathbf{r}}$ and $\mathscr{Q}\mathscr{G}\hat{\pi}_{\mathbf{r}}$ that are at the right in the Green-Kubo integrand. Consider first the line (22.3).

$$\boldsymbol{\nabla}\int d\mathbf{r}'\langle\hat{\boldsymbol{\sigma}}_{\mathbf{r}}\,\|\,\hat{\boldsymbol{\sigma}}_{\mathbf{r}'}\rangle\boldsymbol{\nabla}'\beta(\mathbf{r}')\mathbf{v}(\mathbf{r}') - \boldsymbol{\nabla}\int d\mathbf{r}'\langle\hat{\boldsymbol{\sigma}}_{\mathbf{r}}\,\|\,\hat{\mathbf{Q}}_{\mathbf{r}'}\rangle\boldsymbol{\nabla}'\beta(\mathbf{r}')$$

$$=\boldsymbol{\nabla}\int d\mathbf{r}'\langle\hat{\boldsymbol{\sigma}}_{\mathbf{r}}\,\|\,\hat{\boldsymbol{\sigma}}_{\mathbf{r}'}\rangle^0\boldsymbol{\nabla}'\beta(\mathbf{r}')\mathbf{v}(\mathbf{r}') + \boldsymbol{\nabla}\int d\mathbf{r}'\langle\hat{\boldsymbol{\sigma}}_{\mathbf{r}}\,\|\,\hat{\mathbf{Q}}_{\mathbf{r}'}\rangle^0\boldsymbol{\nabla}'\beta(\mathbf{r}') - \int d\mathbf{r}'\boldsymbol{\nabla}\mathbf{v}(\mathbf{r}')\langle\hat{\boldsymbol{\sigma}}_{\mathbf{r}}\,\|\,\hat{\boldsymbol{\sigma}}_{\mathbf{r}'}\rangle^0\boldsymbol{\nabla}'\beta(\mathbf{r}')$$

For simplicity, we will neglect from now on the terms that depend on $\Delta\boldsymbol{\sigma}_{\mathbf{r}}$. These terms will produce third order derivative terms and are here disregarded. **Comment on this later on.**

In a similar way, the third line (20.3) becomes

$$-\int d\mathbf{r}'\langle\hat{\mathbf{F}}_{\mathbf{r}}\,\|\,\hat{\boldsymbol{\sigma}}_{\mathbf{r}'}\rangle\boldsymbol{\nabla}'\beta(\mathbf{r}')\mathbf{v}(\mathbf{r}') + \int d\mathbf{r}'\langle\hat{\mathbf{F}}_{\mathbf{r}}\,\|\,\hat{\mathbf{Q}}_{\mathbf{r}'}\rangle\boldsymbol{\nabla}'\beta(\mathbf{r}')$$

$$=-\int d\mathbf{r}'\langle\hat{\mathbf{F}}_{\mathbf{r}}\,\|\,\hat{\boldsymbol{\sigma}}_{\mathbf{r}'}\rangle^0\beta(\mathbf{r}')\boldsymbol{\nabla}'\mathbf{v}(\mathbf{r}') + \int d\mathbf{r}'\langle\hat{\mathbf{F}}_{\mathbf{r}}\,\|\,\hat{\mathbf{Q}}_{\mathbf{r}'}\rangle^0\boldsymbol{\nabla}'\beta(\mathbf{r}')$$

On the other hand the second line (20.3) becomes

$$\boldsymbol{\nabla}\int d\mathbf{r}'\langle\hat{\boldsymbol{\sigma}}_{\mathbf{r}}\,\|\,\hat{\mathbf{F}}_{\mathbf{r}'}\rangle(\beta(\mathbf{r}')\mathbf{v}(\mathbf{r}') - \beta_{\mathrm{s}}\mathbf{V}) - \boldsymbol{\nabla}\int d\mathbf{r}'\langle\hat{\boldsymbol{\sigma}}_{\mathbf{r}}\,\|\,\hat{\pi}_{\mathbf{r}'}\rangle(\beta(\mathbf{r}') - \beta_{\mathrm{s}})$$

$$=\boldsymbol{\nabla}\int d\mathbf{r}'\langle\hat{\boldsymbol{\sigma}}_{\mathbf{r}}\,\|\,\hat{\mathbf{F}}_{\mathbf{r}'}\rangle^0(\beta(\mathbf{r}')\mathbf{v}(\mathbf{r}') - \beta_{\mathrm{s}}\mathbf{V}) - \boldsymbol{\nabla}\int d\mathbf{r}'\langle\hat{\boldsymbol{\sigma}}_{\mathbf{r}}\,\|\,\hat{\pi}_{\mathbf{r}'}\rangle^0(\beta(\mathbf{r}') - \beta_{\mathrm{s}}) - \boldsymbol{\nabla}\int d\mathbf{r}'\langle\hat{\boldsymbol{\sigma}}_{\mathbf{r}}\,\|\,\hat{\mathbf{F}}_{\mathbf{r}}\rangle^0\frac{\mathbf{v}(\mathbf{r}) + \mathbf{V}}{2}(\beta(\mathbf{r}') - \beta_{\mathrm{s}})$$

$$=\boldsymbol{\nabla}\int d\mathbf{r}'\langle\hat{\boldsymbol{\sigma}}_{\mathbf{r}}\,\|\,\hat{\mathbf{F}}_{\mathbf{r}'}\rangle^0\left[(\beta(\mathbf{r}')\mathbf{v}(\mathbf{r}') - \beta_{\mathrm{s}}\mathbf{V}) - \frac{\mathbf{v}(\mathbf{r}) + \mathbf{V}}{2}(\beta(\mathbf{r}') - \beta_{\mathrm{s}})\right] - \boldsymbol{\nabla}\int d\mathbf{r}'\langle\hat{\boldsymbol{\sigma}}_{\mathbf{r}}\,\|\,\hat{\pi}_{\mathbf{r}'}\rangle^0(\beta(\mathbf{r}') - \beta_{\mathrm{s}})$$

$$=\boldsymbol{\nabla}\int d\mathbf{r}'\langle\hat{\boldsymbol{\sigma}}_{\mathbf{r}}\,\|\,\hat{\mathbf{F}}_{\mathbf{r}'}\rangle^0\frac{\beta(\mathbf{r}') + \beta_s}{2}(\mathbf{v}(\mathbf{r}') - \mathbf{V}) - \boldsymbol{\nabla}\int d\mathbf{r}'\langle\hat{\boldsymbol{\sigma}}_{\mathbf{r}}\,\|\,\hat{\pi}_{\mathbf{r}'}\rangle^0(\beta(\mathbf{r}') - \beta_{\mathrm{s}})$$

and in a similar way, the fourth line (20.3) becomes

$$-\int d\mathbf{r}'\langle\hat{\mathbf{F}}_{\mathbf{r}}\,\|\,\hat{\mathbf{F}}_{\mathbf{r}'}\rangle(\beta(\mathbf{r}')\mathbf{v}(\mathbf{r}') - \beta_{\mathrm{s}}\mathbf{V}) + \int d\mathbf{r}'\langle\hat{\mathbf{F}}_{\mathbf{r}}\,\|\,\hat{\pi}_{\mathbf{r}'}\rangle(\beta(\mathbf{r}') - \beta_{\mathrm{s}})$$

$$=-\int d\mathbf{r}'\langle\hat{\mathbf{F}}_{\mathbf{r}}\,\|\,\hat{\mathbf{F}}_{\mathbf{r}'}\rangle^0\frac{\beta(\mathbf{r}') + \beta_s}{2}(\mathbf{v}(\mathbf{r}') - \mathbf{V}) + \int d\mathbf{r}'\langle\hat{\mathbf{F}}_{\mathbf{r}}\,\|\,\hat{\pi}_{\mathbf{r}'}\rangle^0(\beta(\mathbf{r}') - \beta_{\mathrm{s}})$$

We now collect the fourth lines in the momentum equation that becomes

$$\partial_t \mathbf{g}(\mathbf{r})|_{\mathrm{irr}} = \boldsymbol{\nabla} \int d\mathbf{r}' \langle \hat{\boldsymbol{\sigma}}_{\mathbf{r}} \| \hat{\boldsymbol{\sigma}}_{\mathbf{r}'} \rangle^0 \beta(\mathbf{r}') \boldsymbol{\nabla}' \mathbf{v}(\mathbf{r}') \qquad \color{red}{-\boldsymbol{\nabla} \int d\mathbf{r}' \langle \hat{\boldsymbol{\sigma}}_{\mathbf{r}} \| \hat{\mathbf{Q}}_{\mathbf{r}'} \rangle^0 \boldsymbol{\nabla}' \beta(\mathbf{r}')}$$

$$+ \boldsymbol{\nabla} \int d\mathbf{r}' \langle \hat{\boldsymbol{\sigma}}_{\mathbf{r}} \| \hat{\mathbf{F}}_{\mathbf{r}'} \rangle^0 \frac{\beta(\mathbf{r}') + \beta_s}{2} \left(\mathbf{v}(\mathbf{r}') - \mathbf{V} \right) \qquad \color{red}{-\boldsymbol{\nabla} \int d\mathbf{r}' \langle \hat{\boldsymbol{\sigma}}_{\mathbf{r}} \| \hat{\pi}_{\mathbf{r}'} \rangle^0 (\beta(\mathbf{r}') - \beta_s)}$$

$$- \int d\mathbf{r}' \langle \hat{\mathbf{F}}_{\mathbf{r}} \| \hat{\boldsymbol{\sigma}}_{\mathbf{r}'} \rangle^0 \beta(\mathbf{r}') \boldsymbol{\nabla}' \mathbf{v}(\mathbf{r}') \qquad \color{red}{+ \int d\mathbf{r}' \langle \hat{\mathbf{F}}_{\mathbf{r}} \| \hat{\mathbf{Q}}_{\mathbf{r}'} \rangle^0 \boldsymbol{\nabla}' \beta(\mathbf{r}')}$$

$$- \int d\mathbf{r}' \langle \hat{\mathbf{F}}_{\mathbf{r}} \| \hat{\mathbf{F}}_{\mathbf{r}'} \rangle^0 \frac{\beta(\mathbf{r}') + \beta_s}{2} \left(\mathbf{v}(\mathbf{r}') - \mathbf{V} \right) \qquad \color{red}{+ \int d\mathbf{r}' \langle \hat{\mathbf{F}}_{\mathbf{r}} \| \hat{\pi}_{\mathbf{r}'} \rangle^0 (\beta(\mathbf{r}') - \beta_s)}$$

We see that quite naturally, the effect of the Galilean operator and the use of the Green-Kubo transport coefficients at rest lead to Galilean invariant terms that depend on relative velocities only.

Note that we may follow identical steps in the energy equation as far as the right hand side of the Green-Kubo integrands is concerned. Therefore, we obtain

$$\partial_t e(\mathbf{r})|_{\mathrm{irr}} = \boldsymbol{\nabla} \int d\mathbf{r}' \langle \mathscr{G}^{-1} \hat{\mathbf{Q}}_{\mathbf{r}} \| \hat{\boldsymbol{\sigma}}_{\mathbf{r}'} \rangle \beta(\mathbf{r}') \boldsymbol{\nabla}' \mathbf{v}(\mathbf{r}') \qquad \color{red}{-\boldsymbol{\nabla} \int d\mathbf{r}' \langle \mathscr{G}^{-1} \hat{\mathbf{Q}}_{\mathbf{r}} \| \hat{\mathbf{Q}}_{\mathbf{r}'} \rangle \boldsymbol{\nabla}' \beta(\mathbf{r}')}$$

$$+ \boldsymbol{\nabla} \int d\mathbf{r}' \langle \mathscr{G}^{-1} \hat{\mathbf{Q}}_{\mathbf{r}} \| \hat{\mathbf{F}}_{\mathbf{r}'} \rangle \frac{\beta(\mathbf{r}') + \beta_s}{2} (\mathbf{v}(\mathbf{r}') - \mathbf{V}) \qquad \color{red}{-\boldsymbol{\nabla} \int d\mathbf{r}' \langle \mathscr{G}^{-1} \hat{\mathbf{Q}}_{\mathbf{r}} \| \hat{\pi}_{\mathbf{r}'} \rangle (\beta(\mathbf{r}') - \beta_s)}$$

$$- \int d\mathbf{r}' \langle \mathscr{G}^{-1} \hat{\pi}_{\mathbf{r}} \| \hat{\boldsymbol{\sigma}}_{\mathbf{r}'} \rangle \beta(\mathbf{r}') \boldsymbol{\nabla}' \mathbf{v}(\mathbf{r}') \qquad \color{red}{+ \int d\mathbf{r}' \langle \mathscr{G}^{-1} \hat{\pi}_{\mathbf{r}} \| \hat{\mathbf{Q}}_{\mathbf{r}'} \rangle \boldsymbol{\nabla}' \beta(\mathbf{r}')}$$

$$- \int d\mathbf{r}' \langle \mathscr{G}^{-1} \hat{\pi}_{\mathbf{r}} \| \hat{\mathbf{F}}_{\mathbf{r}'} \rangle \frac{\beta(\mathbf{r}') + \beta_s}{2} (\mathbf{v}(\mathbf{r}') - \mathbf{V}) \qquad \color{red}{+ \int d\mathbf{r}' \langle \mathscr{G}^{-1} \hat{\pi}_{\mathbf{r}} \| \hat{\pi}_{\mathbf{r}'} \rangle (\beta(\mathbf{r}') - \beta_s)}$$

Now, we have to expand the Galilean operator in the left hand side of the Green-Kubo

terms. This will double the number of terms in the equation,

$$
\begin{aligned}
\partial_t e(\mathbf{r})|_{\mathrm{irr}} = {} & \boldsymbol{\nabla} \int d\mathbf{r}' \langle \hat{\mathbf{Q}}_{\mathbf{r}} \, \| \, \hat{\boldsymbol{\sigma}}_{\mathbf{r}'} \rangle^0 \beta(\mathbf{r}') \boldsymbol{\nabla}' \mathbf{v}(\mathbf{r}') && -\boldsymbol{\nabla} \int d\mathbf{r}' \langle \hat{\mathbf{Q}}_{\mathbf{r}} \, \| \, \hat{\mathbf{Q}}_{\mathbf{r}'} \rangle^0 \boldsymbol{\nabla}' \beta(\mathbf{r}') \\
& + \boldsymbol{\nabla} \left[\mathbf{v}(\mathbf{r}) \int d\mathbf{r}' {\cdot} \langle \hat{\boldsymbol{\sigma}}_{\mathbf{r}} \, \| \, \hat{\boldsymbol{\sigma}}_{\mathbf{r}'} \rangle^0 \beta(\mathbf{r}') \boldsymbol{\nabla}' \mathbf{v}(\mathbf{r}') \right] && -\boldsymbol{\nabla} \left[\mathbf{v}(\mathbf{r}) \int d\mathbf{r}' {\cdot} \langle \hat{\boldsymbol{\sigma}}_{\mathbf{r}} \, \| \, \hat{\mathbf{Q}}_{\mathbf{r}'} \rangle^0 \boldsymbol{\nabla}' \beta(\mathbf{r}') \right] \\
& + \boldsymbol{\nabla} \int d\mathbf{r}' \langle \hat{\mathbf{Q}}_{\mathbf{r}} \, \| \, \hat{\mathbf{F}}_{\mathbf{r}'} \rangle^0 \frac{\beta(\mathbf{r}') + \beta_s}{2} (\mathbf{v}(\mathbf{r}') - \mathbf{V}) && -\boldsymbol{\nabla} \int d\mathbf{r}' \langle \hat{\mathbf{Q}}_{\mathbf{r}} \, \| \, \hat{\pi}_{\mathbf{r}'} \rangle^0 (\beta(\mathbf{r}') - \beta_s) \\
& + \boldsymbol{\nabla} \left[\mathbf{v}(\mathbf{r}) \int d\mathbf{r}' {\cdot} \langle \hat{\boldsymbol{\sigma}}_{\mathbf{r}} \, \| \, \hat{\mathbf{F}}_{\mathbf{r}'} \rangle^0 \frac{\beta(\mathbf{r}') + \beta_s}{2} (\mathbf{v}(\mathbf{r}') - \mathbf{V}) \right] && -\boldsymbol{\nabla} \left[\mathbf{v}(\mathbf{r}) \int d\mathbf{r}' {\cdot} \langle \hat{\boldsymbol{\sigma}}_{\mathbf{r}} \, \| \, \hat{\pi}_{\mathbf{r}'} \rangle^0 (\beta(\mathbf{r}') - \beta_s) \right] \\
& - \int d\mathbf{r}' \langle \hat{\pi}_{\mathbf{r}} \, \| \, \hat{\boldsymbol{\sigma}}_{\mathbf{r}'} \rangle^0 \beta(\mathbf{r}') \boldsymbol{\nabla}' \mathbf{v}(\mathbf{r}') && + \int d\mathbf{r}' \langle \hat{\pi}_{\mathbf{r}} \, \| \, \hat{\mathbf{Q}}_{\mathbf{r}'} \rangle^0 \boldsymbol{\nabla}' \beta(\mathbf{r}') \\
& - \frac{\mathbf{v}(\mathbf{r}) + \mathbf{V}}{2} \int d\mathbf{r}' \langle \hat{\mathbf{F}}_{\mathbf{r}} \, \| \, \hat{\boldsymbol{\sigma}}_{\mathbf{r}'} \rangle^0 \beta(\mathbf{r}') \boldsymbol{\nabla}' \mathbf{v}(\mathbf{r}') && + \frac{\mathbf{v}(\mathbf{r}) + \mathbf{V}}{2} \int d\mathbf{r}' \langle \hat{\mathbf{F}}_{\mathbf{r}} \, \| \, \hat{\mathbf{Q}}_{\mathbf{r}'} \rangle^0 \boldsymbol{\nabla}' \beta(\mathbf{r}') \\
& - \int d\mathbf{r}' \langle \hat{\pi}_{\mathbf{r}} \, \| \, \hat{\mathbf{F}}_{\mathbf{r}'} \rangle^0 \frac{\beta(\mathbf{r}') + \beta_s}{2} (\mathbf{v}(\mathbf{r}') - \mathbf{V}) && + \int d\mathbf{r}' \langle \hat{\pi}_{\mathbf{r}} \, \| \, \hat{\pi}_{\mathbf{r}'} \rangle^0 (\beta(\mathbf{r}') - \beta_s) \\
& - \frac{\mathbf{v}(\mathbf{r}) + \mathbf{V}}{2} \int d\mathbf{r}' \langle \hat{\mathbf{F}}_{\mathbf{r}} \, \| \, \hat{\mathbf{F}}_{\mathbf{r}'} \rangle^0 \frac{\beta(\mathbf{r}') + \beta_s}{2} (\mathbf{v}(\mathbf{r}') - \mathbf{V}) && + \frac{\mathbf{v}(\mathbf{r}) + \mathbf{V}}{2} \int d\mathbf{r}' \langle \hat{\mathbf{F}}_{\mathbf{r}} \, \| \, \hat{\pi}_{\mathbf{r}'} \rangle^0 (\beta(\mathbf{r}') - \beta_s)
\end{aligned}
$$

It is convenient to express this in terms of the internal energy density field by using

$$
\partial_t \epsilon(\mathbf{r})|_{\mathrm{irr}} = \partial_t e(\mathbf{r})|_{\mathrm{irr}} - \mathbf{v}(\mathbf{r}) {\cdot} \partial_t \mathbf{g}(\mathbf{r})|_{\mathrm{irr}}
$$

where we have used the fact that the density field does not evolve in an irreversible

manner. The evolution of the internal energy is

$$
\begin{aligned}
\partial_t \epsilon(\mathbf{r})|_{\text{irr}} = {} & \boldsymbol{\nabla} \int d\mathbf{r}' \langle \hat{\mathbf{Q}}_{\mathbf{r}} \,\|\, \hat{\boldsymbol{\sigma}}_{\mathbf{r}'} \rangle^0 \beta(\mathbf{r}') \boldsymbol{\nabla}' \mathbf{v}(\mathbf{r}') && -\boldsymbol{\nabla} \int d\mathbf{r}' \langle \hat{\mathbf{Q}}_{\mathbf{r}} \,\|\, \hat{\mathbf{Q}}_{\mathbf{r}'} \rangle^0 \boldsymbol{\nabla}' \beta(\mathbf{r}') \\[6pt]
& + \boldsymbol{\nabla}\mathbf{v}(\mathbf{r}) : \left[\int d\mathbf{r}' \!\cdot\! \langle \hat{\boldsymbol{\sigma}}_{\mathbf{r}} \,\|\, \hat{\boldsymbol{\sigma}}_{\mathbf{r}'} \rangle^0 \beta(\mathbf{r}') \boldsymbol{\nabla}' \mathbf{v}(\mathbf{r}') \right] && -\boldsymbol{\nabla}\mathbf{v}(\mathbf{r}) : \left[\int d\mathbf{r}' \!\cdot\! \langle \hat{\boldsymbol{\sigma}}_{\mathbf{r}} \,\|\, \hat{\mathbf{Q}}_{\mathbf{r}'} \rangle^0 \boldsymbol{\nabla}' \beta(\mathbf{r}') \right] \\[6pt]
& + \boldsymbol{\nabla} \int d\mathbf{r}' \langle \hat{\mathbf{Q}}_{\mathbf{r}} \,\|\, \hat{\mathbf{F}}_{\mathbf{r}'} \rangle^0 \frac{\beta(\mathbf{r}') + \beta_s}{2} (\mathbf{v}(\mathbf{r}') - \mathbf{V}) && -\boldsymbol{\nabla} \int d\mathbf{r}' \langle \hat{\mathbf{Q}}_{\mathbf{r}} \,\|\, \hat{\pi}_{\mathbf{r}'} \rangle^0 (\beta(\mathbf{r}') - \beta_s) \\[6pt]
& + \boldsymbol{\nabla}\mathbf{v}(\mathbf{r}) : \left[\int d\mathbf{r}' \!\cdot\! \langle \hat{\boldsymbol{\sigma}}_{\mathbf{r}} \,\|\, \hat{\mathbf{F}}_{\mathbf{r}'} \rangle^0 \frac{\beta(\mathbf{r}') + \beta_s}{2} (\mathbf{v}(\mathbf{r}') - \mathbf{V}) \right] && -\boldsymbol{\nabla}\mathbf{v}(\mathbf{r}) : \left[\int d\mathbf{r}' \!\cdot\! \langle \hat{\boldsymbol{\sigma}}_{\mathbf{r}} \,\|\, \hat{\pi}_{\mathbf{r}'} \rangle^0 (\beta(\mathbf{r}') - \beta_s) \right] \\[6pt]
& - \int d\mathbf{r}' \langle \hat{\pi}_{\mathbf{r}} \,\|\, \hat{\boldsymbol{\sigma}}_{\mathbf{r}'} \rangle^0 \beta(\mathbf{r}') \boldsymbol{\nabla}' \mathbf{v}(\mathbf{r}') && + \int d\mathbf{r}' \langle \hat{\pi}_{\mathbf{r}} \,\|\, \hat{\mathbf{Q}}_{\mathbf{r}'} \rangle^0 \boldsymbol{\nabla}' \beta(\mathbf{r}') \\[6pt]
& + \frac{\mathbf{v}(\mathbf{r}) - \mathbf{V}}{2} \int d\mathbf{r}' \langle \hat{\mathbf{F}}_{\mathbf{r}} \,\|\, \hat{\boldsymbol{\sigma}}_{\mathbf{r}'} \rangle^0 \beta(\mathbf{r}') \boldsymbol{\nabla}' \mathbf{v}(\mathbf{r}') && - \frac{\mathbf{v}(\mathbf{r}) - \mathbf{V}}{2} \int d\mathbf{r}' \langle \hat{\mathbf{F}}_{\mathbf{r}} \,\|\, \hat{\mathbf{Q}}_{\mathbf{r}'} \rangle^0 \boldsymbol{\nabla}' \beta(\mathbf{r}') \\[6pt]
& - \int d\mathbf{r}' \langle \hat{\pi}_{\mathbf{r}} \,\|\, \hat{\mathbf{F}}_{\mathbf{r}'} \rangle^0 \frac{\beta(\mathbf{r}') + \beta_s}{2} (\mathbf{v}(\mathbf{r}') - \mathbf{V}) && + \int d\mathbf{r}' \langle \hat{\pi}_{\mathbf{r}} \,\|\, \hat{\pi}_{\mathbf{r}'} \rangle^0 (\beta(\mathbf{r}') - \beta_s) \\[6pt]
& + \frac{\mathbf{v}(\mathbf{r}) - \mathbf{V}}{2} \int d\mathbf{r}' \langle \hat{\mathbf{F}}_{\mathbf{r}} \,\|\, \hat{\mathbf{F}}_{\mathbf{r}'} \rangle^0 \frac{\beta(\mathbf{r}') + \beta_s}{2} (\mathbf{v}(\mathbf{r}') - \mathbf{V}) && - \frac{\mathbf{v}(\mathbf{r}) - \mathbf{V}}{2} \int d\mathbf{r}' \langle \hat{\mathbf{F}}_{\mathbf{r}} \,\|\, \hat{\pi}_{\mathbf{r}'} \rangle^0 (\beta(\mathbf{r}') - \beta_s)
\end{aligned}
$$

11.5   The full dynamics at the CG level

By collecting the reversible part of the dynamics (11.3) and the irreversible part (11.10) we obtain the final dynamic equations for the relevant variables

$$\partial_t \rho(\mathbf{r}) = -\boldsymbol{\nabla} \cdot \mathbf{g}(\mathbf{r})$$

$$\partial_t \mathbf{g}(\mathbf{r}) = -\boldsymbol{\nabla} \cdot \mathbf{v}(\mathbf{r}) \mathbf{g}(\mathbf{r}) - \boldsymbol{\nabla} \cdot \boldsymbol{\sigma}(\mathbf{r}) + \mathbf{F}(\mathbf{r}) + \partial_t \mathbf{g}(\mathbf{r})|_{\mathrm{irr}}$$

$$\partial_t \epsilon(\mathbf{r}) = -\boldsymbol{\nabla} \cdot \mathbf{v}(\mathbf{r}) \epsilon(\mathbf{r}) - \boldsymbol{\sigma}(\mathbf{r}) : \boldsymbol{\nabla} \mathbf{v}(\mathbf{r}) - \boldsymbol{\nabla} \cdot \Delta \boldsymbol{\sigma}(\mathbf{r}) + \left(\frac{\mathbf{V} - \mathbf{v}(\mathbf{r})}{2} \right) \mathbf{F}(\mathbf{r}) + \partial_t \epsilon(\mathbf{r})|_{\mathrm{irr}}$$

$$\partial_t \mathbf{R} = \mathbf{V}$$

$$\partial_t \mathbf{P} = -\int d\mathbf{r} \mathbf{F}(\mathbf{r}) - \int d\mathbf{r} \, \partial_t \mathbf{g}(\mathbf{r})|_{\mathrm{irr}}$$

$$\partial_t U = \int d\mathbf{r} \left(\frac{\mathbf{v}(\mathbf{r}) - \mathbf{V}}{2} \right) \mathbf{F}(\mathbf{r}) - \int d\mathbf{r} \, \partial_t \epsilon(\mathbf{r})|_{\mathrm{irr}} - \int d\mathbf{r} (\mathbf{v}(\mathbf{r}) - \mathbf{V}) \cdot \partial_t \mathbf{g}(\mathbf{r})|_{\mathrm{irr}}$$

where the irreversible evolution is given by

$$
\begin{aligned}
\partial_t \mathbf{g}(\mathbf{r})|_{\mathrm{irr}} =\ & \boldsymbol{\nabla} \int d\mathbf{r}' \langle \hat{\boldsymbol{\sigma}}_{\mathbf{r}} \| \hat{\boldsymbol{\sigma}}_{\mathbf{r}'} \rangle^0 \beta(\mathbf{r}') \boldsymbol{\nabla}' \mathbf{v}(\mathbf{r}') && -\boldsymbol{\nabla} \int d\mathbf{r}' \langle \hat{\boldsymbol{\sigma}}_{\mathbf{r}} \| \hat{\mathbf{Q}}_{\mathbf{r}'} \rangle^0 \boldsymbol{\nabla}' \beta(\mathbf{r}') \\
& + \boldsymbol{\nabla} \int d\mathbf{r}' \langle \hat{\boldsymbol{\sigma}}_{\mathbf{r}} \| \hat{\mathbf{F}}_{\mathbf{r}'} \rangle^0 \frac{\beta(\mathbf{r}') + \beta_s}{2} \left(\mathbf{v}(\mathbf{r}') - \mathbf{V} \right) && -\boldsymbol{\nabla} \int d\mathbf{r}' \langle \hat{\boldsymbol{\sigma}}_{\mathbf{r}} \| \hat{\pi}_{\mathbf{r}'} \rangle^0 (\beta(\mathbf{r}') - \beta_s) \\
& - \int d\mathbf{r}' \langle \hat{\mathbf{F}}_{\mathbf{r}} \| \hat{\boldsymbol{\sigma}}_{\mathbf{r}'} \rangle^0 \beta(\mathbf{r}') \boldsymbol{\nabla}' \mathbf{v}(\mathbf{r}') && + \int d\mathbf{r}' \langle \hat{\mathbf{F}}_{\mathbf{r}} \| \hat{\mathbf{Q}}_{\mathbf{r}'} \rangle^0 \boldsymbol{\nabla}' \beta(\mathbf{r}') \\
& - \int d\mathbf{r}' \langle \hat{\mathbf{F}}_{\mathbf{r}} \| \hat{\mathbf{F}}_{\mathbf{r}'} \rangle^0 \frac{\beta(\mathbf{r}') + \beta_s}{2} \left(\mathbf{v}(\mathbf{r}') - \mathbf{V} \right) && + \int d\mathbf{r}' \langle \hat{\mathbf{F}}_{\mathbf{r}} \| \hat{\pi}_{\mathbf{r}'} \rangle^0 (\beta(\mathbf{r}') - \beta_s)
\end{aligned}
$$

$$
\begin{aligned}
\partial_t \epsilon(\mathbf{r})|_{\mathrm{irr}} = {} & \boldsymbol{\nabla}\mathbf{v}(\mathbf{r}) : \left[\int d\mathbf{r}' \langle \hat{\boldsymbol{\sigma}}_{\mathbf{r}} \| \hat{\boldsymbol{\sigma}}_{\mathbf{r}'} \rangle^0 \beta(\mathbf{r}') \boldsymbol{\nabla}'\mathbf{v}(\mathbf{r}') \right] && -\boldsymbol{\nabla}\mathbf{v}(\mathbf{r}) : \left[\int d\mathbf{r}' \langle \hat{\boldsymbol{\sigma}}_{\mathbf{r}} \| \hat{\mathbf{Q}}_{\mathbf{r}'} \rangle^0 \boldsymbol{\nabla}'\beta(\mathbf{r}') \right] \\[2mm]
& + \boldsymbol{\nabla} \int d\mathbf{r}' \langle \hat{\mathbf{Q}}_{\mathbf{r}} \| \hat{\boldsymbol{\sigma}}_{\mathbf{r}'} \rangle^0 \beta(\mathbf{r}') \boldsymbol{\nabla}'\mathbf{v}(\mathbf{r}') && -\boldsymbol{\nabla} \int d\mathbf{r}' \langle \hat{\mathbf{Q}}_{\mathbf{r}} \| \hat{\mathbf{Q}}_{\mathbf{r}'} \rangle^0 \boldsymbol{\nabla}'\beta(\mathbf{r}') \\[2mm]
& + \boldsymbol{\nabla}\mathbf{v}(\mathbf{r}) : \left[\int d\mathbf{r}' \langle \hat{\boldsymbol{\sigma}}_{\mathbf{r}} \| \hat{\mathbf{F}}_{\mathbf{r}'} \rangle^0 \frac{\beta(\mathbf{r}') + \beta_s}{2}(\mathbf{v}(\mathbf{r}') - \mathbf{V}) \right] && -\boldsymbol{\nabla}\mathbf{v}(\mathbf{r}) : \left[\int d\mathbf{r}' \langle \hat{\boldsymbol{\sigma}}_{\mathbf{r}} \| \hat{\pi}_{\mathbf{r}'} \rangle^0 (\beta(\mathbf{r}') - \beta_s) \right] \\[2mm]
& + \boldsymbol{\nabla} \int d\mathbf{r}' \langle \hat{\mathbf{Q}}_{\mathbf{r}} \| \hat{\mathbf{F}}_{\mathbf{r}'} \rangle^0 \frac{\beta(\mathbf{r}') + \beta_s}{2}(\mathbf{v}(\mathbf{r}') - \mathbf{V}) && -\boldsymbol{\nabla} \int d\mathbf{r}' \langle \hat{\mathbf{Q}}_{\mathbf{r}} \| \hat{\pi}_{\mathbf{r}'} \rangle^0 (\beta(\mathbf{r}') - \beta_s) \\[2mm]
& - \int d\mathbf{r}' \langle \hat{\pi}_{\mathbf{r}} \| \hat{\boldsymbol{\sigma}}_{\mathbf{r}'} \rangle^0 \beta(\mathbf{r}') \boldsymbol{\nabla}'\mathbf{v}(\mathbf{r}') && + \int d\mathbf{r}' \langle \hat{\pi}_{\mathbf{r}} \| \hat{\mathbf{Q}}_{\mathbf{r}'} \rangle^0 \boldsymbol{\nabla}'\beta(\mathbf{r}') \\[2mm]
& + \frac{\mathbf{v}(\mathbf{r}) - \mathbf{V}}{2} \int d\mathbf{r}' \langle \hat{\mathbf{F}}_{\mathbf{r}} \| \hat{\boldsymbol{\sigma}}_{\mathbf{r}'} \rangle^0 \beta(\mathbf{r}') \boldsymbol{\nabla}'\mathbf{v}(\mathbf{r}') && - \frac{\mathbf{v}(\mathbf{r}) - \mathbf{V}}{2} \int d\mathbf{r}' \langle \hat{\mathbf{F}}_{\mathbf{r}} \| \hat{\mathbf{Q}}_{\mathbf{r}'} \rangle^0 \boldsymbol{\nabla}'\beta(\mathbf{r}') \\[2mm]
& - \int d\mathbf{r}' \langle \hat{\pi}_{\mathbf{r}} \| \hat{\mathbf{F}}_{\mathbf{r}'} \rangle^0 \frac{\beta(\mathbf{r}') + \beta_s}{2}(\mathbf{v}(\mathbf{r}') - \mathbf{V}) && + \int d\mathbf{r}' \langle \hat{\pi}_{\mathbf{r}} \| \hat{\pi}_{\mathbf{r}'} \rangle^0 (\beta(\mathbf{r}') - \beta_s) \\[2mm]
& + \frac{\mathbf{v}(\mathbf{r}) - \mathbf{V}}{2} \int d\mathbf{r}' \langle \hat{\mathbf{F}}_{\mathbf{r}} \| \hat{\mathbf{F}}_{\mathbf{r}'} \rangle^0 \frac{\beta(\mathbf{r}') + \beta_s}{2}(\mathbf{v}(\mathbf{r}') - \mathbf{V}) && - \frac{\mathbf{v}(\mathbf{r}) - \mathbf{V}}{2} \int d\mathbf{r}' \langle \hat{\mathbf{F}}_{\mathbf{r}} \| \hat{\pi}_{\mathbf{r}'} \rangle^0 (\beta(\mathbf{r}') - \beta_s)
\end{aligned}
$$

The equations (11.5) are closed equations for the relevant variables, because all the averages involved in $\boldsymbol{\sigma}(\mathbf{r}), \mathbf{F}(\mathbf{r}), \Delta\boldsymbol{\sigma}(\mathbf{r})$ and in the Green-Kubo kernels are given in terms of the relevant ensemble that depends implicitly on the relevant variables. However, for this very reason, they are not very *explicit* in the relevant variables and we seek now approximations that allows one to obtain the different averages in more explicit form. A second problem that we will need to solve is the explicit connection between the conjugate variables $\beta(\mathbf{r}), \mu(\mathbf{r}), \boldsymbol{\lambda}_R, \beta_s$ and the relevant variables.

11.6 The theory for a quiescent fluid

In the simulations presented, we have observed that after the initial flash, the solid expands slightly, and the fluid also moves due to thermal expansion. However, after a relatively small time in which the fluid adopts a non-homogeneous density field, the fluid stops moving, and there is only heat conduction in the system. In these situations, the equations simplify considerably.

After this transient time, we may use Eqs. (11.5) with $\mathbf{v}(\mathbf{r}) = 0$. In this way we obtain $\partial_t \rho(\mathbf{r}) = 0$, $\partial_t \mathbf{g}(\mathbf{r}) = 0$, $\partial_t \mathbf{R} = 0$, $\partial_t \mathbf{P} = 0$. The only non-trivial equations are

$$0 = -\boldsymbol{\nabla}\cdot\boldsymbol{\sigma}(\mathbf{r}) + \mathbf{F}(\mathbf{r}) - \boldsymbol{\nabla} \int d\mathbf{r}' \langle \hat{\boldsymbol{\sigma}}_{\mathbf{r}} \,\|\, \hat{\mathbf{Q}}_{\mathbf{r}'} \rangle^0 \boldsymbol{\nabla}' \beta(\mathbf{r}') - \boldsymbol{\nabla} \int d\mathbf{r}' \langle \hat{\boldsymbol{\sigma}}_{\mathbf{r}} \,\|\, \hat{\pi}_{\mathbf{r}'} \rangle^0 (\beta(\mathbf{r}') - \beta_{\mathrm{s}})$$

$$+ \int d\mathbf{r}' \langle \hat{\mathbf{F}}_{\mathbf{r}} \,\|\, \hat{\mathbf{Q}}_{\mathbf{r}'} \rangle^0 \boldsymbol{\nabla}' \beta(\mathbf{r}') + \int d\mathbf{r}' \langle \hat{\mathbf{F}}_{\mathbf{r}} \,\|\, \hat{\pi}_{\mathbf{r}'} \rangle^0 (\beta(\mathbf{r}') - \beta_{\mathrm{s}})$$

$$\partial_t \epsilon(\mathbf{r}) = -\boldsymbol{\nabla} \int d\mathbf{r}' \langle \hat{\mathbf{Q}}_{\mathbf{r}} \,\|\, \hat{\mathbf{Q}}_{\mathbf{r}'} \rangle^0 \boldsymbol{\nabla}' \beta(\mathbf{r}') - \boldsymbol{\nabla} \int d\mathbf{r}' \langle \hat{\mathbf{Q}}_{\mathbf{r}} \,\|\, \hat{\pi}_{\mathbf{r}'} \rangle^0 (\beta(\mathbf{r}') - \beta_{\mathrm{s}})$$

$$+ \int d\mathbf{r}' \langle \hat{\pi}_{\mathbf{r}} \,\|\, \hat{\mathbf{Q}}_{\mathbf{r}'} \rangle^0 \boldsymbol{\nabla}' \beta(\mathbf{r}') + \int d\mathbf{r}' \langle \hat{\pi}_{\mathbf{r}} \,\|\, \hat{\pi}_{\mathbf{r}'} \rangle^0 (\beta(\mathbf{r}') - \beta_{\mathrm{s}})$$

$$\partial_t U = - \int d\mathbf{r} \partial_t \epsilon(\mathbf{r})$$

The first equation is a mechanical balance equation in which the reversible fluid stress and force that the solid exerts on the fluid are balanced with irreversible forces due to temperature gradients and differences. **[I think that this equation fixes the density profile, but perhaps the Gibbs-Duhem relation is enough for fixing the density!]** The last equation is just an expression of total energy conservation, this is the energy lost by the solid is gained by the fluid.

Therefore, we will focus in the evolution equation for the internal energy, that takes the form

$$\partial_t \epsilon(\mathbf{r}) = -\boldsymbol{\nabla} \int d\mathbf{r}' \kappa_{\mathbf{r}\mathbf{r}'} \boldsymbol{\nabla}' \beta(\mathbf{r}') - \boldsymbol{\nabla} \int d\mathbf{r}' L_{\mathbf{r}\mathbf{r}'} (\beta(\mathbf{r}') - \beta_{\mathrm{s}}) + \int d\mathbf{r}' N_{\mathbf{r}\mathbf{r}'} \boldsymbol{\nabla}' \beta(\mathbf{r}') + \int d\mathbf{r}' S_{\mathbf{r}\mathbf{r}'} (\beta(\mathbf{r}') - \beta_{\mathrm{s}})$$

where we have introduced the following non-local kernels

$$\kappa_{\mathbf{r}\mathbf{r}'} = \langle \hat{\mathbf{Q}}_{\mathbf{r}} \,\|\, \hat{\mathbf{Q}}_{\mathbf{r}'} \rangle^0$$
$$L_{\mathbf{r}\mathbf{r}'} = \langle \hat{\mathbf{Q}}_{\mathbf{r}} \,\|\, \hat{\pi}_{\mathbf{r}'} \rangle^0$$
$$N_{\mathbf{r}\mathbf{r}'} = \langle \hat{\pi}_{\mathbf{r}} \,\|\, \hat{\mathbf{Q}}_{\mathbf{r}'} \rangle^0$$
$$S_{\mathbf{r}\mathbf{r}'} = \langle \hat{\pi}_{\mathbf{r}} \,\|\, \hat{\pi}_{\mathbf{r}'} \rangle^0$$

For future convenience the equation (11.6) may be expressed as

$$\partial_t \epsilon(\mathbf{r}) = -\boldsymbol{\nabla} \int d\mathbf{r}' \kappa_{\mathbf{r}\mathbf{r}'} \boldsymbol{\nabla}' (\beta(\mathbf{r}') - \beta_s) - \boldsymbol{\nabla} \int d\mathbf{r}' L_{\mathbf{r}\mathbf{r}'} (\beta(\mathbf{r}') - \beta_{\mathrm{s}}) + \int d\mathbf{r}' N_{\mathbf{r}\mathbf{r}'} \boldsymbol{\nabla}' (\beta(\mathbf{r}') - \beta_s) + \int d\mathbf{r}' S_{\mathbf{r}\mathbf{r}'} (\beta(\mathbf{r}') - \beta_{\mathrm{s}})$$

Because microscopic power $\hat{\pi}_\mathbf{r}$ is different from zero only near the solid, the kernels $L_{\mathbf{rr'}}$, $H_{\mathbf{rr'}}$, $K_{\mathbf{rr'}}$ are different from zero only if $\mathbf{r}$ and $\mathbf{r'}$ are close to the solid surface. Therefore, last three terms in (11.6) are localised terms near the surface of the solid. The first term involving second derivatives is a non-local version of Fourier law of heat conduction.

Onsager symmetry now takes the form

$$\mathbf{K_{rr'}} = \mathbf{K_{r'r}}$$
$$\mathbf{H_{rr'}} = \mathbf{H_{r'r}}$$
$$S_{\mathbf{rr'}} = S_{\mathbf{r'r}}$$

Eq. (11.6) should allow to predict the evolution of the energy profile, given an initial profile of the energy once the fluid has settled down to zero motion. The temperature field $\beta(\mathbf{r})$ and the temperature of the solid β_s are the derivatives of the entropy function that depends

11.7   The discrete version of the full dynamics at the CG level

There are many possibilities to numerically discretize the above equations. As we want to have integrated quantities that can be measured in MD simulaitons, we choose a Galerkin finite element method. Because of traslational invariance along the walls, we will bin the system in layers paralel to the planar walls. The box length L_z is divided in M bins labelled with an index μ. The bins are separated by $M+1$ nodes (actually, nodal planes) located at $z_\mu = (i-1)\Delta z$, $i = 1, \cdots, M+1$ with $\Delta z = L_z/M$. We carefully distinguish between *nodes* and *bins*: nodes are points in the z axis, while bins are segments in this axis. In 3D, nodes are planes, while bins are slabs. As it will become apparent, from a microscopic point of view, mass, momentum, and force densities are defined at the nodes, while stress is defined at the bin. Each bin is a layer of dimensions $L_x, L_y, \Delta z$, where $\Delta z = L_z/M$. We introduce the characteristic function of the bin $\chi_\mu(\mathbf{r})$ that takes the value 1 if $\mathbf{r}$ is in the bin and zero otherwise. Its explicit form is given by the unit function

$$\chi_\mu(\mathbf{r}) = \theta(z_{\mu+1} - x_3)\theta(x_3 - z_\mu) = \chi_\mu(x_3)$$

where $\theta(x)$ is the Heaviside step function, $z_{\mu+1}$ is the position of the upper boundary of the layer, and z_μ is the corresponding position of the lower boundary of the layer. The *node* μ is located at z_μ. The set of characteristic functions form a partition of unity, in the sense that, by summing over all the bins we have

$$\sum_{\mu=1}^{M} \chi_\mu(\mathbf{r}) = 1$$

The volume integral of the characteristic function gives the volume $\mathscr{V}_\mu$ of the bin

$$\int d\mathbf{r}\chi_\mu(\mathbf{r}) = \mathscr{V}_\mu = L_x L_y \Delta z$$

For each node μ, we introduce a linear basis function $\psi_\mu(\mathbf{r})$

$$\psi_\mu(\mathbf{r}) = \chi_\mu(x_3)\frac{z_{\mu+1} - x_3}{\Delta z} + \chi_{\mu-1}(x_3)\frac{x_3 - z_{\mu-1}}{\Delta z}$$

that depends only on the x_3 component of $\mathbf{r}$. The only non-zero partial derivative is given by

$$\frac{\partial}{\partial x_3}\psi_\mu(\mathbf{r}) = -\frac{\chi_\mu(x_3) - \chi_{\mu-1}(x_3)}{\Delta z}$$

These phase functions, as opposed to the microscopic functions $\hat{\rho}_\mathbf{r}(z), \hat{\mathbf{g}}_\mathbf{r}(z)$, can be measured directly in an MD simulation. Note that the integral of the basis functions $\psi_\mu(\mathbf{r})$

gives the volume of bin μ, this is

$$\int d\mathbf{r}\psi_\mu(\mathbf{r}) = \mathscr{V}_\mu$$

In the Galerkin method, we assume that the temperature field, $\beta(\mathbf{r})$, is well approximated by the linearly interpolated field

$$\beta(\mathbf{r}) \simeq \sum_\nu \psi_\nu(\mathbf{r})\beta_\nu$$

Therefore, we may express $\beta(\mathbf{r}) - \beta_s$ as

$$\beta(\mathbf{r}) - \beta_s \simeq \sum_\nu \psi_\nu(\mathbf{r})(\beta_\nu - \beta_s)$$

This results in the following discrete equation

$$\begin{aligned}
\partial_t \epsilon_\mu(t) = &- \sum_{\nu=1}^{M+1} \mathscr{V}_\nu \int \frac{d\mathbf{r}}{\mathscr{V}_\mu} \int \frac{d\mathbf{r}'}{\mathscr{V}_\nu} \boldsymbol{\nabla}\psi_\mu(\mathbf{r})\boldsymbol{\kappa_{rr'}}\boldsymbol{\nabla}'\left[\psi_\nu(\mathbf{r}')(\beta_\nu - \beta_s)\right] \\
&- \sum_{\nu=1}^{M+1} \mathscr{V}_\nu \int \frac{d\mathbf{r}}{\mathscr{V}_\mu} \int \frac{d\mathbf{r}'}{\mathscr{V}_\nu} \boldsymbol{\nabla}\psi_\mu(\mathbf{r})\mathbf{L_{rr'}}\left[\psi_\nu(\mathbf{r}')(\beta_\nu - \beta_s)\right] \\
&+ \sum_{\nu=1}^{M+1} \mathscr{V}_\nu \frac{d\mathbf{r}}{\mathscr{V}_\mu} \int \frac{d\mathbf{r}'}{\mathscr{V}_\nu} \psi_\mu(\mathbf{r})\mathbf{N_{rr'}}\boldsymbol{\nabla}'\left[\psi_\nu(\mathbf{r}')(\beta_\nu - \beta_s)\right] \\
&+ \sum_{\nu=1}^{M+1} \mathscr{V}_\nu \int \frac{d\mathbf{r}}{\mathscr{V}_\mu} \int \frac{d\mathbf{r}'}{\mathscr{V}_\nu} \psi_\mu(\mathbf{r})S_{rr'}\left[\psi_\nu(\mathbf{r}')(\beta_\nu - \beta_s)\right]
\end{aligned}$$

Because ψ depends only on the z component of r, the eq. (11.7) takes the form

$$\begin{aligned}
\partial_t \epsilon_\mu(t) = &- \sum_{\nu=1}^{M+1} \mathscr{V}_\nu \int \frac{d\mathbf{r}}{\mathscr{V}_\mu} \int \frac{d\mathbf{r}'}{\mathscr{V}_\nu} \frac{\partial}{\partial x_3}\psi_\mu(\mathbf{r})\boldsymbol{\kappa_{rr'}}\frac{\partial}{\partial x_3}\left[\psi_\nu(\mathbf{r}')(\beta_\nu - \beta_s)\right] \\
&- \sum_{\nu=1}^{M+1} \mathscr{V}_\nu \int \frac{d\mathbf{r}}{\mathscr{V}_\mu} \int \frac{d\mathbf{r}'}{\mathscr{V}_\nu} \frac{\partial}{\partial x_3}\psi_\mu(\mathbf{r})\mathbf{L_{rr'}}\left[\psi_\nu(\mathbf{r}')(\beta_\nu - \beta_s)\right] \\
&+ \sum_{\nu=1}^{M+1} \mathscr{V}_\nu \int \frac{d\mathbf{r}}{\mathscr{V}_\mu} \int \frac{d\mathbf{r}'}{\mathscr{V}_\nu} \psi_\mu(\mathbf{r})\mathbf{N_{rr'}}\frac{\partial}{\partial x_3}\left[\psi_\nu(\mathbf{r}')(\beta_\nu - \beta_s)\right] \\
&+ \sum_{\nu=1}^{M+1} \mathscr{V}_\nu \int \frac{d\mathbf{r}}{\mathscr{V}_\mu} \int \frac{d\mathbf{r}'}{\mathscr{V}_\nu} \psi_\mu(\mathbf{r})S_{rr'}\left[\psi_\nu(\mathbf{r}')(\beta_\nu - \beta_s)\right]
\end{aligned}$$

We now consider each term within square brackets. The first one is, after using the

expression (11.7) for the derivatives of the basis functions

$$\int \frac{d\mathbf{r}}{\mathscr{V}_\mu} \int \frac{d\mathbf{r}'}{\mathscr{V}_\nu} \frac{\partial}{\partial x_3} \psi_\mu(\mathbf{r}) \boldsymbol{\kappa}_{\mathbf{rr}'} \frac{\partial}{\partial x_3'} \psi_\nu(\mathbf{r}')$$

$$= \frac{1}{\Delta z^2} \int \frac{d\mathbf{r}}{\mathscr{V}_\mu} \int \frac{d\mathbf{r}'}{\mathscr{V}_\nu} (\chi_\mu(x_3) - \chi_{\mu-1}(x_3))$$

$$\times \boldsymbol{\kappa}_{\mathbf{rr}'} (\chi_\nu(x_3) - \chi_{\nu-1}(x_3))$$

$$= \frac{1}{\Delta z^2} \left[\kappa_{\mu\nu} - \kappa_{\mu-1\nu} - \kappa_{\mu\nu-1} + \kappa_{\mu-1\nu-1} \right]$$

where we have introduced the discrete kernels as

$$\kappa_{\mu\nu} \equiv \int \frac{d\mathbf{r}}{\mathscr{V}_\mu} \int \frac{d\mathbf{r}'}{\mathscr{V}_\nu} \chi_\mu(\mathbf{r}) \boldsymbol{\kappa}_{\mathbf{rr}'} \chi_\nu(\mathbf{r}')$$

$$= \int_0^\infty dt' \langle \mathscr{Q}\hat{Q}_\mu(t') \mathscr{Q}\hat{Q}_\nu \rangle$$

The second bracket in (11.7) is

$$\frac{1}{\Delta z} \int \frac{d\mathbf{r}}{\mathscr{V}_\mu} \int \frac{d\mathbf{r}'}{\mathscr{V}_\nu} (\chi_\mu(\mathbf{r}) - \chi_{\mu-1}(\mathbf{r})) \mathbf{L}_{\mathbf{rr}'} \psi_\nu(\mathbf{r}')$$

$$= \frac{1}{\Delta z} \left[L_{\mu\nu} - L_{\mu-1\nu} \right]$$

where

$$L_{\mu\nu} \equiv \int \frac{d\mathbf{r}}{\mathscr{V}_\mu} \int \frac{d\mathbf{r}'}{\mathscr{V}_\nu} \chi_\mu(\mathbf{r}) \mathbf{L}_{\mathbf{rr}'} \psi_\nu(\mathbf{r}')$$

$$= \int_0^\infty dt' \langle \mathscr{Q}\hat{Q}_\mu(t') \mathscr{Q}\hat{\pi}_\nu \rangle$$

The third one is

$$= -\frac{1}{\Delta z} \int \frac{d\mathbf{r}}{\mathscr{V}_\mu} \int \frac{d\mathbf{r}'}{\mathscr{V}_\nu} \psi_\mu(\mathbf{r}) \mathbf{N}_{\mathbf{rr}'} (\chi_\nu(\mathbf{r}') - \chi_{\nu-1}(\mathbf{r}'))$$

$$= -\frac{1}{\Delta z} \left[N_{\mu\nu} - N_{\mu\nu-1} \right]$$

where we have introduced

$$N_{\mu\nu} \equiv \int \frac{d\mathbf{r}}{\mathscr{V}_\mu} \int \frac{d\mathbf{r}'}{\mathscr{V}_\nu} \psi_\mu(\mathbf{r}) \mathbf{N}_{\mathbf{rr}'} \chi_\nu(\mathbf{r}')$$

$$= \int_0^\infty dt' \langle \mathscr{Q}\hat{\pi}_\mu(t') \mathscr{Q}\hat{Q}_\nu \rangle$$

and the last one is

$$S_{\mu\nu} \equiv \int \frac{d\mathbf{r}}{\mathscr{V}_\mu} \frac{d\mathbf{r}'}{\mathscr{V}_\nu} \psi_\mu(\mathbf{r}) S_{rr'} \psi_\nu(\mathbf{r}')$$

$$= \int_0^\infty dt' \langle \mathscr{Q}\hat{\pi}_\mu(t') \mathscr{Q}\hat{\pi}_\nu \rangle$$

In these expressions, we have introduced

$$\int \frac{d\mathbf{r}}{\mathscr{V}_\mu} \chi_\mu(\mathbf{r}) \hat{Q}_{\mathbf{r}} = \hat{\boldsymbol{Q}}_\mu$$

$$\int \frac{d\mathbf{r}}{\mathscr{V}_\nu} \psi_\nu(\mathbf{r}) \hat{\pi}_{\mathbf{r}} = \hat{\pi}_\mu$$

and the non-local kernels (11.6).

The final form of the discrete equation is

$$\partial_t \epsilon_\mu(t) = -\sum_{\nu=1}^{M+1} \mathscr{V}_\nu \frac{[\kappa_{\mu\nu} - \kappa_{\mu-1\nu} - \kappa_{\mu\nu-1} + \kappa_{\mu-1\nu-1}]}{\Delta z^2} [\beta_\nu - \beta_s]$$

$$+ \sum_{\nu=1}^{M+1} \mathscr{V}_\nu \frac{[L_{\mu\nu} - L_{\mu\nu-1}]}{\Delta z} [\beta_\nu - \beta_s]$$

$$- \sum_{\nu=1}^{M+1} \mathscr{V}_\nu \frac{[N_{\mu\nu} - N_{\mu-1\nu}]}{\Delta z} [\beta_\nu - \beta_s]$$

$$+ \sum_{\nu=1}^{M+1} \mathscr{V}_\nu S_{\mu\nu} [\beta_\nu - \beta_s]$$

In order to compute the unknown terms $\kappa_{\mu\nu}, L_{\mu\nu}, N_{\mu\nu}$ and $S_{\mu\nu}$ we need to discretize them. Therefore, we have to discretize $\mathscr{Q}_t \hat{Q}_{\mathbf{r}}$ and $\mathscr{Q}_t \hat{\pi}_{\mathbf{r}}$. See appendix for more detail. **[Este salto está en el ejercicio Discrete version. Hay que adaptarlo para añadirlo aquí]**

$$\mathscr{Q}_t \hat{\mathbf{Q}}_\mu = \hat{\mathbf{Q}}_\mu - \mathrm{Tr}\left[\bar{\rho}_t \hat{\mathbf{Q}}_\mu\right]$$

$$- \sum_\mu \sum_{\mu'} (\hat{\rho}_\mu - \rho_\mu) \langle \delta\hat{\boldsymbol{\rho}}_\mu \delta\hat{\boldsymbol{\rho}}_{\mu'} \rangle^{-1} \left\langle \hat{\boldsymbol{\rho}}_{\mu'} \delta\hat{\mathbf{Q}}_\mu \right\rangle$$

$$- \sum_\mu \sum_{\mu'} (\hat{\mathbf{g}}_\mu - \mathbf{g}_\mu) \langle \delta\hat{\mathbf{g}}_\mu \delta\hat{\mathbf{g}}_{\mu'} \rangle^{-1} \mathbf{v}(\mu') \left\langle \hat{\boldsymbol{\rho}}_{\mu'} \delta\hat{\mathbf{Q}}_\mu \right\rangle$$

$$- \sum_\mu \sum_{\mu'} (\hat{\mathbf{e}}_\mu - \mathbf{e}_\mu) \langle \delta\hat{\mathbf{e}}_\mu \delta\hat{\mathbf{e}}_{\mu'} \rangle^{-1} \left\langle \hat{\mathbf{e}}_{\mu'} \delta\hat{\mathbf{Q}}_\mu \right\rangle$$

and

$$
\begin{aligned}
\mathscr{Q}_t \hat{\pi}_\mu = \hat{\pi}_\mu &- \text{Tr}\left[\overline{\rho}_t \hat{\pi}_\mu\right] \\
&- \sum_\mu \sum_{\mu'} (\hat{\rho}_\mu - \rho_\mu) \langle \delta\hat{\rho}_\mu \delta\hat{\rho}_{\mu'}\rangle^{-1} \langle \hat{\rho}_{\mu'} \delta\hat{\pi}_\mu\rangle \\
&- \sum_\mu \sum_{\mu'} (\hat{\mathbf{g}}_\mu - \mathbf{g}_\mu) \langle \delta\hat{\mathbf{g}}_\mu \delta\hat{\mathbf{g}}_{\mu'}\rangle^{-1} \mathbf{v}(\mu') \langle \hat{\rho}_{\mu'} \delta\hat{\pi}_\mu\rangle \\
&- \sum_\mu \sum_{\mu'} (\hat{\mathbf{e}}_\mu - \mathbf{e}_\mu) \langle \delta\hat{\mathbf{e}}_\mu \delta\hat{\mathbf{e}}_{\mu'}\rangle^{-1} \langle \hat{\mathbf{e}}_{\mu'} \delta\hat{\pi}_\mu\rangle
\end{aligned}
$$

11.7.1 The discrete version of the full dynamics at equilibrium

At equilibrium the equations for $\mathscr{Q}_t\hat{\mathbf{Q}}_\mu$ and $\mathscr{Q}_t\hat{\pi}_\mu$ takes the form

$$
\mathscr{Q}_t\hat{\mathbf{Q}}_\mu = \hat{\mathbf{Q}}_\mu - \sum_\mu \sum_{\mu'} (\hat{\boldsymbol{\epsilon}}_\mu - \boldsymbol{\epsilon}_\mu) \langle \delta\hat{\boldsymbol{\epsilon}}_\mu \delta\hat{\boldsymbol{\epsilon}}_{\mu'}\rangle^{-1} \left\langle \hat{\boldsymbol{\epsilon}}_{\mu'} \delta\hat{\mathbf{Q}}_\mu\right\rangle
$$

and

$$
\mathscr{Q}_t\hat{\pi}_\mu = \hat{\pi}_\mu - \sum_\mu \sum_{\mu'} (\hat{\boldsymbol{\epsilon}}_\mu - \boldsymbol{\epsilon}_\mu) \langle \delta\hat{\boldsymbol{\epsilon}}_\mu \delta\hat{\boldsymbol{\epsilon}}_{\mu'}\rangle^{-1} \langle \hat{\boldsymbol{\epsilon}}_{\mu'} \delta\hat{\pi}_\mu\rangle
$$

This shows that at equilibrium the action of the Kawasaki-Gunton projection operator on $\hat{\mathbf{Q}}_\mu$ and $\hat{\pi}_\mu$ does nothing. This implies that we only have to compute the discrete version of $\hat{\mathbf{Q}}_\mu$ and $\hat{\pi}_\mu$. See appendix por more detail.

$$
\hat{\mathbf{Q}}_\mu = \sum_i \mathbf{v}_i e_i \frac{\chi_\mu(\mathbf{r}_i)}{\mathscr{V}_\mu} + \frac{1}{2\mathscr{V}_\mu} \sum_{ij}^{NN} \frac{(\mathbf{v}_i + \mathbf{v}_j)}{2} \cdot \mathbf{F}_{ij} \mathbf{q}_{ij} z_\mu(i,j)
$$

and

$$
\hat{\pi}_\mu = \sum_{ij'}^{NN'} \mathbf{F}_{ij'} \cdot \frac{(\mathbf{v}_i + \mathbf{v}_{j'})}{2} \frac{\psi_\mu(\mathbf{r}_i)}{\mathscr{V}_\mu}
$$

Therefore, at equilibrium the equations (11.7), (11.7), (11.7) and (11.7) takes the form

$$
\kappa_{\mu\nu} = \int_0^\infty dt' \langle \hat{\mathbf{Q}}_\mu(t') \hat{\mathbf{Q}}_\nu\rangle
$$

$$
L_{\mu\nu} = \int_0^\infty dt' \langle \hat{\mathbf{Q}}_\mu(t') \hat{\pi}_\nu\rangle
$$

$$
N_{\mu\nu} = \int_0^\infty dt' \langle \hat{\pi}_\mu(t') \hat{\mathbf{Q}}_\nu\rangle
$$

$$S_{\mu\nu} = \int_0^\infty dt' \langle \hat{\pi}_\mu(t') \hat{\pi}_\nu \rangle$$

The equation (11.7) can be written compactly in matrix form as

$$\partial_t \boldsymbol{\epsilon}(t) = -\mathbf{M} \cdot \boldsymbol{\beta}(t)$$

where $\boldsymbol{\beta}$ is a vector with components β_ν and $\mathbf{M}$ contains the information about the transport coefficients

$$\mathbf{M} = \mathcal{V} \left[\frac{\kappa_{\mu\nu} - \kappa_{\mu-1\nu} - \kappa_{\mu\nu-1} + \kappa_{\mu-1\nu-1}}{\Delta z^2} - \frac{L_{\mu\nu} - L_{\mu\nu-1}}{\Delta z} - \frac{N_{\mu\nu} - N_{\mu-1\nu}}{\Delta z} + S_{\mu\nu} \right]$$

We may introduce the bi-diagonal forward finite difference operator $\mathbf{F}$ in order to obtain a more compact form of $\mathbf{M}$.

$$\mathbf{F} = \frac{1}{\Delta z} \begin{pmatrix} 1 & -1 & 0 & \cdots & 0 \\ 0 & 1 & -1 & \cdots & 0 \\ \vdots & & \ddots & & \\ 0 & \cdots & 0 & 1 & -1 \\ 0 & \cdots & 0 & 0 & 1 \end{pmatrix}$$

Therefore,

$$\mathbf{M} \equiv \mathcal{V} \left[\mathbf{F}^T \boldsymbol{\kappa} \mathbf{F} - \mathbf{F}^T \mathbf{L} - \mathbf{N}\mathbf{F} + \mathbf{S} \right]$$

where $\boldsymbol{\kappa}$, $\mathbf{L}$, $\mathbf{N}$ and $\mathbf{S}$ are matrix with components $\kappa_{\mu\nu}$, $L_{\mu\nu}$, $N_{\mu\nu}$ and $S_{\mu\nu}$, respectively.

11.8   Local equilibrium approximation

In this section we show that if the conjugate fields vary little in the length scale of molecular correlations, we may approximate the relevant ensemble of local functions with an ordinary equilibrium ensemble with temperature and chemical potentials matched to the local values of the conjugate fields.

Consider the rest ensemble averages of local functions like $\boldsymbol{\sigma}(\mathbf{r}), \mathbf{F}^{\mathrm{s}\to\mathrm{f}}(\mathbf{r}), \Delta\boldsymbol{\sigma}(\mathbf{r})$. For the sake of the discussion, choose first the stress tensor

$$\boldsymbol{\sigma}(\mathbf{r}) = \mathrm{Tr}\left[\overline{\rho}^{\mathrm{rest}}\hat{\boldsymbol{\sigma}}_{\mathbf{r}}\right] = \frac{\rho_0}{\Xi_{\mathrm{rest}}[\lambda]}\mathrm{Tr}\left[\exp\left\{-\int d\mathbf{r}'\beta(\mathbf{r}')\left(\hat{e}_{\mathbf{r}'} - \mu(\mathbf{r}')\hat{\rho}_{\mathbf{r}'}\right) - \boldsymbol{\lambda}_R\cdot\hat{\mathbf{R}} - \beta_{\mathrm{s}}\hat{E}\right\}\hat{\boldsymbol{\sigma}}_{\mathbf{r}}\right]$$

By expanding the conjugate fields $\beta(\mathbf{r}'), \mu(\mathbf{r}')$ around $\mathbf{r}$ in the numerator and denominator (within $\Xi_{\mathrm{rest}}[\lambda]$), we have

$$\boldsymbol{\sigma}(\mathbf{r}) = \frac{\mathrm{Tr}\left[\exp\left\{-\int d\mathbf{r}'(\beta(\mathbf{r}) + \Delta\beta(\mathbf{r}')\left(\hat{e}_{\mathbf{r}'} + (\beta\mu(\mathbf{r}) + \Delta\beta\mu(\mathbf{r}'))\hat{\rho}_{\mathbf{r}'}\right) - \boldsymbol{\lambda}_R\cdot\hat{\mathbf{R}} - \beta_{\mathrm{s}}\hat{E}\right\}\hat{\boldsymbol{\sigma}}_{\mathbf{r}}\right]}{\mathrm{Tr}\left[\exp\left\{-\int d\mathbf{r}'(\beta(\mathbf{r}) + \Delta\beta(\mathbf{r}')\left(\hat{e}_{\mathbf{r}'} + (\beta\mu(\mathbf{r}) + \Delta\beta\mu(\mathbf{r}'))\hat{\rho}_{\mathbf{r}'}\right) - \boldsymbol{\lambda}_R\cdot\hat{\mathbf{R}} - \beta_{\mathrm{s}}\hat{E}\right\}\right]}$$

$$= \frac{\mathrm{Tr}\left[\rho_{\mathbf{r}}^{\mathrm{loc}}\left(1 - \int d\mathbf{r}'\Delta\beta(\mathbf{r}')\left(\hat{e}_{\mathbf{r}'} - (\beta\mu(\mathbf{r}) + \Delta\beta\mu(\mathbf{r}'))\hat{\rho}_{\mathbf{r}'} + \cdots\right)\right)\hat{\boldsymbol{\sigma}}_{\mathbf{r}}\right]}{\mathrm{Tr}\left[\rho_{\mathbf{r}}^{\mathrm{loc}}\left(1 - \int d\mathbf{r}'\Delta\beta(\mathbf{r}')\left(\hat{e}_{\mathbf{r}'} - (\beta\mu(\mathbf{r}) + \Delta\beta\mu(\mathbf{r}'))\hat{\rho}_{\mathbf{r}'}\right) + \cdots\right)\right]}$$

where $\Delta\beta(\mathbf{r}) = \beta(\mathbf{r}') - \beta(\mathbf{r})$ and $\Delta\beta\mu(\mathbf{r}) = \beta\mu(\mathbf{r}') - \beta\mu(\mathbf{r})$. We have introduced the local ensemble, etc., and we have introduced the local ensemble

$$\rho_{\mathbf{r}}^{\mathrm{loc}} \equiv \frac{1}{\Xi_{\mathbf{r}}}\exp\left\{-\beta(\mathbf{r})\hat{H}^{\mathrm{s}} + \beta\mu(\mathbf{r})mN - \boldsymbol{\lambda}_R\cdot\hat{\mathbf{R}} - \beta_{\mathrm{s}}\hat{E}\right\}$$

$$\Xi_{\mathbf{r}} = \mathrm{Tr}\left[\exp\left\{-\beta(\mathbf{r})\hat{H}^{\mathrm{s}} + \beta\mu(\mathbf{r})mN - \boldsymbol{\lambda}_R\cdot\hat{\mathbf{R}} - \beta_{\mathrm{s}}\hat{E}\right\}\right]$$

Note that the local ensemble is conceptually close to the equilibrium ensemble, where the temperature and chemical potential are matched to the local field values. However, it is not exactly the same as an equilibrium ensemble because the two temperatures $\beta(\mathbf{r})$ and β_{s} are not identical in general. In addition, the ensemble contains the term $\boldsymbol{\lambda}_R$ that accounts for the presence of the solid sphere with its center of mass at the average position $\mathbf{R}$.

The first two terms in the expansion (11.8) are

$$\boldsymbol{\sigma}(\mathbf{r}) = \mathrm{Tr}\left[\rho_{\mathbf{r}}^{\mathrm{loc}}\hat{\boldsymbol{\sigma}}_{\mathbf{r}}\right] - \int d\mathbf{r}'\Delta\beta(\mathbf{r}')\mathrm{Tr}\left[\rho_{\mathbf{r}}^{\mathrm{loc}}\left(\hat{e}_{\mathbf{r}'} - \langle\hat{e}_{\mathbf{r}'}\rangle_{\mathbf{r}}^{\mathrm{loc}}\right)\hat{\boldsymbol{\sigma}}_{\mathbf{r}}\right] + \int d\mathbf{r}'\Delta\beta\mu(\mathbf{r}')\mathrm{Tr}\left[\rho_{\mathbf{r}}^{\mathrm{loc}}\left(\hat{\rho}_{\mathbf{r}'} - \langle\hat{\rho}_{\mathbf{r}'}\rangle_{\mathbf{r}}^{\mathrm{loc}}\right)\hat{\boldsymbol{\sigma}}_{\mathbf{r}}\right] + \cdots$$

Note that the linear term in the expansion involves correlations between the hydrodynamic fields at $\mathbf{r}'$ and the stress tensor at $\mathbf{r}$. These correlations decay in typical length scales of molecular size, i.e. in the range of the interactions. If the conjugate fields $\beta(\mathbf{r}), \mu(\mathbf{r})$ vary little in these length scales, we may neglect all the linear and higher order

terms, leading to the *local approximation*

$$\boldsymbol{\sigma}(\mathbf{r}) \simeq \mathrm{Tr}\left[\rho_\mathbf{r}^{\mathrm{loc}} \hat{\boldsymbol{\sigma}}_\mathbf{r}\right]$$

11.8.1   The entropy under the local approximation

The local approximation assumes that the relevant ensemble can be approximated by

$$\overline{\rho}_t = \rho_\mathbf{r}^{\mathrm{loc}}\left(1 - \int d\mathbf{r}' \Delta\beta(\mathbf{r}')\left(\hat{e}_{\mathbf{r}'} - (\beta\mu(\mathbf{r}) + \Delta\beta\mu(\mathbf{r}'))\hat{\rho}_{\mathbf{r}'} + \cdots\right)\right)$$

[Far from the solid sphere, the average of the stress tensor is seen to be identical to the pressure.]

[It should be remarked that the theory presented is valid, as the H-theorem clearly testifies, for the decaying dynamics towards the equilibrium state in isolated systems. It is, therefore, a theory that describes, given initial values for the averages of the CG variables, the subsequent average evolution towards equilibrium. One situation in which we will be interested is when the solid particle is very large and therefore, very massive. In these situations, we may assume that the spherical particle has initial (average) position $\mathbf{R}_0$ and initial (average) momentum $\mathbf{P}_0 = 0$ and that, for all the decay evolution of the hydrodynamic fields, these values do not change appreciably because the forces that the fluid exerts on the particle during its evolution are not sufficiently strong to modify these variables.] In principle, the relevant ensemble depends (in a functional way) on the averages of all the relevant variables of the system. We will evaluate the transport kernels for the *equilibrium* values of the relevant variables and will assume that for any other value of the average value of the relevant variables obtained in the course of the dynamics, the transport kernels do not change sensibly. The equilibrium values of the average relevant variables have been obtained in Eqs. (11.10.2), (20.3) and are characterized by the following conjugate variables (see Eq. (22.5) and (10))

$$\mu(\mathbf{r}, \mathbf{R}) = \mu_0$$
$$\boldsymbol{\lambda}_g(\mathbf{r}) = 0$$
$$\boldsymbol{\lambda}_P = 0$$
$$\boldsymbol{\lambda}_R = 0$$

Substitution of these conjugate variables into the relevant ensemble (12.4) shows that the relevant ensemble becomes just the equilibrium ensemble. Of course an equilibrium average of the microscopic system is one in which the sampling of the microscopic state involves states where the solid sphere may be located in any one position of the physical space, due to Brownian motion. When the solid particle is infinitely massive, the position of the center of mass will not change appreciably in the time scale at which the solvent becomes equilibrated. This is, when the number of particles of the solid object is very large, we expect that the instantaneous values of their centers of mass $\hat{\mathbf{R}}$ is always very similar to their average values. For massive solid objects and, in particular, planar walls, we should understand the averages over the equilibrium ensemble as a conditional averages where the solid object is fixed in space. These equilibrium averages can

be, therefore, sampled through the ergodic hypothesis, as time averages over long MD simulations in which the solid remains fixed.

The projected currents are computed explicitly in the appendix.

As it is well-known, if two phase space variables $\hat{A}(z), \hat{B}(z)$ transform under time reversal with the same parity, the property of microscopic reversibility together with the stationarity of the equilibrium ensemble imply

$$\langle A(t)B \rangle^{\text{eq}} = \langle AB(t) \rangle^{\text{eq}}$$

The microscopic reversibility property reflects into the following

$$\langle \mathscr{Q}\mathbf{F_r}(t)\mathscr{Q}\boldsymbol{\sigma_{r'}} \rangle^{\text{eq}} = \langle \mathscr{Q}\boldsymbol{\sigma_{r'}}(t)\mathscr{Q}\mathbf{F_r} \rangle^{\text{eq}}$$

This results in the following symmetry properties (Onsager relations) for the transport kernels

$$\boldsymbol{\eta}_{\mathbf{rr'}}^{\alpha\beta\alpha'\beta'} = \boldsymbol{\eta}_{\mathbf{r'r}}^{\alpha'\beta'\alpha\beta}$$
$$\mathbf{H}_{\mathbf{rr'}}^{\alpha\beta\alpha'} = \mathbf{G}_{\mathbf{r'r}}^{\alpha'\alpha\beta}$$
$$\boldsymbol{\gamma}_{\mathbf{rr'}}^{\alpha\alpha'} = \boldsymbol{\gamma}_{\mathbf{r'r}}^{\alpha'\alpha}$$

11.8.2   Connection between conjugate and relevant variables

11.8.3   Model for the entropy

The explicit functional form of the entropy functional $S_{\text{rest}}[\rho, \epsilon, \mathbf{R}, U]$ is not known in general and constructing models is not an easy task in general. We will restrict in the present work to one of the simplest models, the quadratic model. The quadratic model for the entropy is based on an expansion to second order of the entropy around the equilibrium state. In general terms we have

$$S_{\text{rest}}(a) = S_{\text{rest}}(a^{\text{eq}}) + \frac{\partial S_{\text{rest}}}{\partial a}(a^{\text{eq}})\delta a + \frac{1}{2}\frac{\partial^2 S_{\text{rest}}}{\partial a \partial a}(a^{\text{eq}})\delta a \delta a + \cdots$$
$$\simeq S(a^{\text{eq}}) + \frac{1}{2}\frac{\partial^2 S}{\partial a \partial a}(a^{\text{eq}})\delta a \delta a + \cdots$$

where $\delta a = a - a^{\text{eq}}$ and the linear term vanishes because the entropy attains its maximum value at the equilibrium state. Note that the Hessian matrix of second derivatives of the entropy is given by the inverse of the Hessian matrix of the thermodynamic potential $\Phi(\lambda)$, as can be easily seen from the fact that the both are Legendre transform of each other. In turn, the matrix of second derivatives of the thermodynamic potential are just the covariances of the relevant variables. In this way, we end up with the quadratic model

for the entropy

$$S(a) = S(a^{\mathrm{eq}}) - \frac{1}{2} \left\langle \delta\hat{A}\delta\hat{A} \right\rangle_{\mathrm{eq}}^{-1} \delta a \delta a$$

Here $\langle \cdots \rangle_{\mathrm{eq}}$ denotes an average with the equilibrium ensemble. This model uses as information the equilibrium average and covariance of the relevant variables. As such, is not a highly predictive model. As compared with density functional models for hard spheres, for example, that allow to predict the average density profile as an output, the present approximation requires the equilibrium average as input. In addition, the quadratic model is valid for describing situations relatively close to equilibrium. However, it is the simplest minimal non-trivial model that already captures structure of the fluid (i.e. layering) and allows for a non-equilibrium description of the evolution of the system. The conjugate parameters of this model are linear in the deviations of the relevant variables from equilibrium, this is

$$\lambda(a) = - \left\langle \delta\hat{A}\delta\hat{A} \right\rangle_{\mathrm{eq}}^{-1} \delta a$$

This gives an explicit expression for the conjugate parameters entering the dynamic equation.

For the case that the entropy is (11.2.2) we have the following conjugate variables (11.2.2)

$$\beta(\mathbf{r})\mu(\mathbf{r}) = - \int d\mathbf{r} \left[\langle \delta\hat{\rho}_{\mathbf{r}} \delta\hat{\rho}_{\mathbf{r}'} \rangle_{\mathrm{eq}} \right]^{-1} \delta\rho_{\mathbf{r}'} - \int d\mathbf{r} \left[\langle \delta\hat{\rho}_{\mathbf{r}} \delta\hat{\epsilon}_{\mathbf{r}'} \rangle_{\mathrm{eq}} \right]^{-1} \delta\epsilon_{\mathbf{r}'} - \left[\left\langle \delta\hat{\rho}_{\mathbf{r}} \delta\hat{\mathbf{R}}_{\mathbf{r}'} \right\rangle_{\mathrm{eq}} \right]^{-1} \delta\mathbf{R} - \left[\left\langle \delta\hat{\rho}_{\mathbf{r}} \delta\hat{U}_{\mathbf{r}'} \right\rangle_{\mathrm{eq}} \right]^{-1} \delta U$$

$$\beta(\mathbf{r}) = - \int d\mathbf{r} \left[\langle \delta\hat{\epsilon}_{\mathbf{r}} \delta\hat{\rho}_{\mathbf{r}'} \rangle_{\mathrm{eq}} \right]^{-1} \delta\rho_{\mathbf{r}'} - \int d\mathbf{r} \left[\langle \delta\hat{\epsilon}_{\mathbf{r}} \delta\hat{\epsilon}_{\mathbf{r}'} \rangle_{\mathrm{eq}} \right]^{-1} \delta\epsilon_{\mathbf{r}'} - \left[\left\langle \delta\hat{\epsilon}_{\mathbf{r}} \delta\hat{\mathbf{R}}_{\mathbf{r}'} \right\rangle_{\mathrm{eq}} \right]^{-1} \delta\mathbf{R} - \left[\left\langle \delta\hat{\epsilon}_{\mathbf{r}} \delta\hat{U}_{\mathbf{r}'} \right\rangle_{\mathrm{eq}} \right]^{-1} \delta U$$

$$\boldsymbol{\lambda}_R = - \int d\mathbf{r} \left[\left\langle \delta\hat{\mathbf{R}} \delta\hat{\rho}_{\mathbf{r}'} \right\rangle_{\mathrm{eq}} \right]^{-1} \delta\rho_{\mathbf{r}'} - \int d\mathbf{r} \left[\left\langle \delta\hat{\mathbf{R}} \delta\hat{\epsilon}_{\mathbf{r}'} \right\rangle_{\mathrm{eq}} \right]^{-1} \delta\epsilon_{\mathbf{r}'} - \left[\left\langle \delta\hat{\mathbf{R}} \delta\hat{\mathbf{R}}_{\mathbf{r}'} \right\rangle_{\mathrm{eq}} \right]^{-1} \delta\mathbf{R} - \left[\left\langle \delta\hat{\mathbf{R}} \delta\hat{U}_{\mathbf{r}'} \right\rangle_{\mathrm{eq}} \right]^{-1} \delta U$$

$$\beta_{\mathrm{s}} = - \int d\mathbf{r} \left[\left\langle \delta\hat{U} \delta\hat{\rho}_{\mathbf{r}'} \right\rangle_{\mathrm{eq}} \right]^{-1} \delta\rho_{\mathbf{r}'} - \int d\mathbf{r} \left[\left\langle \delta\hat{U} \delta\hat{\epsilon}_{\mathbf{r}'} \right\rangle_{\mathrm{eq}} \right]^{-1} \delta\epsilon_{\mathbf{r}'} - \left[\left\langle \delta\hat{U} \delta\hat{\mathbf{R}}_{\mathbf{r}'} \right\rangle_{\mathrm{eq}} \right]^{-1} \delta\mathbf{R} - \left[\left\langle \delta\hat{U} \delta\hat{U}_{\mathbf{r}'} \right\rangle_{\mathrm{eq}} \right]^{-1} \delta U$$

.

[We have to plot the conjugate variables, given the MD profiles of the relevant variables. This should allow us to figure out whether the density variable is important or not. If the contribution to the temperature due to the density field is important, we need to construct a theory for energy transport that includes the density field.]

11.9   Appendix. Two exact identities

11.9.1   Gibbs-Duhem identity

Consider the following integral, which is inspired by the form of the partition function (18.4),

$$
\mathbf{I} = \frac{1}{\Xi N!} \int \prod_i^N \frac{d\mathbf{q}_i}{\Lambda_f^3(\mathbf{q}_i)} \int \prod_{i'}^{N'} \frac{d\mathbf{q}_{i'}}{\Lambda_s^3} \exp\left\{ \sum_i^N m\beta(\mathbf{q}_i)\mu(\mathbf{q}_i) - \boldsymbol{\lambda}_R{\cdot}\hat{\mathbf{R}} \right\}
$$
$$
\times \left[\sum_j^N \delta(\mathbf{r} - \mathbf{q}_j)\frac{\partial}{\partial \mathbf{q}_j} \right] \exp\left\{ -\sum_j^N \beta(\mathbf{q}_j)\phi_j - \sum_{j'}^{N'} \beta_s\phi_{j'} \right\}
$$

where the operator within square brackets acts on its right. We use this integral as a way to get an identity by developing, on one hand the action of the operator on the exponential and, on the other, an integration by parts.

First perform the derivative

$$
\mathbf{I} = \frac{1}{\Xi N!} \int \prod_i^N \frac{d\mathbf{q}_i}{\Lambda_f^3(\mathbf{q}_i)} \int \prod_{i'}^{N'} \frac{d\mathbf{q}_{i'}}{\Lambda_s^3} \exp\left\{ \sum_i^N m\beta(\mathbf{q}_i)\mu(\mathbf{q}_i) - \boldsymbol{\lambda}_R{\cdot}\hat{\mathbf{R}} - \sum_j^N \beta(\mathbf{q}_j)\phi_j - \sum_{j'}^{N'} \beta_s\phi_{j'} \right\}
$$
$$
\times \left[\sum_j^N \delta(\mathbf{r} - \mathbf{q}_j)\frac{\partial}{\partial \mathbf{q}_j} \right] \left[-\sum_k^N \beta(\mathbf{q}_k)\phi_k - \sum_{k'}^{N'} \beta_s\phi_{k'} \right]
$$
$$
= \left\langle \left[\sum_j^N \delta(\mathbf{r} - \mathbf{q}_j)\frac{\partial}{\partial \mathbf{q}_j} \right] \left[-\sum_k^N \beta(\mathbf{q}_k)\phi_k - \sum_{k'}^{N'} \beta_s\phi_{k'} \right] \right\rangle^\lambda
$$
$$
= -\boldsymbol{\nabla}\beta(\mathbf{r}) \left\langle \sum_j^N \delta(\mathbf{r} - \mathbf{q}_j)\phi_j \right\rangle^\lambda - \left\langle \sum_j^N \delta(\mathbf{r} - \mathbf{q}_j)\sum_k^N \beta(\mathbf{q}_k)\frac{\partial\phi_k}{\partial\mathbf{q}_j} \right\rangle^\lambda - \left\langle \sum_j^N \delta(\mathbf{r} - \mathbf{q}_j)\sum_{k'}^{N'} \beta_s\frac{\partial\phi_{k'}}{\partial\mathbf{q}_j} \right\rangle^\lambda
$$

The derivative of the potential gives forces

$$
\frac{\partial\phi_k}{\partial\mathbf{q}_j} = \frac{1}{2}\sum_i^N \frac{\partial\phi_{ik}}{\partial\mathbf{q}_j} + \frac{1}{2}\sum_{i'}^{N'} \frac{\partial\phi_{i'k}}{\partial\mathbf{q}_j} = -\frac{1}{2}\sum_i^N \mathbf{F}_{ik}(\delta_{ij} - \delta_{jk}) + \frac{1}{2}\sum_{i'}^{N'} \mathbf{F}_{i'k}\delta_{jk}
$$

and then, the second term

$$
-\left\langle \sum_j^N \delta(\mathbf{r} - \mathbf{q}_j) \sum_k^N \beta(\mathbf{q}_k) \frac{\partial \phi_k}{\partial \mathbf{q}_j} \right\rangle^\lambda = \frac{1}{2} \left\langle \sum_j^N \delta(\mathbf{r} - \mathbf{q}_j) \sum_k^N \beta(\mathbf{q}_k) \sum_i^N \mathbf{F}_{ik}(\delta_{ij} - \delta_{jk}) \right\rangle^\lambda
$$

$$
- \frac{1}{2} \left\langle \sum_j^N \delta(\mathbf{r} - \mathbf{q}_j) \sum_k^N \beta(\mathbf{q}_k) \sum_{i'}^{N'} \mathbf{F}_{i'k} \delta_{jk} \right\rangle^\lambda
$$

$$
= \frac{1}{2} \left\langle \sum_{ij}^N [\delta(\mathbf{r} - \mathbf{q}_i) - \delta(\mathbf{r} - \mathbf{q}_j)] \beta(\mathbf{q}_j) \mathbf{F}_{ij} \right\rangle^\lambda + \frac{1}{2}\beta(\mathbf{r}) \left\langle \sum_i^N \delta(\mathbf{r} - \mathbf{q}_i) \sum_{i'}^{N'} \mathbf{F}_{ii'} \right\rangle^\lambda
$$

$$
= \frac{1}{2} \left\langle \sum_{ij}^N \delta(\mathbf{r} - \mathbf{q}_i) [\beta(\mathbf{q}_i) + \beta(\mathbf{q}_j)] \mathbf{F}_{ij} \right\rangle^\lambda + \frac{1}{2}\beta(\mathbf{r}) \left\langle \sum_i^N \delta(\mathbf{r} - \mathbf{q}_i) \sum_{i'}^{N'} \mathbf{F}_{ii'} \right\rangle^\lambda
$$

where it is understood that in the sum over i, j, the term $i = j$ is excluded, as it involves the force that particle i exerts on particle i, which is zero.

The third term is

$$
-\left\langle \sum_j^N \delta(\mathbf{r} - \mathbf{q}_j) \sum_{k'}^{N'} \beta_{\mathrm{s}} \frac{\partial \phi_{k'}}{\partial \mathbf{q}_j} \right\rangle^\lambda = \frac{1}{2} \left\langle \sum_i^N \delta(\mathbf{r} - \mathbf{q}_i) \sum_{i'}^{N'} \beta_{\mathrm{s}} \mathbf{F}_{ii'} \right\rangle^\lambda = \frac{1}{2}\beta_{\mathrm{s}} \mathbf{F}(\mathbf{r})
$$

In summary, (11.9.1) becomes

$$
\mathbf{I} = -\left\langle \sum_j^N \delta(\mathbf{r} - \mathbf{q}_j) \phi_j \right\rangle^\lambda \boldsymbol{\nabla}\beta(\mathbf{r}) + \left\langle \sum_{ij}^N \delta(\mathbf{r} - \mathbf{q}_i) \left[\frac{\beta(\mathbf{q}_i) + \beta(\mathbf{q}_j)}{2} \right] \mathbf{F}_{ij} \right\rangle^\lambda + \left\langle \sum_{ij'}^N \delta(\mathbf{r} - \mathbf{q}_i) \left[\frac{\beta(\mathbf{q}_i) + \beta_{\mathrm{s}}}{2} \right] \mathbf{F}_{ij'} \right\rangle^\lambda
$$

$$
= -\left\langle \sum_j^N \delta(\mathbf{r} - \mathbf{q}_j) \phi_j \right\rangle^\lambda \boldsymbol{\nabla}\beta(\mathbf{r}) + \left\langle \sum_{ij}^N \delta(\mathbf{r} - \mathbf{q}_i) \left[\frac{\beta(\mathbf{q}_i) + \beta(\mathbf{q}_j)}{2} \right] \mathbf{F}_{ij} \right\rangle^\lambda + \frac{\beta(\mathbf{r}) + \beta_{\mathrm{s}}}{2} \mathbf{F}(\mathbf{r})
$$

Now, we integrate by parts (11.9.1)

$$\mathbf{I} = -\frac{1}{\Xi N!} \int \prod_i^N d\mathbf{q}_i \int \prod_{i'}^{N'} \frac{d\mathbf{q}_{i'}}{\Lambda_\mathrm{s}^3} \exp\left\{-\sum_j^N \beta(\mathbf{q}_j)\phi_j - \sum_{j'}^{N'} \beta_\mathrm{s}\phi_{j'}\right\}$$

$$\times \sum_j^N \frac{\partial}{\partial \mathbf{q}_j} \left[\delta(\mathbf{r} - \mathbf{q}_j) \exp\left\{-\sum_i^N \ln \Lambda_\mathrm{f}^3(\mathbf{q}_i) + \sum_i^N m\beta(\mathbf{q}_i)\mu(\mathbf{q}_i) - \boldsymbol{\lambda}_R{\cdot}\hat{\mathbf{R}}\right\}\right]$$

$$= \boldsymbol{\nabla} n(\mathbf{r}) - \left\langle \sum_j^N \delta(\mathbf{r} - \mathbf{q}_j) \frac{\partial}{\partial \mathbf{q}_j} \left[-\sum_i^N \ln \Lambda_\mathrm{f}^3(\mathbf{q}_i) + \sum_i^N m\beta(\mathbf{q}_i)\mu(\mathbf{q}_i)\right]\right\rangle^\lambda$$

$$= \boldsymbol{\nabla} n(\mathbf{r}) - \left\langle \sum_j^N \delta(\mathbf{r} - \mathbf{q}_j) \left[-\frac{\partial}{\partial \mathbf{q}_j} \ln \Lambda_\mathrm{f}^3(\mathbf{q}_j) + m\boldsymbol{\nabla}(\beta(\mathbf{q}_j)\mu(\mathbf{q}_j))\right]\right\rangle^\lambda$$

$$= \boldsymbol{\nabla} n(\mathbf{r}) + \frac{3n(\mathbf{r})}{2\beta(\mathbf{r})} \boldsymbol{\nabla}\beta(\mathbf{r}) - \rho(\mathbf{r})\boldsymbol{\nabla}(\beta(\mathbf{r})\mu(\mathbf{r}))$$

By collecting (11.9.1) and (11.9.1) we obtain

$$-e(\mathbf{r})\boldsymbol{\nabla}\beta(\mathbf{r}) + \rho(\mathbf{r})\boldsymbol{\nabla}(\beta(\mathbf{r})\mu(\mathbf{r})) - \boldsymbol{\nabla} n(\mathbf{r}) + \left\langle \sum_{ij}^N \delta(\mathbf{r} - \mathbf{q}_i) \left[\frac{\beta(\mathbf{q}_i) + \beta(\mathbf{q}_j)}{2}\right] \mathbf{F}_{ij}\right\rangle^\lambda + \frac{\beta(\mathbf{r}) + \beta_\mathrm{s}}{2}\mathbf{F}(\mathbf{r}) = 0$$

where we have used (22.4). Let us arrange now the averages

$$\left\langle \sum_{ij}^N \delta(\mathbf{r} - \mathbf{q}_i) \left[\frac{\beta(\mathbf{q}_i) + \beta(\mathbf{q}_j)}{2}\right] \mathbf{F}_{ij}\right\rangle^\lambda = \frac{1}{2}\left\langle \sum_{ij}^N (\delta(\mathbf{r} - \mathbf{q}_i) - \delta(\mathbf{r} - \mathbf{q}_j)) \left[\frac{\beta(\mathbf{q}_i) + \beta(\mathbf{q}_j)}{2}\right] \mathbf{F}_{ij}\right\rangle^\lambda =$$

$$= -\boldsymbol{\nabla}\left\langle \frac{1}{2}\sum_{ij}^N \mathbf{q}_{ij} \left[\frac{\beta(\mathbf{q}_i) + \beta(\mathbf{q}_j)}{2}\right] \mathbf{F}_{ij} \int_0^1 d\epsilon \delta(\mathbf{r} - \mathbf{q}_j - \epsilon \mathbf{q}_{ij})\right\rangle^\lambda$$

We recognize in this expression a modified version of the stress tensor. In fact, when the temperature of the fluid is constant, we get inside the average the usual definition of the virial part of the stress tensor (up to a factor $(k_B T)^{-1}$). It seems natural to introduce the stress tensor in the non-isothermal case as

$$\tilde{\boldsymbol{\sigma}}(\mathbf{r}) = k_B T(\mathbf{r})\left[n(\mathbf{r})\boldsymbol{\delta} + \left\langle \frac{1}{2}\sum_{ij}^N \mathbf{q}_{ij} \left[\frac{\beta(\mathbf{q}_i) + \beta(\mathbf{q}_j)}{2}\right] \mathbf{F}_{ij} \int_0^1 d\epsilon \delta(\mathbf{r} - \mathbf{q}_j - \epsilon \mathbf{q}_{ij})\right\rangle^\lambda\right]$$

The virial part differs from the usual virial part of the stress tensor in the temperature factors.

With these definitions, Eq. (11.9.1) becomes

$$
- e(\mathbf{r})\boldsymbol{\nabla}\beta(\mathbf{r}) + \rho(\mathbf{r})\boldsymbol{\nabla}(\beta(\mathbf{r})\mu(\mathbf{r})) - \boldsymbol{\nabla}\left(\beta(\mathbf{r})\tilde{\boldsymbol{\sigma}}(\mathbf{r})\right) + \left[\frac{\beta(\mathbf{r}) + \beta_{\mathrm{s}}}{2}\right]\mathbf{F}(\mathbf{r}) = 0
$$

This exact and rigorous equation has the form of the usual Gibbs-Duhem relationship, modified with the presence of the interactions with the solid.

11.9.2 Traslation invariance

Consider the generalized potential (11.2.-1), with the partition function (18.4) and perform the change of variables $\mathbf{q}_i \rightarrow \mathbf{q}_i + \mathbf{a}$, $\mathbf{q}_{i'} \rightarrow \mathbf{q}_{i'} + \mathbf{a}$ corresponding to a simple translation in the integrals. We obtain

$$
\Phi = -\ln\frac{1}{N!}\int\prod_i^N\frac{d\mathbf{q}_i}{\Lambda_{\mathrm{f}}^3(\mathbf{q}_i + \mathbf{a})}\int\prod_{i'}^{N'}\frac{d\mathbf{q}_{i'}}{\Lambda_{\mathrm{s}}^3}\exp\left\{-\sum_j^N\beta(\mathbf{q}_j + \mathbf{a})\phi_j - \sum_{j'}^{N'}\beta_{\mathrm{s}}\phi_{j'} + \sum_i^N\beta(\mathbf{q}_i + \mathbf{a})m\mu(\mathbf{q}_i + \mathbf{a}) - \boldsymbol{\lambda}_R\cdot(\hat{\mathbf{R}} + \mathbf{a})\right\}
$$

where we have used the fact that the potentials of interaction are translation invariant. The above identity is true for any $\mathbf{a}$, impliying that the derivative with respect to $\mathbf{a}$ of the left hand side is zero. Therefore

$$
0 = \frac{1}{\Xi}\frac{1}{N!}\int dq dq'\frac{\partial}{\partial\mathbf{a}}\exp\left\{-\sum_i^N\frac{3}{2}\ln\beta(\mathbf{q}_i + \mathbf{a}) - \sum_{i'}^{N'}\frac{3}{2}\ln\beta_{\mathrm{s}} - \sum_j^N\beta(\mathbf{q}_j + \mathbf{a})\phi_j - \sum_{j'}^{N'}\beta_{\mathrm{s}}\phi_{j'}\right\}
$$

$$
\times\exp\left\{\sum_i^N\beta(\mathbf{q}_i + \mathbf{a})m\mu(\mathbf{q}_i + \mathbf{a}) - \boldsymbol{\lambda}_R\cdot(\hat{\mathbf{R}} + \mathbf{a})\right\}
$$

where the terms proportional to $3/2$ are due to the thermal wavelengths.

$$
0 = \frac{1}{\Xi}\frac{1}{N!}\int dq dq'\exp\left\{\cdots\right\}\frac{\partial}{\partial\mathbf{a}}\left[-\sum_i^N\frac{3}{2}\ln\beta(\mathbf{q}_i + \mathbf{a}) - \sum_j^N\beta(\mathbf{q}_j + \mathbf{a})\phi_j + \sum_i^N\beta(\mathbf{q}_i + \mathbf{a})m\mu(\mathbf{q}_i + \mathbf{a}) - \boldsymbol{\lambda}_R\cdot\mathbf{a}\right]
$$

Introduce the identities

$$
\int d\mathbf{r}\delta(\mathbf{r} - \mathbf{q}_i) = 1 \qquad \int d\mathbf{r}\delta(\mathbf{r} - \mathbf{q}_{i'}) = 1
$$

$$
0 = \frac{1}{\Xi}\frac{1}{N!}\int dq dq'\exp\left\{\cdots\right\}\frac{\partial}{\partial\mathbf{a}}\left[-\int d\mathbf{r}\frac{3}{2}\ln\beta(\mathbf{r} + \mathbf{a})\hat{n}_{\mathbf{r}} - \int d\mathbf{r}\beta(\mathbf{r} + \mathbf{a})\phi_{\mathbf{r}} + \int d\mathbf{r}\beta(\mathbf{r} + \mathbf{a})\mu(\mathbf{r} + \mathbf{a})\hat{\rho}_{\mathbf{r}} - \boldsymbol{\lambda}_R\cdot\mathbf{a}\right]
$$

This is

$$0 = \frac{\partial}{\partial \mathbf{a}} \left[-\int d\mathbf{r} \frac{3}{2} \ln \beta(\mathbf{r} + \mathbf{a}) \langle \hat{n}_{\mathbf{r}} \rangle^{\lambda} - \int d\mathbf{r} \beta(\mathbf{r} + \mathbf{a}) \langle \phi_{\mathbf{r}} \rangle^{\lambda} + \int d\mathbf{r} \rho(\mathbf{r}) \beta(\mathbf{r} + \mathbf{a}) \mu(\mathbf{r} + \mathbf{a}) - \boldsymbol{\lambda}_R \cdot \mathbf{a} \right]$$

The final result encoding translation invariance is

$$\int d\mathbf{r} \left[-e(\mathbf{r}) \boldsymbol{\nabla} \beta(\mathbf{r}) + \rho(\mathbf{r}) \boldsymbol{\nabla} \beta(\mathbf{r}) \mu(\mathbf{r}) \right] = \boldsymbol{\lambda}_R$$

Note that we may use now the exact Gibbs-Duhem relation (11.9.1) and end up with

$$-\int d\mathbf{r} \left[\frac{\beta(\mathbf{r}) + \beta_{\mathrm{s}}}{2} \right] \mathbf{F}(\mathbf{r}) = \boldsymbol{\lambda}_R$$

that shows the close connection of the conjugate variable $\boldsymbol{\lambda}_R$ with the force that the solid exerts on the fluid.

11.10   Appendix: The projected currents

[**Describir que si uno hace la teoria del CG con las variables discretas directamente, obtiene las mismas expresiones que discretizar la ecuacion del continuo. Esto permite escribir las corrientes proyectadas directamente en terminos de las variables discretas.**]

In this appendix we consider the explicit form of the projected currents $\mathcal{Q}_t i\mathcal{L}A$ for the present selection of relevant variables. The projector defined in (20.2.1) gives rise to the following four projected currents $\mathcal{Q}_t\hat{\mathbf{F}}_{\mathbf{r}}, \mathcal{Q}_t\hat{\boldsymbol{\sigma}}_{\mathbf{r}}, \mathcal{Q}_t\hat{\pi}_{\mathbf{r}}, \mathcal{Q}_t\hat{\mathbf{Q}}_{\mathbf{r}}$ given explicitly by

$$
\begin{aligned}
\mathcal{Q}_t\hat{\mathbf{F}}_{\mathbf{r}} = {}& \hat{\mathbf{F}}_{\mathbf{r}} - \mathrm{Tr}\left[\overline{\rho}_t\hat{\mathbf{F}}_{\mathbf{r}}\right] \\
& - (\hat{\mathbf{R}} - \mathbf{R}(t))\left\langle \delta\hat{\mathbf{R}}\hat{\mathbf{F}}_{\mathbf{r}}\right\rangle \\
& - (\hat{\mathbf{P}} - \mathbf{P}(t))\left\langle \delta\hat{\mathbf{P}}\hat{\mathbf{F}}_{\mathbf{r}}\right\rangle \\
& - (\hat{\mathbf{E}} - \mathbf{E}(t))\left\langle \delta\hat{\mathbf{E}}\hat{\mathbf{F}}_{\mathbf{r}}\right\rangle \\
& - \int d\mathbf{r}' \int d\mathbf{r}''(\hat{\rho}_{\mathbf{r}'} - \rho(\mathbf{r}',t))\left\langle \delta\hat{\rho}_{\mathbf{r}'}\delta\hat{\rho}_{\mathbf{r}''}\right\rangle^{-1}\left\langle \delta\hat{\rho}_{\mathbf{r}''}\hat{\mathbf{F}}_{\mathbf{r}}\right\rangle \\
& - \int d\mathbf{r}' \int d\mathbf{r}''(\hat{\mathbf{g}}_{\mathbf{r}'} - \mathbf{g}(\mathbf{r}',t))\left\langle \delta\hat{\mathbf{g}}_{\mathbf{r}'}\delta\hat{\mathbf{g}}_{\mathbf{r}''}\right\rangle^{-1}\left\langle \delta\hat{\mathbf{g}}_{\mathbf{r}''}\hat{\mathbf{F}}_{\mathbf{r}}\right\rangle \\
& - \int d\mathbf{r}' \int d\mathbf{r}''(\hat{\mathbf{e}}_{\mathbf{r}'} - \mathbf{e}(\mathbf{r}',t))\left\langle \delta\hat{\mathbf{e}}_{\mathbf{r}'}\delta\hat{\mathbf{e}}_{\mathbf{r}''}\right\rangle^{-1}\left\langle \delta\hat{\mathbf{e}}_{\mathbf{r}''}\hat{\mathbf{F}}_{\mathbf{r}}\right\rangle
\end{aligned}
$$

$$
\begin{aligned}
\mathcal{Q}_t\hat{\boldsymbol{\sigma}}_{\mathbf{r}} = {}& \hat{\boldsymbol{\sigma}}_{\mathbf{r}} - \mathrm{Tr}\left[\overline{\rho}_t\hat{\boldsymbol{\sigma}}_{\mathbf{r}}\right] \\
& - (\hat{\mathbf{R}} - \mathbf{R}(t))\left\langle \delta\hat{\mathbf{R}}\hat{\boldsymbol{\sigma}}_{\mathbf{r}}\right\rangle \\
& - (\hat{\mathbf{P}} - \mathbf{P}(t))\left\langle \delta\hat{\mathbf{P}}\hat{\boldsymbol{\sigma}}_{\mathbf{r}}\right\rangle \\
& - (\hat{\mathbf{E}} - \mathbf{E}(t))\left\langle \delta\hat{\mathbf{E}}\hat{\boldsymbol{\sigma}}_{\mathbf{r}}\right\rangle \\
& - \int d\mathbf{r}' \int d\mathbf{r}''(\hat{\rho}_{\mathbf{r}'} - \rho(\mathbf{r}',t))\left\langle \delta\hat{\rho}_{\mathbf{r}'}\delta\hat{\rho}_{\mathbf{r}''}\right\rangle^{-1}\left\langle \delta\hat{\rho}_{\mathbf{r}''}\hat{\boldsymbol{\sigma}}_{\mathbf{r}}\right\rangle \\
& - \int d\mathbf{r}' \int d\mathbf{r}''(\hat{\mathbf{g}}_{\mathbf{r}'} - \mathbf{g}(\mathbf{r}',t))\left\langle \delta\hat{\mathbf{g}}_{\mathbf{r}'}\delta\hat{\mathbf{g}}_{\mathbf{r}''}\right\rangle^{-1}\left\langle \delta\hat{\mathbf{g}}_{\mathbf{r}''}\hat{\boldsymbol{\sigma}}_{\mathbf{r}}\right\rangle \\
& - \int d\mathbf{r}' \int d\mathbf{r}''(\hat{\mathbf{e}}_{\mathbf{r}'} - \mathbf{e}(\mathbf{r}',t))\left\langle \delta\hat{\mathbf{e}}_{\mathbf{r}'}\delta\hat{\mathbf{e}}_{\mathbf{r}''}\right\rangle^{-1}\left\langle \delta\hat{\mathbf{e}}_{\mathbf{r}''}\hat{\boldsymbol{\sigma}}_{\mathbf{r}}\right\rangle
\end{aligned}
$$

$$\mathcal{Q}_t \hat{\pi}_{\mathbf{r}} = \hat{\pi}_{\mathbf{r}} - \mathrm{Tr}\left[\overline{\rho}_t \hat{\pi}_{\mathbf{r}}\right]$$
$$- (\hat{\mathbf{R}} - \mathbf{R}(t))\left\langle \delta\hat{\mathbf{R}}\hat{\pi}_{\mathbf{r}}\right\rangle$$
$$- (\hat{\mathbf{P}} - \mathbf{P}(t))\left\langle \delta\hat{\mathbf{P}}\hat{\pi}_{\mathbf{r}}\right\rangle$$
$$- (\hat{\mathbf{E}} - \mathbf{E}(t))\left\langle \delta\hat{\mathbf{E}}\hat{\pi}_{\mathbf{r}}\right\rangle$$
$$- \int d\mathbf{r}' \int d\mathbf{r}'' (\hat{\rho}_{\mathbf{r}'} - \rho(\mathbf{r}',t))\langle \delta\hat{\rho}_{\mathbf{r}'}\delta\hat{\rho}_{\mathbf{r}''}\rangle^{-1}\langle \delta\hat{\rho}_{\mathbf{r}''}\hat{\pi}_{\mathbf{r}}\rangle$$
$$- \int d\mathbf{r}' \int d\mathbf{r}'' (\hat{\mathbf{g}}_{\mathbf{r}'} - \mathbf{g}(\mathbf{r}',t))\langle \delta\hat{\mathbf{g}}_{\mathbf{r}'}\delta\hat{\mathbf{g}}_{\mathbf{r}''}\rangle^{-1}\langle \delta\hat{\mathbf{g}}_{\mathbf{r}''}\hat{\pi}_{\mathbf{r}}\rangle$$
$$- \int d\mathbf{r}' \int d\mathbf{r}'' (\hat{\mathbf{e}}_{\mathbf{r}'} - \mathbf{e}(\mathbf{r}',t))\langle \delta\hat{\mathbf{e}}_{\mathbf{r}'}\delta\hat{\mathbf{e}}_{\mathbf{r}''}\rangle^{-1}\langle \delta\hat{\mathbf{e}}_{\mathbf{r}''}\hat{\pi}_{\mathbf{r}}\rangle$$

and

$$\mathcal{Q}_t \hat{\mathbf{Q}}_{\mathbf{r}} = \hat{\mathbf{Q}}_{\mathbf{r}} - \mathrm{Tr}\left[\overline{\rho}_t \hat{\mathbf{Q}}_{\mathbf{r}}\right]$$
$$- (\hat{\mathbf{R}} - \mathbf{R}(t))\left\langle \delta\hat{\mathbf{R}}\hat{\mathbf{Q}}_{\mathbf{r}}\right\rangle$$
$$- (\hat{\mathbf{P}} - \mathbf{P}(t))\left\langle \delta\hat{\mathbf{P}}\hat{\mathbf{Q}}_{\mathbf{r}}\right\rangle$$
$$- (\hat{\mathbf{E}} - \mathbf{E}(t))\left\langle \delta\hat{\mathbf{E}}\hat{\mathbf{Q}}_{\mathbf{r}}\right\rangle$$
$$- \int d\mathbf{r}' \int d\mathbf{r}'' (\hat{\rho}_{\mathbf{r}'} - \rho(\mathbf{r}',t))\langle \delta\hat{\rho}_{\mathbf{r}'}\delta\hat{\rho}_{\mathbf{r}''}\rangle^{-1}\left\langle \delta\hat{\rho}_{\mathbf{r}''}\hat{\mathbf{Q}}_{\mathbf{r}}\right\rangle$$
$$- \int d\mathbf{r}' \int d\mathbf{r}'' (\hat{\mathbf{g}}_{\mathbf{r}'} - \mathbf{g}(\mathbf{r}',t))\langle \delta\hat{\mathbf{g}}_{\mathbf{r}'}\delta\hat{\mathbf{g}}_{\mathbf{r}''}\rangle^{-1}\left\langle \delta\hat{\mathbf{g}}_{\mathbf{r}''}\hat{\mathbf{Q}}_{\mathbf{r}}\right\rangle$$
$$- \int d\mathbf{r}' \int d\mathbf{r}'' (\hat{\mathbf{e}}_{\mathbf{r}'} - \mathbf{e}(\mathbf{r}',t))\langle \delta\hat{\mathbf{e}}_{\mathbf{r}'}\delta\hat{\mathbf{e}}_{\mathbf{r}''}\rangle^{-1}\left\langle \delta\hat{\mathbf{e}}_{\mathbf{r}''}\hat{\mathbf{Q}}_{\mathbf{r}}\right\rangle$$

Under the assumption that the solid particle is sufficiently large, the actual values $\hat{\mathbf{R}}, \hat{\mathbf{P}}, \hat{\mathbf{E}}$ of the microscopic functions will not differ too much from its average values, and the corresponding terms in (11.10), (11.10), (11.10) and (11.10) may be neglected. The projected currents become

$$\mathcal{Q}_t \hat{\mathbf{F}}_{\mathbf{r}} = \hat{\mathbf{F}}_{\mathbf{r}} - \mathrm{Tr}\left[\overline{\rho}_t \hat{\mathbf{F}}_{\mathbf{r}}\right]$$
$$- \int d\mathbf{r}' \int d\mathbf{r}'' (\hat{\rho}_{\mathbf{r}'} - \rho(\mathbf{r}',t))\langle \delta\hat{\rho}_{\mathbf{r}'}\delta\hat{\rho}_{\mathbf{r}''}\rangle^{-1}\left\langle \delta\hat{\rho}_{\mathbf{r}''}\hat{\mathbf{F}}_{\mathbf{r}}\right\rangle$$
$$- \int d\mathbf{r}' \int d\mathbf{r}'' (\hat{\mathbf{g}}_{\mathbf{r}'} - \mathbf{g}(\mathbf{r}',t))\langle \delta\hat{\mathbf{g}}_{\mathbf{r}'}\delta\hat{\mathbf{g}}_{\mathbf{r}''}\rangle^{-1}\left\langle \delta\hat{\mathbf{g}}_{\mathbf{r}''}\hat{\mathbf{F}}_{\mathbf{r}}\right\rangle$$
$$- \int d\mathbf{r}' \int d\mathbf{r}'' (\hat{\mathbf{e}}_{\mathbf{r}'} - \mathbf{e}(\mathbf{r}',t))\langle \delta\hat{\mathbf{e}}_{\mathbf{r}'}\delta\hat{\mathbf{e}}_{\mathbf{r}''}\rangle^{-1}\left\langle \delta\hat{\mathbf{e}}_{\mathbf{r}''}\hat{\mathbf{F}}_{\mathbf{r}}\right\rangle$$

$$\mathscr{Q}_t\hat{\boldsymbol{\sigma}}_\mathbf{r} = \hat{\boldsymbol{\sigma}}_\mathbf{r} - \mathrm{Tr}\left[\overline{\rho}_t\hat{\boldsymbol{\sigma}}_\mathbf{r}\right]$$

$$- \int d\mathbf{r}' \int d\mathbf{r}'' (\hat{\rho}_{\mathbf{r}'} - \rho(\mathbf{r}', t)) \langle \delta\hat{\boldsymbol{\rho}}_{\mathbf{r}'}\delta\hat{\boldsymbol{\rho}}_{\mathbf{r}''}\rangle^{-1} \langle \delta\hat{\boldsymbol{\rho}}_{\mathbf{r}''}\hat{\boldsymbol{\sigma}}_\mathbf{r}\rangle$$

$$- \int d\mathbf{r}' \int d\mathbf{r}'' (\hat{\mathbf{g}}_{\mathbf{r}'} - \mathbf{g}(\mathbf{r}', t)) \langle \delta\hat{\mathbf{g}}_{\mathbf{r}'}\delta\hat{\mathbf{g}}_{\mathbf{r}''}\rangle^{-1} \langle \delta\hat{\mathbf{g}}_{\mathbf{r}''}\hat{\boldsymbol{\sigma}}_\mathbf{r}\rangle$$

$$- \int d\mathbf{r}' \int d\mathbf{r}'' (\hat{\mathbf{e}}_{\mathbf{r}'} - \mathbf{e}(\mathbf{r}', t)) \langle \delta\hat{\mathbf{e}}_{\mathbf{r}'}\delta\hat{\mathbf{e}}_{\mathbf{r}''}\rangle^{-1} \langle \delta\hat{\mathbf{e}}_{\mathbf{r}''}\hat{\boldsymbol{\sigma}}_\mathbf{r}\rangle$$

$$\mathscr{Q}_t\hat{\pi}_\mathbf{r} = \hat{\pi}_\mathbf{r} - \mathrm{Tr}\left[\overline{\rho}_t\hat{\pi}_\mathbf{r}\right]$$

$$- \int d\mathbf{r}' \int d\mathbf{r}'' (\hat{\rho}_{\mathbf{r}'} - \rho(\mathbf{r}', t)) \langle \delta\hat{\boldsymbol{\rho}}_{\mathbf{r}'}\delta\hat{\boldsymbol{\rho}}_{\mathbf{r}''}\rangle^{-1} \langle \delta\hat{\boldsymbol{\rho}}_{\mathbf{r}''}\hat{\pi}_\mathbf{r}\rangle$$

$$- \int d\mathbf{r}' \int d\mathbf{r}'' (\hat{\mathbf{g}}_{\mathbf{r}'} - \mathbf{g}(\mathbf{r}', t)) \langle \delta\hat{\mathbf{g}}_{\mathbf{r}'}\delta\hat{\mathbf{g}}_{\mathbf{r}''}\rangle^{-1} \langle \delta\hat{\mathbf{g}}_{\mathbf{r}''}\hat{\pi}_\mathbf{r}\rangle$$

$$- \int d\mathbf{r}' \int d\mathbf{r}'' (\hat{\mathbf{e}}_{\mathbf{r}'} - \mathbf{e}(\mathbf{r}', t)) \langle \delta\hat{\mathbf{e}}_{\mathbf{r}'}\delta\hat{\mathbf{e}}_{\mathbf{r}''}\rangle^{-1} \langle \delta\hat{\mathbf{e}}_{\mathbf{r}''}\hat{\pi}_\mathbf{r}\rangle$$

and

$$\mathscr{Q}_t\hat{\mathbf{Q}}_\mathbf{r} = \hat{\mathbf{Q}}_\mathbf{r} - \mathrm{Tr}\left[\overline{\rho}_t\hat{\mathbf{Q}}_\mathbf{r}\right]$$

$$- \int d\mathbf{r}' \int d\mathbf{r}'' (\hat{\rho}_{\mathbf{r}'} - \rho(\mathbf{r}', t)) \langle \delta\hat{\boldsymbol{\rho}}_{\mathbf{r}'}\delta\hat{\boldsymbol{\rho}}_{\mathbf{r}''}\rangle^{-1} \left\langle \delta\hat{\boldsymbol{\rho}}_{\mathbf{r}''}\hat{\mathbf{Q}}_\mathbf{r}\right\rangle$$

$$- \int d\mathbf{r}' \int d\mathbf{r}'' (\hat{\mathbf{g}}_{\mathbf{r}'} - \mathbf{g}(\mathbf{r}', t)) \langle \delta\hat{\mathbf{g}}_{\mathbf{r}'}\delta\hat{\mathbf{g}}_{\mathbf{r}''}\rangle^{-1} \left\langle \delta\hat{\mathbf{g}}_{\mathbf{r}''}\hat{\mathbf{Q}}_\mathbf{r}\right\rangle$$

$$- \int d\mathbf{r}' \int d\mathbf{r}'' (\hat{\mathbf{e}}_{\mathbf{r}'} - \mathbf{e}(\mathbf{r}', t)) \langle \delta\hat{\mathbf{e}}_{\mathbf{r}'}\delta\hat{\mathbf{e}}_{\mathbf{r}''}\rangle^{-1} \left\langle \delta\hat{\mathbf{e}}_{\mathbf{r}''}\hat{\mathbf{Q}}_\mathbf{r}\right\rangle$$

Last term

$$\left\langle \delta\hat{\boldsymbol{\rho}}_{\mathbf{r}''}\hat{F}_\mathbf{r}\right\rangle = \left\langle \delta\hat{\boldsymbol{\rho}}_{\mathbf{r}''}\delta\hat{\mathbf{F}}_\mathbf{r}\right\rangle = \left\langle \hat{\boldsymbol{\rho}}_{\mathbf{r}''}\delta\hat{\mathbf{F}}_\mathbf{r}\right\rangle - \rho(\mathbf{r}'', t)\left\langle \delta\hat{\mathbf{F}}_\mathbf{r}\right\rangle$$

The last term vanishes. Therefore,

$$\left\langle \delta\hat{\boldsymbol{\rho}}_{\mathbf{r}''}\hat{F}_\mathbf{r}\right\rangle = \left\langle \hat{\boldsymbol{\rho}}_{\mathbf{r}''}\delta\hat{\mathbf{F}}_\mathbf{r}\right\rangle$$

Doing the same for all terms in equations (11.10), (11.10), (11.10) and (11.10) we obtain

$$
\begin{aligned}
\mathscr{Q}_t \hat{\mathbf{F}}_{\mathbf{r}} = \hat{\mathbf{F}}_{\mathbf{r}} &- \mathrm{Tr}\left[\overline{\rho}_t \hat{\mathbf{F}}_{\mathbf{r}}\right] \\
&- \int d\mathbf{r}' \int d\mathbf{r}'' (\hat{\rho}_{\mathbf{r}'} - \rho(\mathbf{r}',t)) \langle \delta\hat{\boldsymbol{\rho}}_{\mathbf{r}'}\delta\hat{\boldsymbol{\rho}}_{\mathbf{r}''}\rangle^{-1} \left\langle \hat{\boldsymbol{\rho}}_{\mathbf{r}''}\delta\hat{\mathbf{F}}_{\mathbf{r}} \right\rangle \\
&- \int d\mathbf{r}' \int d\mathbf{r}'' (\hat{\mathbf{g}}_{\mathbf{r}'} - \mathbf{g}(\mathbf{r}',t)) \langle \delta\hat{\mathbf{g}}_{\mathbf{r}'}\delta\hat{\mathbf{g}}_{\mathbf{r}''}\rangle^{-1} \mathbf{v}(\mathbf{r}'') \left\langle \hat{\boldsymbol{\rho}}_{\mathbf{r}''}\delta\hat{\mathbf{F}}_{\mathbf{r}} \right\rangle \\
&- \int d\mathbf{r}' \int d\mathbf{r}'' (\hat{\mathbf{e}}_{\mathbf{r}'} - \mathbf{e}(\mathbf{r}',t)) \langle \delta\hat{\mathbf{e}}_{\mathbf{r}'}\delta\hat{\mathbf{e}}_{\mathbf{r}''}\rangle^{-1} \langle \hat{\mathbf{e}}_{\mathbf{r}''}\delta\mathbf{F}_{\mathbf{r}} \rangle
\end{aligned}
$$

$$
\begin{aligned}
\mathscr{Q}_t \hat{\boldsymbol{\sigma}}_{\mathbf{r}} = \hat{\boldsymbol{\sigma}}_{\mathbf{r}} &- \mathrm{Tr}\left[\overline{\rho}_t \hat{\boldsymbol{\sigma}}_{\mathbf{r}}\right] \\
&- \int d\mathbf{r}' \int d\mathbf{r}'' (\hat{\rho}_{\mathbf{r}'} - \rho(\mathbf{r}',t)) \langle \delta\hat{\boldsymbol{\rho}}_{\mathbf{r}'}\delta\hat{\boldsymbol{\rho}}_{\mathbf{r}''}\rangle^{-1} \langle \hat{\boldsymbol{\rho}}_{\mathbf{r}''}\delta\hat{\boldsymbol{\sigma}}_{\mathbf{r}} \rangle \\
&- \int d\mathbf{r}' \int d\mathbf{r}'' (\hat{\mathbf{g}}_{\mathbf{r}'} - \mathbf{g}(\mathbf{r}',t)) \langle \delta\hat{\mathbf{g}}_{\mathbf{r}'}\delta\hat{\mathbf{g}}_{\mathbf{r}''}\rangle^{-1} \mathbf{v}(\mathbf{r}'') \langle \hat{\boldsymbol{\rho}}_{\mathbf{r}''}\delta\hat{\boldsymbol{\sigma}}_{\mathbf{r}} \rangle \\
&- \int d\mathbf{r}' \int d\mathbf{r}'' (\hat{\mathbf{e}}_{\mathbf{r}'} - \mathbf{e}(\mathbf{r}',t)) \langle \delta\hat{\mathbf{e}}_{\mathbf{r}'}\delta\hat{\mathbf{e}}_{\mathbf{r}''}\rangle^{-1} \langle \hat{\mathbf{e}}_{\mathbf{r}''}\delta\hat{\boldsymbol{\sigma}}_{\mathbf{r}} \rangle
\end{aligned}
$$

$$
\begin{aligned}
\mathscr{Q}_t \hat{\pi}_{\mathbf{r}} = \hat{\pi}_{\mathbf{r}} &- \mathrm{Tr}\left[\overline{\rho}_t \hat{\pi}_{\mathbf{r}}\right] \\
&- \int d\mathbf{r}' \int d\mathbf{r}'' (\hat{\rho}_{\mathbf{r}'} - \rho(\mathbf{r}',t)) \langle \delta\hat{\boldsymbol{\rho}}_{\mathbf{r}'}\delta\hat{\boldsymbol{\rho}}_{\mathbf{r}''}\rangle^{-1} \langle \hat{\boldsymbol{\rho}}_{\mathbf{r}''}\delta\hat{\pi}_{\mathbf{r}} \rangle \\
&- \int d\mathbf{r}' \int d\mathbf{r}'' (\hat{\mathbf{g}}_{\mathbf{r}'} - \mathbf{g}(\mathbf{r}',t)) \langle \delta\hat{\mathbf{g}}_{\mathbf{r}'}\delta\hat{\mathbf{g}}_{\mathbf{r}''}\rangle^{-1} \mathbf{v}(\mathbf{r}'') \langle \hat{\boldsymbol{\rho}}_{\mathbf{r}''}\delta\hat{\pi}_{\mathbf{r}} \rangle \\
&- \int d\mathbf{r}' \int d\mathbf{r}'' (\hat{\mathbf{e}}_{\mathbf{r}'} - \mathbf{e}(\mathbf{r}',t)) \langle \delta\hat{\mathbf{e}}_{\mathbf{r}'}\delta\hat{\mathbf{e}}_{\mathbf{r}''}\rangle^{-1} \langle \hat{\mathbf{e}}_{\mathbf{r}''}\delta\hat{\pi}_{\mathbf{r}} \rangle
\end{aligned}
$$

and

$$
\begin{aligned}
\mathscr{Q}_t \hat{\mathbf{Q}}_{\mathbf{r}} = \hat{\mathbf{Q}}_{\mathbf{r}} &- \mathrm{Tr}\left[\overline{\rho}_t \hat{\mathbf{Q}}_{\mathbf{r}}\right] \\
&- \int d\mathbf{r}' \int d\mathbf{r}'' (\hat{\rho}_{\mathbf{r}'} - \rho(\mathbf{r}',t)) \langle \delta\hat{\boldsymbol{\rho}}_{\mathbf{r}'}\delta\hat{\boldsymbol{\rho}}_{\mathbf{r}''}\rangle^{-1} \left\langle \hat{\boldsymbol{\rho}}_{\mathbf{r}''}\delta\hat{\mathbf{Q}}_{\mathbf{r}} \right\rangle \\
&- \int d\mathbf{r}' \int d\mathbf{r}'' (\hat{\mathbf{g}}_{\mathbf{r}'} - \mathbf{g}(\mathbf{r}',t)) \langle \delta\hat{\mathbf{g}}_{\mathbf{r}'}\delta\hat{\mathbf{g}}_{\mathbf{r}''}\rangle^{-1} \mathbf{v}(\mathbf{r}'') \left\langle \hat{\boldsymbol{\rho}}_{\mathbf{r}''}\delta\hat{\mathbf{Q}}_{\mathbf{r}} \right\rangle \\
&- \int d\mathbf{r}' \int d\mathbf{r}'' (\hat{\mathbf{e}}_{\mathbf{r}'} - \mathbf{e}(\mathbf{r}',t)) \langle \delta\hat{\mathbf{e}}_{\mathbf{r}'}\delta\hat{\mathbf{e}}_{\mathbf{r}''}\rangle^{-1} \left\langle \hat{\mathbf{e}}_{\mathbf{r}''}\delta\hat{\mathbf{Q}}_{\mathbf{r}} \right\rangle
\end{aligned}
$$

In order to compute the unknown terms in (11.7), we need the discrete version of

$\mathscr{Q}\hat{Q}_{\mathbf{r}}$ and $\mathscr{Q}_t\hat{\pi}_{\mathbf{r}}$

$$\mathscr{Q}_t\hat{\mathbf{Q}}_\mu = \hat{\mathbf{Q}}_\mu - \mathrm{Tr}\left[\overline{\rho}_t\hat{\mathbf{Q}}_\mu\right]$$

$$-\sum_\mu\sum_{\mu'}(\hat{\rho}_\mu - \rho_\mu)\langle\delta\hat{\boldsymbol{\rho}}_\mu\delta\hat{\boldsymbol{\rho}}_{\mu'}\rangle^{-1}\left\langle\hat{\boldsymbol{\rho}}_{\mu'}\delta\hat{\mathbf{Q}}_\mu\right\rangle$$

$$-\sum_\mu\sum_{\mu'}(\hat{\mathbf{g}}_\mu - \mathbf{g}_\mu)\langle\delta\hat{\mathbf{g}}_\mu\delta\hat{\mathbf{g}}_{\mu'}\rangle^{-1}\mathbf{v}(\mu')\left\langle\hat{\boldsymbol{\rho}}_{\mu'}\delta\hat{\mathbf{Q}}_\mu\right\rangle$$

$$-\sum_\mu\sum_{\mu'}(\hat{\mathbf{e}}_\mu - \mathbf{e}_\mu)\langle\delta\hat{\mathbf{e}}_\mu\delta\hat{\mathbf{e}}_{\mu'}\rangle^{-1}\left\langle\hat{\mathbf{e}}_{\mu'}\delta\hat{\mathbf{Q}}_\mu\right\rangle$$

and

$$\mathscr{Q}_t\hat{\pi}_\mu = \hat{\pi}_\mu - \mathrm{Tr}\left[\overline{\rho}_t\hat{\pi}_\mu\right]$$

$$-\sum_\mu\sum_{\mu'}(\hat{\rho}_\mu - \rho_\mu)\langle\delta\hat{\boldsymbol{\rho}}_\mu\delta\hat{\boldsymbol{\rho}}_{\mu'}\rangle^{-1}\langle\hat{\boldsymbol{\rho}}_{\mu'}\delta\hat{\pi}_\mu\rangle$$

$$-\sum_\mu\sum_{\mu'}(\hat{\mathbf{g}}_\mu - \mathbf{g}_\mu)\langle\delta\hat{\mathbf{g}}_\mu\delta\hat{\mathbf{g}}_{\mu'}\rangle^{-1}\mathbf{v}(\mu')\langle\hat{\boldsymbol{\rho}}_{\mu'}\delta\hat{\pi}_\mu\rangle$$

$$-\sum_\mu\sum_{\mu'}(\hat{\mathbf{e}}_\mu - \mathbf{e}_\mu)\langle\delta\hat{\mathbf{e}}_\mu\delta\hat{\mathbf{e}}_{\mu'}\rangle^{-1}\langle\hat{\mathbf{e}}_{\mu'}\delta\hat{\pi}_\mu\rangle$$

where we have introduce the discrete variables

$$\hat{\rho}_\mu(z) = \sum_{i=1}^N m_i\frac{1}{\mathscr{V}_\mu}\psi_\mu(q_i)$$

$$\hat{g}_\mu(z) = \sum_{i=1}^N p_i\frac{1}{\mathscr{V}_\mu}\psi_\mu(q_i)$$

$$\hat{e}_\mu(z) = \sum_{i=1}^N e_i\frac{1}{\mathscr{V}_\mu}\psi_\mu(q_i)$$

We need a discrete expression for $\hat{\mathbf{Q}}_{\mathbf{r}}$ and $\hat{\pi}_{\mathbf{r}}$.

Let us start with $\hat{\mathbf{Q}}_{\mathbf{r}}$

$$\hat{\mathbf{Q}}_{\mathbf{r}} \equiv \sum_i^N \mathbf{v}_i e_i\delta(\mathbf{r} - \mathbf{r}_i) + \frac{1}{2}\sum_{ij}^{NN}\frac{(\mathbf{v}_i + \mathbf{v}_j)}{2}\cdot\mathbf{F}_{ij}\mathbf{q}_{ij}\int_0^1 d\epsilon\delta(\mathbf{r} - \mathbf{q}_j - \epsilon\mathbf{q}_{ij})$$

The first term

$$\int d\mathbf{r}\frac{\chi_\mu}{\mathscr{V}_\mu}\sum_i \mathbf{v}_i e_i\delta(r - r_i) = \sum_i \mathbf{v}_i e_i\frac{\chi_\mu(\mathbf{r}_i)}{\mathscr{V}_\mu}$$

And the second one

$$\frac{1}{2\mathscr{V}_\mu}\int d\mathbf{r}\chi_\mu(\mathbf{r})\sum_{ij}^{NN}\frac{(\mathbf{v}_i+\mathbf{v}_j)}{2}\cdot\mathbf{F}_{ij}\mathbf{q}_{ij}\int_0^1 d\epsilon\delta(\mathbf{r}-\mathbf{q}_j-\epsilon\mathbf{q}_{ij})=\frac{1}{2\mathscr{V}_\mu}\sum_{ij}^{NN}\frac{(\mathbf{v}_i+\mathbf{v}_j)}{2}\cdot\mathbf{F}_{ij}\mathbf{q}_{ij}z_\mu(i,j)$$

where we have introduced the geometric factor

$$
\begin{aligned}
z_\mu(i,j) &= \int_0^1 d\epsilon\chi_\mu(\mathbf{r}_i-\epsilon\mathbf{r}_{ij})\\
&= \int_0^1 d\epsilon\theta(z_{\mu+1}-z_i+\epsilon z_{ij})\theta(z_i-\epsilon z_{ij}-z_\mu)\\
&= \frac{1}{z_{ij}}\int_0^{z_{ij}} dz\theta(z_{\mu+1}-z_i+z)\theta(z_i-z_\mu-z)
\end{aligned}
$$

The integral can be easily computed with Mathematica with the result

$$
\begin{aligned}
z_\mu(i,j) =\frac{1}{z_{ij}}[&(z_j-z_\mu)\theta(z_{\mu+1}-z_j,z_\mu-z_j)\\
&-(z_i-z_\mu)\theta(z_{\mu+1}-z_i,z_\mu-z_i)\\
&-(z_j-z_{\mu+1})\theta(z_{\mu+1}-z_j)\\
&+(z_i-z_{\mu+1})\theta(z_{\mu+1}-z_i)]
\end{aligned}
$$

where $\theta(a,b)$ takes the value 1 if both $a,b>0$ and zero otherwise. Note that $z_\mu(i,j)=z_\mu(j,i)$. If both particles are within the bin, then $z_\mu(i,j)=1$. If the line joining the particles does not cross the bin (for example, $z_i,z_j<z_\mu$) then $z_\mu(i,j)=0$. If both particles are outside the bin, but the line joining the particles crosses the bin (for example, $z_i<z_\mu,z_j>z_{\mu+1}$) then $z_\mu(i,j)=\frac{z_{\mu+1}-z_\mu}{z_j-z_i}$. Finally, if one particle is in the bin, and the other outside (for example $z_\mu<z_i<z_{\mu+1},z_j>z_{\mu+1}$) then $z_\mu(i,j)=\frac{z_{\mu+1}-z_i}{z_j-z_i}$. In summary, $z_\mu(i,j)$ is the fraction of the segment of the *vertical* distance between particles i,j that happens to be within the bin μ. Note that by Thale's theorem this fraction is equal to the fraction of the *length* of the segment joining particles i,j that happens to be inside the bin.

Finally, the discrete version of $\hat{\mathbf{Q}}_\mathbf{r}$ is

$$\hat{\mathbf{Q}}_\mu=\sum_i \mathbf{v}_i e_i\frac{\chi_\mu(\mathbf{r}_i)}{\mathscr{V}_\mu}+\frac{1}{2\mathscr{V}_\mu}\sum_{ij}^{NN}\frac{(\mathbf{v}_i+\mathbf{v}_j)}{2}\cdot\mathbf{F}_{ij}\mathbf{q}_{ij}z_\mu(i,j)$$

Let us move to $\hat{\pi}_\mathbf{r}$

$$\hat{\pi}_\mathbf{r}\equiv\sum_{ij'}^{NN'}\mathbf{F}_{ij'}\cdot\frac{(\mathbf{v}_i+\mathbf{v}_{j'})}{2}\delta(\mathbf{r}-\mathbf{q}_i)$$

$$\hat{\pi}_\mu = \int d\mathbf{r} \frac{\psi_\mu(\mathbf{r})}{\mathscr{V}_\mu} \sum_{ij'}^{NN'} \mathbf{F}_{ij'} \cdot \frac{(\mathbf{v}_i + \mathbf{v}_{j'})}{2} \delta(\mathbf{r} - \mathbf{q}_i)$$

Therefore, the discrete version is

$$\hat{\pi}_\mu = \sum_{ij'}^{NN'} \mathbf{F}_{ij'} \cdot \frac{(\mathbf{v}_i + \mathbf{v}_{j'})}{2} \frac{\psi_\mu(\mathbf{r}_i)}{\mathscr{V}_\mu}$$

In this appendix we consider the explicit form of the projected currents $\mathscr{Q}_t i \mathcal{L} A$ for the present selection of relevant variables. The projector defined in (20.2.1) gives rise to the following four projected currents $\mathscr{Q}_t \hat{\mathbf{F}}_{\mathbf{r}}, \mathscr{Q}_t \hat{\boldsymbol{\sigma}}_{\mathbf{r}}, \mathscr{Q}_t \hat{\boldsymbol{\pi}}_{\mathbf{r}}, \mathscr{Q}_t \hat{\mathbf{Q}}_{\mathbf{r}}$ given explicitly by **[Faltan terminos con energia!]**

$$\mathscr{Q}_t \hat{\mathbf{F}}_{\mathbf{r}} = \hat{\mathbf{F}}_{\mathbf{r}} - \mathrm{Tr}\left[\overline{\rho}_t \hat{\mathbf{F}}_{\mathbf{r}}\right] - (\hat{\mathbf{R}} - \mathbf{R}(t)) \frac{\partial}{\partial \mathbf{R}(t)} \mathrm{Tr}\left[\overline{\rho}_t \hat{\mathbf{F}}_{\mathbf{r}}\right] - (\hat{\mathbf{P}} - \mathbf{P}(t)) \frac{\partial}{\partial \mathbf{P}(t)} \mathrm{Tr}\left[\overline{\rho}_t \hat{\mathbf{F}}_{\mathbf{r}}\right]$$
$$- \int d\mathbf{r}' (\hat{\rho}_{\mathbf{r}'} - \rho(\mathbf{r}', t)) \frac{\delta}{\delta \rho(\mathbf{r}', t)} \mathrm{Tr}\left[\overline{\rho}_{t'} \hat{\mathbf{F}}_{\mathbf{r}}\right] - \int d\mathbf{r}' (\hat{\mathbf{g}}_{\mathbf{r}'} - \mathbf{g}(\mathbf{r}', t)) \frac{\delta}{\delta \mathbf{g}(\mathbf{r}', t)} \mathrm{Tr}\left[\overline{\rho}_{t'} \hat{\mathbf{F}}_{\mathbf{r}}\right]$$

and

$$\mathscr{Q}_t \hat{\boldsymbol{\sigma}}_{\mathbf{r}} = \hat{\boldsymbol{\sigma}}_{\mathbf{r}} - \mathrm{Tr}\left[\overline{\rho}_t \hat{\boldsymbol{\sigma}}_{\mathbf{r}}\right] - (\hat{\mathbf{R}} - \mathbf{R}(t)) \frac{\partial}{\partial \mathbf{R}(t)} \mathrm{Tr}\left[\overline{\rho}_t \hat{\boldsymbol{\sigma}}_{\mathbf{r}}\right] - (\hat{\mathbf{P}} - \mathbf{P}(t)) \frac{\partial}{\partial \mathbf{P}(t)} \mathrm{Tr}\left[\overline{\rho}_t \hat{\boldsymbol{\sigma}}_{\mathbf{r}}\right]$$
$$- \int d\mathbf{r}' (\hat{\rho}_{\mathbf{r}'} - \rho(\mathbf{r}', t)) \frac{\delta}{\delta \rho(\mathbf{r}', t)} \mathrm{Tr}\left[\overline{\rho}_{t'} \hat{\boldsymbol{\sigma}}_{\mathbf{r}}\right] - \int d\mathbf{r}' (\hat{\mathbf{g}}_{\mathbf{r}'} - \mathbf{g}(\mathbf{r}', t)) \frac{\delta}{\delta \mathbf{g}(\mathbf{r}', t)} \mathrm{Tr}\left[\overline{\rho}_{t'} \hat{\boldsymbol{\sigma}}_{\mathbf{r}}\right]$$

[Faltan el flujo de calor y la potencia!]

Under the assumption that the solid particle is sufficiently large, the actual values $\hat{\mathbf{R}}, \hat{\mathbf{P}}$ of the microscopic functions will not differ too much from its average values, and the corresponding terms in (11.10), (11.10) may be neglected. The projected currents become

$$\mathscr{Q}_t \hat{\mathbf{F}}_{\mathbf{r}} = \hat{\mathbf{F}}_{\mathbf{r}} - \mathrm{Tr}\left[\overline{\rho}_t \hat{\mathbf{F}}_{\mathbf{r}}\right] - \int d\mathbf{r}' (\hat{\rho}_{\mathbf{r}'} - \rho(\mathbf{r}', t)) \frac{\delta}{\delta \rho(\mathbf{r}', t)} \mathrm{Tr}\left[\overline{\rho}_{t'} \hat{\mathbf{F}}_{\mathbf{r}}\right] - \int d\mathbf{r}' (\hat{\mathbf{g}}_{\mathbf{r}'} - \mathbf{g}(\mathbf{r}', t)) \frac{\delta}{\delta \mathbf{g}(\mathbf{r}', t)} \mathrm{Tr}\left[\overline{\rho}_{t'} \hat{\mathbf{F}}_{\mathbf{r}}\right]$$

Las t' serán t, ¿no? and

$$\mathscr{Q}_t \hat{\boldsymbol{\sigma}}_{\mathbf{r}} = \hat{\boldsymbol{\sigma}}_{\mathbf{r}} - \mathrm{Tr}\left[\overline{\rho}_t \hat{\boldsymbol{\sigma}}_{\mathbf{r}}\right] - \int d\mathbf{r}' (\hat{\rho}_{\mathbf{r}'} - \rho(\mathbf{r}', t)) \frac{\delta}{\delta \rho(\mathbf{r}', t)} \mathrm{Tr}\left[\overline{\rho}_{t'} \hat{\boldsymbol{\sigma}}_{\mathbf{r}}\right] - \int d\mathbf{r}' (\hat{\mathbf{g}}_{\mathbf{r}'} - \mathbf{g}(\mathbf{r}', t)) \frac{\delta}{\delta \mathbf{g}(\mathbf{r}', t)} \mathrm{Tr}\left[\overline{\rho}_{t'} \hat{\boldsymbol{\sigma}}_{\mathbf{r}}\right]$$

Let us start with the projected current (11.10), that requires the average with the relevant

ensemble of the force density that the solid exerts on the fluid

$$\mathrm{Tr}\left[\overline{\rho}_t \hat{\mathbf{F}}_\mathbf{r}\right] = \mathrm{Tr}[\mathscr{G}\overline{\rho}_t\mathscr{G}\hat{\mathbf{F}}_\mathbf{r}]$$

Because the force does not depend on velocities, the Galilean operator does nothing on it. Therefore, we need to compute

$$\mathrm{Tr}\left[\overline{\rho}_t \hat{\mathbf{F}}_\mathbf{r}\right] = \frac{1}{\Xi[\lambda(t)]}\mathrm{Tr}\left[\rho^{\mathrm{eq}}(z)\exp\left\{\beta\int d\mathbf{r}\mu(\mathbf{r})\hat{\rho}_\mathbf{r}(z) - \beta\boldsymbol{\lambda}_R(t){\cdot}\hat{\mathbf{R}} - \beta\boldsymbol{\lambda}_P(t){\cdot}\hat{\mathbf{P}}\right\}\hat{\mathbf{F}}_\mathbf{r}\right]$$

which does not depend on the momentum of the fluid (because none of the conjugate variables does). Note that the average of the force density that the solid exerts on the fluid does not depend on the momentum variable, and the last term in (11.10) vanishes. We end up, therefore, with the following result

$$\mathscr{Q}_t\hat{\mathbf{F}}_\mathbf{r} = \hat{\mathbf{F}}_\mathbf{r} - \mathrm{Tr}\left[\overline{\rho}_t\hat{\mathbf{F}}_\mathbf{r}\right] - \int d\mathbf{r}'(\hat{\rho}_{\mathbf{r}'} - \rho(\mathbf{r}',t))\frac{\delta}{\delta\rho(\mathbf{r}',t)}\mathrm{Tr}\left[\overline{\rho}_t\hat{\mathbf{F}}_\mathbf{r}\right]$$

Note that the functional derivative of the relevant ensemble is

$$\frac{\delta}{\delta\rho(\mathbf{r}',t)}\overline{\rho}_t = \frac{\delta}{\delta\rho(\mathbf{r}',t)}\frac{1}{\Xi[\lambda(t)]}\rho^{\mathrm{eq}}(z)\exp\left\{\beta\int d\mathbf{r}\mu(\mathbf{r})\hat{\rho}_\mathbf{r}(z) - \beta\boldsymbol{\lambda}_R(t){\cdot}\hat{\mathbf{R}} - \beta\boldsymbol{\lambda}_P(t){\cdot}\hat{\mathbf{P}}\right\}$$

$$= \overline{\rho}_t\left[\frac{\delta}{\delta\rho(\mathbf{r}',t)}\beta\int d\mathbf{r}\mu(\mathbf{r})\hat{\rho}_\mathbf{r}(z) - \frac{\delta}{\delta\rho(\mathbf{r}',t)}\ln\Xi[\lambda(t)]\right]$$

$$= \overline{\rho}_t\beta\int d\mathbf{r}'\frac{\delta\mu(\mathbf{r}'')}{\delta\rho(\mathbf{r}',t)}\delta\hat{\rho}_{\mathbf{r}''}(z)$$

where $\delta\hat{\rho}_{\mathbf{r}''}(z) = \hat{\rho}_{\mathbf{r}''}(z) - \rho(\mathbf{r}'',t)$. We have neglected terms that involve the functional derivative of $\boldsymbol{\lambda}_\mathbf{R}$ and $\boldsymbol{\lambda}_\mathbf{P}$ because they accompany fluctuations of $\mathbf{R}$ and $\mathbf{P}$ which are assumed to be negligible.

We need to evaluate the functional derivative of the chemical potential with respect to the number density field. This can be achieved by noting that

$$\frac{\delta}{\delta\mu(\mathbf{r})}\ln\Xi[\lambda] = \beta\rho(\mathbf{r})$$

$$\frac{\delta^2}{\delta\mu(\mathbf{r})\delta\mu(\mathbf{r}')}\ln\Xi[\lambda] = \beta_\mathrm{s}\left\langle\delta\hat{\rho}(\mathbf{r})\delta\hat{\rho}(\mathbf{r})\right\rangle$$

which both imply

$$\frac{\delta\rho(\mathbf{r}')}{\delta\mu(\mathbf{r})} = \beta\left\langle\delta\hat{\rho}_\mathbf{r}\delta\hat{\rho}_{\mathbf{r}'}\right\rangle$$

The functional derivative appearing in (11.10) is, therefore, the inverse of the density

correlation matrix, this is

$$\frac{\delta\mu(\mathbf{r})}{\delta\rho(\mathbf{r}')} = \beta_{-1}\left\langle\delta\hat{\rho}_{\mathbf{r}}\delta\hat{\rho}_{\mathbf{r}'}\right\rangle^{-1}$$

Therefore, the projected current (11.10) is

$$\mathcal{Q}_t\hat{\mathbf{F}}_{\mathbf{r}} = \hat{\mathbf{F}}_{\mathbf{r}} - \mathrm{Tr}\left[\overline{\rho}_t\hat{\mathbf{F}}_{\mathbf{r}}\right] - \int d\mathbf{r}' \int d\mathbf{r}''(\hat{\rho}_{\mathbf{r}'} - \rho(\mathbf{r}',t))\left\langle\delta\hat{\rho}_{\mathbf{r}'}\delta\hat{\rho}_{\mathbf{r}''}\right\rangle^{-1}\left\langle\delta\hat{\rho}_{\mathbf{r}''}\hat{\mathbf{F}}_{\mathbf{r}}\right\rangle$$

Let us now move to the projected current $\mathcal{Q}_t\hat{\boldsymbol{\sigma}}_{\mathbf{r}}$.

$$\mathcal{Q}_t\hat{\boldsymbol{\sigma}}_{\mathbf{r}} = \hat{\boldsymbol{\sigma}}_{\mathbf{r}} - \mathrm{Tr}\left[\overline{\rho}_t\hat{\boldsymbol{\sigma}}_{\mathbf{r}}\right] - \int d\mathbf{r}'(\hat{\rho}_{\mathbf{r}'} - \rho(\mathbf{r}',t))\frac{\delta}{\delta\rho(\mathbf{r}',t)}\mathrm{Tr}\left[\overline{\rho}_{t'}\hat{\boldsymbol{\sigma}}_{\mathbf{r}}\right] - \int d\mathbf{r}'(\hat{\mathbf{g}}_{\mathbf{r}'} - \mathbf{g}(\mathbf{r}',t))\frac{\delta}{\delta\mathbf{g}(\mathbf{r}',t)}\mathrm{Tr}\left[\overline{\rho}_{t'}\hat{\boldsymbol{\sigma}}_{\mathbf{r}}\right]$$

$$= \hat{\boldsymbol{\sigma}}_{\mathbf{r}} - \mathrm{Tr}\left[\overline{\rho}_t\hat{\boldsymbol{\sigma}}_{\mathbf{r}}\right]$$
$$- \int d\mathbf{r}'(\hat{\rho}_{\mathbf{r}'} - \rho(\mathbf{r}',t))\frac{\delta}{\delta\rho(\mathbf{r}',t)}\left[\mathrm{Tr}\left[\overline{\rho}_t\hat{\mathbf{K}}_{\mathbf{r}}\right] + \mathrm{Tr}\left[\overline{\rho}_t\hat{\boldsymbol{\Pi}}_{\mathbf{r}}\right]\right]$$
$$- \int d\mathbf{r}'(\hat{\mathbf{g}}_{\mathbf{r}'} - \mathbf{g}(\mathbf{r}',t))\frac{\delta}{\delta\mathbf{g}(\mathbf{r}',t)}\left[\mathrm{Tr}\left[\overline{\rho}_t\hat{\mathbf{K}}_{\mathbf{r}}\right] + \mathrm{Tr}\left[\overline{\rho}_t\hat{\boldsymbol{\Pi}}_{\mathbf{r}}\right]\right]$$

$$= \hat{\boldsymbol{\sigma}}_{\mathbf{r}} - \mathrm{Tr}\left[\overline{\rho}_t\hat{\boldsymbol{\sigma}}_{\mathbf{r}}\right]$$
$$- \int d\mathbf{r}'(\hat{\rho}_{\mathbf{r}'} - \rho(\mathbf{r}',t))\frac{\delta}{\delta\rho(\mathbf{r}',t)}\left[\frac{k_BT}{m}\rho(\mathbf{r})\boldsymbol{\delta} + \frac{\mathbf{g}(\mathbf{r})\mathbf{g}(\mathbf{r})}{\rho(\mathbf{r})} + \mathrm{Tr}\left[\overline{\rho}_t\hat{\boldsymbol{\Pi}}_{\mathbf{r}}\right]\right]$$
$$- \int d\mathbf{r}'(\hat{\mathbf{g}}_{\mathbf{r}'} - \mathbf{g}(\mathbf{r}',t))\frac{\delta}{\delta\mathbf{g}(\mathbf{r}',t)}\left[\frac{k_BT}{m}\rho(\mathbf{r})\boldsymbol{\delta} + \frac{\mathbf{g}(\mathbf{r})\mathbf{g}(\mathbf{r})}{\rho(\mathbf{r})} + \mathrm{Tr}\left[\overline{\rho}_t\hat{\boldsymbol{\Pi}}_{\mathbf{r}}\right]\right]$$

where we have decomposed the kinetic and virial parts of the stress tensor and used (10.2). The ideal part and the virial part are independent of momentum variables, the latter because the virial stress tensor $\hat{\boldsymbol{\Pi}}_{\mathbf{r}}$ does not depend on velocities of the particles.

The only term that depends on momentum is the convective term. Therefore,

$$
\mathcal{Q}_t \hat{\boldsymbol{\sigma}}_{\mathbf{r}}^{\alpha\beta} = \hat{\boldsymbol{\sigma}}_{\mathbf{r}}^{\alpha\beta} - \mathrm{Tr}\left[\overline{\rho}_t \hat{\boldsymbol{\sigma}}_{\mathbf{r}}^{\alpha\beta}\right]
$$
$$
- \int d\mathbf{r}'(\hat{\rho}_{\mathbf{r}'} - \rho(\mathbf{r}',t)) \frac{\delta}{\delta\rho(\mathbf{r}',t)} \left[\frac{k_B T}{m}\rho(\mathbf{r})\delta^{\alpha\beta} + \frac{\mathbf{g}^\alpha(\mathbf{r})\mathbf{g}^\beta(\mathbf{r})}{\rho(\mathbf{r})} + \mathrm{Tr}\left[\overline{\rho}_t \hat{\boldsymbol{\Pi}}_{\mathbf{r}}^{\alpha\beta}\right]\right]
$$
$$
- \int d\mathbf{r}'(\hat{\mathbf{g}}_{\mathbf{r}'}^\gamma - \mathbf{g}^\gamma(\mathbf{r}',t)) \frac{\delta}{\delta\mathbf{g}^\gamma(\mathbf{r}',t)} \frac{\mathbf{g}^\alpha(\mathbf{r})\mathbf{g}^\beta(\mathbf{r})}{\rho(\mathbf{r})}
$$
$$
= \hat{\boldsymbol{\sigma}}_{\mathbf{r}}^{\alpha\beta} - \mathrm{Tr}\left[\overline{\rho}_t \hat{\boldsymbol{\sigma}}_{\mathbf{r}}^{\alpha\beta}\right]
$$
$$
- \int d\mathbf{r}'(\hat{\rho}_{\mathbf{r}'} - \rho(\mathbf{r}',t))\delta(\mathbf{r} - \mathbf{r}')\left[\frac{k_B T}{m}\delta^{\alpha\beta} - \mathbf{v}^\alpha(\mathbf{r})\mathbf{v}^\beta(\mathbf{r})\right]
$$
$$
- \int d\mathbf{r}'(\hat{\rho}_{\mathbf{r}'} - \rho(\mathbf{r}',t)) \frac{\delta}{\delta\rho(\mathbf{r}',t)} \mathrm{Tr}\left[\overline{\rho}_t \hat{\boldsymbol{\Pi}}_{\mathbf{r}}^{\alpha\beta}\right]
$$
$$
- \int d\mathbf{r}'(\hat{\mathbf{g}}_{\mathbf{r}'}^\gamma - \mathbf{g}^\gamma(\mathbf{r}',t))\delta(\mathbf{r} - \mathbf{r}')\left[\delta^{\gamma\beta}\mathbf{v}^\alpha(\mathbf{r}) + \delta^{\alpha\gamma}\mathbf{v}^\beta(\mathbf{r})\right]
$$

Simplifying

$$
\mathcal{Q}_t \hat{\boldsymbol{\sigma}}_{\mathbf{r}}^{\alpha\beta} = \hat{\boldsymbol{\sigma}}_{\mathbf{r}}^{\alpha\beta} - \mathrm{Tr}\left[\overline{\rho}_t \hat{\boldsymbol{\sigma}}_{\mathbf{r}}^{\alpha\beta}\right] - (\hat{\mathbf{g}}_{\mathbf{r}}^\beta - \mathbf{g}^\beta(\mathbf{r},t))\mathbf{v}^\alpha(\mathbf{r}) + (\hat{\mathbf{g}}_{\mathbf{r}}^\alpha - \mathbf{g}^\alpha(\mathbf{r},t))\mathbf{v}^\beta(\mathbf{r})
$$
$$
- \int d\mathbf{r}'(\hat{\rho}_{\mathbf{r}'} - \rho(\mathbf{r}',t)) \frac{\delta}{\delta\rho(\mathbf{r}',t)} \mathrm{Tr}\left[\overline{\rho}_t \hat{\boldsymbol{\Pi}}_{\mathbf{r}}^{\alpha\beta}\right] - (\hat{\rho}_{\mathbf{r}'} - \rho(\mathbf{r}',t)) \frac{k_B T}{m}
$$

We may use now the same argument as in the case of the projected force for computing the last functional derivative. The final result for the projected currents is

$$
\mathcal{Q}_t \hat{\mathbf{F}}_{\mathbf{r}} = \hat{\mathbf{F}}_{\mathbf{r}} - \mathrm{Tr}\left[\overline{\rho}_t \hat{\mathbf{F}}_{\mathbf{r}}\right] - \int d\mathbf{r}' \int d\mathbf{r}''(\hat{\rho}_{\mathbf{r}'} - \rho(\mathbf{r}',t)) \langle\delta\hat{\rho}_{\mathbf{r}'}\delta\hat{\rho}_{\mathbf{r}''}\rangle^{-1} \left\langle\delta\hat{\rho}_{\mathbf{r}''}\hat{\mathbf{F}}_{\mathbf{r}}\right\rangle
$$
$$
\mathcal{Q}_t \hat{\boldsymbol{\sigma}}_{\mathbf{r}}^{\alpha\beta} = \hat{\boldsymbol{\sigma}}_{\mathbf{r}}^{\alpha\beta} - \mathrm{Tr}\left[\overline{\rho}_t \hat{\boldsymbol{\sigma}}_{\mathbf{r}}^{\alpha\beta}\right] - (\hat{\mathbf{g}}_{\mathbf{r}}^\beta - \mathbf{g}^\beta(\mathbf{r},t))\mathbf{v}^\alpha(\mathbf{r}) + (\hat{\mathbf{g}}_{\mathbf{r}}^\alpha - \mathbf{g}^\alpha(\mathbf{r},t))\mathbf{v}^\beta(\mathbf{r})
$$
$$
- \int d\mathbf{r}' \int d\mathbf{r}''(\hat{\rho}_{\mathbf{r}'} - \rho(\mathbf{r}',t)) \langle\delta\hat{\rho}_{\mathbf{r}'}\delta\hat{\rho}_{\mathbf{r}''}\rangle^{-1} \left\langle\delta\hat{\rho}_{\mathbf{r}''}\hat{\boldsymbol{\Pi}}_{\mathbf{r}}^{\alpha\beta}\right\rangle - (\hat{\rho}_{\mathbf{r}'} - \rho(\mathbf{r}',t)) \frac{k_B T}{m}
$$

Under the approximation that the system is close to equilibrium, the relevant ensemble is very similar to the equilibrium ensemble, and we may take $\mathbf{v}(\mathbf{r},t) \simeq 0$ and $\rho(\mathbf{r},t) \simeq \rho^{\mathrm{eq}}(\mathbf{r})$. This results in

$$
\mathcal{Q}_t \hat{\mathbf{F}}_{\mathbf{r}} = \hat{\mathbf{F}}_{\mathbf{r}} - \mathrm{Tr}\left[\rho_{\mathrm{eq}}\hat{\mathbf{F}}_{\mathbf{r}}\right] - \int d\mathbf{r}' \int d\mathbf{r}''(\hat{\rho}_{\mathbf{r}'} - \rho_{\mathrm{eq}}(\mathbf{r}')) \langle\delta\hat{\rho}_{\mathbf{r}'}\delta\hat{\rho}_{\mathbf{r}''}\rangle_{\mathrm{eq}}^{-1} \left\langle\delta\hat{\rho}_{\mathbf{r}''}\hat{\mathbf{F}}_{\mathbf{r}}\right\rangle_{\mathrm{eq}}
$$
$$
\mathcal{Q}_t \hat{\boldsymbol{\sigma}}_{\mathbf{r}}^{\alpha\beta} = \hat{\boldsymbol{\sigma}}_{\mathbf{r}}^{\alpha\beta} - \mathrm{Tr}\left[\overline{\rho}_t \hat{\boldsymbol{\sigma}}_{\mathbf{r}}^{\alpha\beta}\right] - \int d\mathbf{r}' \int d\mathbf{r}''(\hat{\rho}_{\mathbf{r}'} - \rho_{\mathrm{eq}}(\mathbf{r}')) \langle\delta\hat{\rho}_{\mathbf{r}'}\delta\hat{\rho}_{\mathbf{r}''}\rangle^{-1} \left\langle\delta\hat{\rho}_{\mathbf{r}''}\hat{\boldsymbol{\sigma}}_{\mathbf{r}}^{\alpha\beta}\right\rangle_{\mathrm{eq}}
$$

Physically, the last integral terms are the responsible to substract from the equilibrium fluctuations of the force density and stress tensor that part that may still have a systematic dependence on the fluctuations of the density.

[In the appendix we have derived two exact identities, the Gibbs-Duhem identity

given by

$$-e(\mathbf{r})\boldsymbol{\nabla}\beta(\mathbf{r}) + \rho(\mathbf{r})\boldsymbol{\nabla}(\beta(\mathbf{r})\mu(\mathbf{r})) - \boldsymbol{\nabla}\beta(\mathbf{r})\tilde{\boldsymbol{\sigma}}(\mathbf{r}) + \left[\frac{\beta(\mathbf{r}) + \beta_\mathrm{s}}{2}\right]\mathbf{F}(\mathbf{r}) = 0$$

and the translation invariance identity given by

$$\int d\mathbf{r}\left[-e(\mathbf{r})\boldsymbol{\nabla}\beta(\mathbf{r}) + \rho(\mathbf{r})\boldsymbol{\nabla}\beta(\mathbf{r})\mu(\mathbf{r})\right] = \boldsymbol{\lambda}_R$$

The combination of these two identities leads to

$$\boldsymbol{\lambda}_R = \int d\mathbf{r}\left[\frac{\beta(\mathbf{r}) + \beta_\mathrm{s}}{2}\right]\mathbf{F}(\mathbf{r})$$

Recall that $\boldsymbol{\lambda}_R$ is given by the derivative of the entropy with respect to the position $\mathbf{R}$, as shown in Eq. (11.2.1). Therefore,

$$\frac{\partial S}{\partial \mathbf{R}} = \int d\mathbf{r}\left[\frac{\beta(\mathbf{r}) + \beta_\mathrm{s}}{2}\right]\mathbf{F}(\mathbf{r})$$

This equation allows shows that the gradient of the entropy gives the force $\mathbf{F}^{\mathrm{s}\rightarrow\mathrm{f}}(\mathbf{r})$ that solid exerts on the fluid.

We have the following definitions of "stress"

$$\boldsymbol{\sigma}(\mathbf{r}) = k_B T(\mathbf{r})n(\mathbf{r})\boldsymbol{\delta} + \left\langle\frac{1}{2}\sum_{ij}^{NN}\mathbf{F}_{ij}\mathbf{q}_{ij}\int_0^1 d\epsilon\delta(\mathbf{r} - \mathbf{q}_j + \epsilon\mathbf{q}_{ij})\right\rangle^\lambda$$

$$\tilde{\boldsymbol{\sigma}}(\mathbf{r}) = k_B T(\mathbf{r})n(\mathbf{r})\boldsymbol{\delta} + k_B T(\mathbf{r})\left\langle\frac{1}{2}\sum_{ij}^{N}\left[\frac{\beta(\mathbf{q}_i) + \beta(\mathbf{q}_j)}{2}\right]\mathbf{q}_{ij}\mathbf{F}_{ij}\int_0^1 d\epsilon\delta(\mathbf{r} - \mathbf{q}_j - \epsilon\mathbf{q}_{ij})\right\rangle^\lambda$$

$$\Delta\boldsymbol{\sigma}(\mathbf{r}) = k_B T(\mathbf{r})n(\mathbf{r})\mathbf{v}(\mathbf{r}) + \left\langle\frac{1}{2}\sum_{ij}^{NN}\frac{(\mathbf{v}(\mathbf{q}_i) + \mathbf{v}(\mathbf{q}_j))}{2}\cdot\mathbf{F}_{ij}\mathbf{q}_{ij}\int_0^1 d\epsilon\delta(\mathbf{r} - \mathbf{q}_j + \epsilon\mathbf{q}_{ij})\right\rangle^\lambda$$

In the smooth conjugate fields approximation in which both, the velocity and temperature fields vary slowly in the range of the fluid interactions, these stress tensors become

$$\tilde{\boldsymbol{\sigma}}(\mathbf{r}) \simeq \boldsymbol{\sigma}(\mathbf{r})$$
$$\Delta\boldsymbol{\sigma}(\mathbf{r}) \simeq \boldsymbol{\sigma}(\mathbf{r})\cdot\mathbf{v}(\mathbf{r})$$

]

[

$$\partial_t \rho(\mathbf{r}) = -\boldsymbol{\nabla} \cdot \mathbf{g}(\mathbf{r})$$

$$\partial_t \mathbf{g}(\mathbf{r}) = -\boldsymbol{\nabla} \cdot \mathbf{g}(\mathbf{r})\mathbf{v}_{\mathrm{f}}(\mathbf{r}) - \rho(\mathbf{r})\boldsymbol{\nabla}\frac{\delta\mathscr{F}}{\delta\rho(\mathbf{r})}[\rho,\mathbf{R}] + \boldsymbol{\nabla}\boldsymbol{\Sigma}(\mathbf{r}) + \mathscr{S}(\mathbf{r})$$

$$\dot{\mathbf{R}} = \frac{\mathbf{P}}{M}$$

$$\dot{\mathbf{P}} = -\frac{\partial\mathscr{F}}{\partial\mathbf{R}} - \int d\mathbf{r}\,\mathscr{S}(\mathbf{r})$$

where the free energy functional $\mathscr{F}[\rho,\mathbf{R}]$ is introduced in Eq. (10), the velocity field is $\mathbf{v}_{\mathrm{f}}(\mathbf{r}) = \mathbf{g}(\mathbf{r})/\rho(\mathbf{r})$, the fluid stress tensor $\boldsymbol{\Sigma}(\mathbf{r})$ is given in (11.10), and the irreversible force $\mathscr{S}(\mathbf{r})$ is given in Eq. (11.10), that we reproduce here

$$\boldsymbol{\Sigma}^{\alpha\beta}(\mathbf{r}) = \int d\mathbf{r}'\,\eta_{\mathbf{rr}'}^{\alpha\beta\alpha'\beta'}\boldsymbol{\nabla}_{\mathbf{r}'}^{\beta'}\mathbf{v}^{\alpha'}(\mathbf{r}')$$

$$\mathscr{S}^{\alpha}(\mathbf{r}) = \int d\mathbf{r}'\,\mathbf{G}_{\mathbf{rr}'}^{\alpha\alpha'\beta'}\boldsymbol{\nabla}_{\mathbf{r}'}^{\beta'}\mathbf{v}^{\alpha'}(\mathbf{r}') - \boldsymbol{\nabla}_{\mathbf{r}}^{\beta}\int d\mathbf{r}'\,\mathbf{H}_{\mathbf{rr}'}^{\alpha\beta\alpha'}(\mathbf{v}^{\alpha'}(\mathbf{r}') - \mathbf{V}^{\alpha'}) - \int d\mathbf{r}'\,\gamma_{\mathbf{rr}'}^{\alpha\alpha'}(\mathbf{v}^{\alpha'}(\mathbf{r}') - \mathbf{V}^{\alpha'})$$

Eqs. (11.10) are the main results of the present paper. They describe the non-local hydrodynamics of a simple isothermal fluid coupled with the motion of an immersed structureless solid sphere. These equations generalize Equilibrium Density Functional Theory for a simple fluid to situations in which the fluid may be moving and, therefore, in a non-equilibrium situation.

The only approximation that has been taken is the Markovian approximation that neglects memory effects in the dissipative part of the dynamics. The equation for the evolution of the mass density field is just the continuity equation. The equation for the momentum density field involves the usual convective term plus a term involving the gradient of the functional derivative of the free energy. This term describes the reversible coupling between the fluid and solid sphere. The viscous term $\boldsymbol{\nabla}\boldsymbol{\Sigma}$ in Eqs. (11.10) describes the internal friction of the fluid due to its self-interaction. This viscous term involving second derivatives is the usual viscosity term of the Navier-Stokes equations, which is here expressed in a non-local form. The use of non-local viscosities has been advocated recently in the field of nano-hydrodynamics [?]. The fourth order viscosity tensor is given in terms of the correlation of the fluctuations of the fluid stress tensor. Away from the walls, it is expected that the viscosity tensor becomes fully isotropic and dependent only on the distance between the points $\mathbf{r},\mathbf{r}'$.

The force density $\mathscr{S}(\mathbf{r})$ involving the non-local transport kernels $\mathbf{H}_{\mathbf{rr}'}, \mathbf{G}_{\mathbf{rr}'}, \gamma_{\mathbf{rr}'}$ describes the irreversible interaction between the solid and the fluid. Note that these kernels are defined in terms of correlations involving the force density $\hat{\mathbf{F}}_{\mathbf{r}}^{s\to l}$ that the solid sphere exerts on the fluid particles. These terms should be understood, therefore, as the responsible for transmitting the irreversible forces that the solid sphere exert on the fluid.

Note that because the force $\hat{\mathbf{F}}_{\mathbf{r}'}$ and the power $\hat{\pi}_{\mathbf{r}}$ are different from zero only near the solid "surface", the kernels that involve F and π are also localised near the solid surface.

The only terms that survive away from the solid are those with second derivatives.

By using Eqs. (10.1) and (11.1.2) and inserting the result in the equation of motion (11.4) one obtains

$$\partial_t \mathbf{g}^\alpha(\mathbf{r})|_{\mathrm{irr}} = \boldsymbol{\nabla}_{\mathbf{r}}^\beta \boldsymbol{\Sigma}^{\alpha\beta} + \mathscr{S}^\alpha(\mathbf{r})$$

$$\frac{d}{dt}\mathbf{P}^\alpha\bigg|_{\mathrm{irr}} = -\int d\mathbf{r}'\, \mathscr{S}^\alpha(\mathbf{r}')$$

where the fluid stress tensor is

$$\boldsymbol{\Sigma}^{\alpha\beta}(\mathbf{r}) = \int d\mathbf{r}'\, \boldsymbol{\eta}_{\mathbf{rr}'}^{\alpha\beta\alpha'\beta'}\, \boldsymbol{\nabla}_{\mathbf{r}'}^{\beta'}\mathbf{v}^{\alpha'}(\mathbf{r}')$$

and the *irreversible surface force density* on the fluid is defined as

$$\mathscr{S}^\alpha(\mathbf{r}) = \int d\mathbf{r}'\, \mathbf{G}_{\mathbf{rr}'}^{\alpha\alpha'\beta'}\, \boldsymbol{\nabla}_{\mathbf{r}'}^{\beta'}\mathbf{v}^{\alpha'}(\mathbf{r}') - \boldsymbol{\nabla}_{\mathbf{r}}^\beta \int d\mathbf{r}'\, \mathbf{H}_{\mathbf{rr}'}^{\alpha\beta\alpha'}(\mathbf{v}^{\alpha'}(\mathbf{r}') - \mathbf{V}^{\alpha'}) - \int d\mathbf{r}'\, \boldsymbol{\gamma}_{\mathbf{rr}'}^{\alpha\alpha'}(\mathbf{v}^{\alpha'}(\mathbf{r}') - \mathbf{V}^{\alpha'})$$

In these expressions we have introduced the following *non-local* transport coefficients: the viscosity kernel $\boldsymbol{\eta}_{\mathbf{rr}'}$ (fourth order tensor), the slip kernels $\mathbf{H}_{\mathbf{rr}'}, \mathbf{G}_{\mathbf{rr}'}$ (third order tensors), and the friction kernel $\boldsymbol{\gamma}_{\mathbf{rr}'}$ (second order tensor) . They are defined by the Green-Kubo formulae

11.10.1   The structure of the transport kernels

We have divided the irreversible change of fluid momentum in two parts. The first part is a viscous part that will lead to the usual second derivative terms corresponding to viscous effects with a viscosity tensor involving correlations of the fluid stress tensor. The second part is in the form of a surface irreversible force, involving the transport kernels $\mathbf{G}_{\mathbf{rr}'}, \mathbf{H}_{\mathbf{rr}'}, \boldsymbol{\gamma}_{\mathbf{rr}'}$. These transport kernels contain the fluctuations of the force density $\hat{\mathbf{F}}_{\mathbf{r}}^{\mathrm{s}\to\mathrm{f}}(z)$ that the solid exerts on the fluid, defined in (10.1). This is the force per unit volume that the particles of the solid sphere exert on the fluid particles that are around the point $\mathbf{r}$ in space. Only for those points $\mathbf{r}$ that are near the surface of the solid sphere this force density will be different from zero. This means that the transport kernels $\mathbf{G}_{\mathbf{rr}'}, \mathbf{H}_{\mathbf{rr}'}, \boldsymbol{\gamma}_{\mathbf{rr}'}$ are highly localized near the solid surface. Note, however, that *the concept of solid surface does not enter this theory.* There is no such a solid surface in microscopic terms. This surface can be defined operationally though by looking precisely at the singular behaviour of the above transport kernels. In general, the force density $\hat{\mathbf{F}}_{\mathbf{r}}(z)$ will be a fluctuating vector on the surface of the solid sphere. If the interaction between fluid and solid particles is purely repulsive, this force will be most of the time directed outwards the surface of the solid sphere. At the same time, because the interaction between solid and fluid particles is singular upon approaching distance, we expect that $\mathbf{F}_{\mathbf{r}}^{\mathrm{s}\to\mathrm{f}}$ will diverge as we approach the solid boundary. This divergence will translate into diverging forms for the transport kernels as $\mathbf{r}$ or $\mathbf{r}'$ approach the boundary of the solid. In a similar way, the stress tensor $\hat{\boldsymbol{\sigma}}_{\mathbf{r}}$ that depends only on fluid particle coordinates will be non-zero only outside the solid sphere because the interaction with the solid sphere

refrains to have fluid particles inside the solid sphere (more on this later).

The force density and the stress tensor are assumed to vary in time in a time scale much shorter than the typical time scale in which the mass and momentum density of the solvent, and the position and momentum of the solid sphere particle appreciably changes. This separation of time scales is at the core of the Markovian form of the evolution of the CG dynamics in the projection operator technique. Whether the selected relevant variables do actually comply with this separation of time scales can only be assesed from the validity of the predictions of the resulting theory as compared with actual simulations or experiments.

11.10.2 Conserved quantities, H-theorem and the equilibrium state

The equations (11.10) are the equations of hydrodynamics in the presence of a solid spherical particle. We stress that the above equations conserve total mass and momentum, given by

$$M_T = M' + \int d\mathbf{r}\rho(\mathbf{r})$$

$$\mathbf{P}_T = \mathbf{P} + \int d\mathbf{r}\mathbf{g}(\mathbf{r})$$

Mass conservation follows inmediately from the continuity equation. Momentum conservation is a consequence of the invariance under translations of the free energy functional expressed in Eq. (10.4) that ensures that the reversible part of the dynamics conserves momentum The irreversible part conserves also total momentum because, apart from a global divergence term, the momentum lost by the fluid is gained by the solid sphere.

In addition, the function H evolves in time in a strictly decreasing way, this is

$$\frac{dH}{dt}(t) \geq 0$$

where the equality sign occurs when the system has reached its equilibrium state. This is because, while the reversible part of the dynamics conserves H, the irreversible part of the dynamics fullfils (11.10.2), due to the positive semidefinite character of the friction matrix.

As a consequence, the equilibrium state of Eqs. (11.10) is the one that maximizes H subject to give the actual values of the total mass and momentum. In order to obtain the equilirium values of the relevant variables, one should minimize the following functional without constraints

$$H - \mu_0 \int d\mathbf{r}\rho(\mathbf{r}) - \mathbf{V}_0 \left[\int d\mathbf{r}\mathbf{g}(\mathbf{r}) + \mathbf{P} \right]$$

where $\mu_0, \mathbf{V}_0$ are the corresponding Lagrange multipliers. Setting to zero the derivatives

of the above functional gives

$$\frac{\mathbf{v}_{\mathrm{f}}^2(\mathbf{r})}{2} + \frac{\delta\mathscr{F}}{\delta\rho(\mathbf{r})}[\rho, \mathbf{R}] - \mu_0 = 0, \qquad\qquad \frac{\partial\mathscr{F}}{\partial\mathbf{R}}[\rho, \mathbf{R}] = 0$$

$$\mathbf{v}(\mathbf{r}) - \mathbf{V}_0 = 0, \qquad\qquad \mathbf{V} - \mathbf{V}_0 = 0$$

This means that the state of equilibrium has a constant velocity field equal to the velocity of the solid particle and, without losing generality, we may take $\mathbf{V}_0 = 0$. We then have the following two coupled equations for the equilibrium value that take the density field and the position of the sphere

$$\frac{\delta\mathscr{F}}{\delta\rho(\mathbf{r})}[\rho, \mathbf{R}] = \mu_0, \qquad\qquad \frac{\partial\mathscr{F}}{\partial\mathbf{R}}[\rho, \mathbf{R}] = 0$$

From Eqs. (10), the first equation (20.3) simply states that the equilibrium state has a constant value of the chemical potential $\mu(\mathbf{r}) = \mu_0$ while the second equation states that the total force on the solid sphere vanishes at equilibrium. This set of two coupled equations should be understood as a set of nonlinear equations for the equilibrium density field $\rho(\mathbf{r})$ and the equilibrium value of the center of mass of the sphere. Translational invariance of the system implies that if $\mathbf{R}, \rho(\mathbf{r})$ is a solution of (20.3), then $\mathbf{R}+\mathbf{a}, \rho(\mathbf{r}+\mathbf{a})$ is also a solution. Therefore, without loose of generality we may chose the origin of coordinates at the center of the sphere an $\mathbf{R} = 0$. Then the equilibrium density field is the solution of the first equation. Note that for realistic models of the free energy functional, the density field will display oscillations at short length scales due to the packing of the fluid near the solid sphere.

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11.10.3   Simple models

The partition function (11.2.2) and hence the entropy functional (11.2.2) cannot be computed analytically for a general interaction potential. However, this is possible for some particular simple systems. These simpler systems should offer intuition to propose realistic models in a more general case. The cases that we will consider are:

- The fluid and the solid do not interact.

- The fluid and the solid do interact and the fluid is an ideal gas.

- The fluid and the solid do interact and the solid is very stiff.

- Quadratic model.

The fluid and the solid do not interact.

In this case, the potential energy terms $\phi_{ij'} = 0$ and the integrals over fluid and solid degrees of freedom decouple

$$
\begin{aligned}
\Phi_{\text{rest}}[\mu, \beta, \boldsymbol{\lambda}_R, \beta_{\text{s}}] = {} & -\ln \sum_{N=0}^{\infty} \frac{1}{N!} \int \prod_i^N \frac{d\mathbf{q}_i}{\Lambda_{\text{f}}^3(\mathbf{q}_i)} \exp\left\{ -\sum_j^N \beta(\mathbf{q}_j)\phi_j + \sum_i^N m\beta(\mathbf{q}_i)\mu(\mathbf{q}_i) \right\} \\
& \times \int \prod_{i'}^{N'} \frac{d\mathbf{q}_{i'}}{\Lambda_{\text{s}}^3} \exp\left\{ -\boldsymbol{\lambda}_R \cdot \hat{\mathbf{R}} - \sum_{j'}^{N'} \beta_{\text{s}} \phi_{j'} \right\} \\
= {} & \Phi_{\text{rest}}^{\text{f}}[\mu, \beta] + \Phi_{\text{rest}}^{\text{s}}[\boldsymbol{\lambda}_R, \beta_{\text{s}}]
\end{aligned}
$$

In this case, both the free energy (11.2.2) and the entropy (11.2.2) become additive. In particular

$$
S_{\text{rest}}[\rho, e, \mathbf{R}, E] = S_{\text{rest}}^{\text{f}}[\rho, e] + S_{\text{rest}}^{\text{s}}(\mathbf{R}, E)
$$

It is not easy to compute the fluid entropy in general. Two notable exceptions are when the fluid is an ideal gas or a hard sphere fluid, see Ref. [] for the explicit functional forms.

The entropy of the solid can be computed in the harmonic approximation, in which the interaction is given by harmonic springs.

The fluid and the solid do interact and the fluid is an ideal gas.

In this case the potential ϕ_i of fluid particle i and the potential $\phi_{j'}$ of solid particle j' are given by

$$
\phi_i = \frac{1}{2} \sum_{j'}^{N'} \phi_{ij'}
$$

$$
\phi_{j'} = \frac{1}{2} \sum_i^N \phi_{ij'} + \frac{1}{2} \sum_{i'j'}^{N'N'} \phi_{i'j'} + \phi_{j'}^{\text{ext}}
$$

The rest thermodynamic potential (11.2.2) becomes

$$
\Phi_{\text{rest}}[\mu, \beta, \boldsymbol{\lambda}_R, \beta_{\text{s}}] = -\ln \int \prod_{i'}^{N'} \frac{d\mathbf{q}_{i'}}{\Lambda_{\text{s}}^3} \exp\left\{ -\boldsymbol{\lambda}_R \cdot \hat{\mathbf{R}} - \frac{\beta_{\text{s}}}{2} \sum_{i'j'}^{N'} \phi_{i'j'} - \beta_{\text{s}} \sum_{i'}^{N'} \phi_{i'}^{\text{ext}} \right\}
$$

$$
\times \sum_{N=0}^{\infty} \frac{1}{N!} \int \prod_{i}^{N} \frac{d\mathbf{q}_i}{\Lambda_{\text{f}}^3(\mathbf{q}_i)} \exp\left\{ \sum_{i}^{N} \left(m\beta(\mathbf{q}_i)\mu(\mathbf{q}_i) - \frac{\beta(\mathbf{q}_i) + \beta_{\text{s}}}{2} \sum_{i'}^{N'} \phi_{ii'} \right) \right\}
$$

$$
= -\ln \int \prod_{i'}^{N'} \frac{d\mathbf{q}_{i'}}{\Lambda_{\text{s}}^3} \exp\left\{ -\boldsymbol{\lambda}_R \cdot \hat{\mathbf{R}} - \frac{\beta_{\text{s}}}{2} \sum_{i'j'}^{N'} \phi_{i'j'} - \beta_{\text{s}} \sum_{i'}^{N'} \phi_{i'}^{\text{ext}} \right\}
$$

$$
\times \sum_{N=0}^{\infty} \frac{1}{N!} \left[\int \frac{d\mathbf{q}}{\Lambda_{\text{f}}^3(\mathbf{q})} \exp\left\{ \mu_0 + m\beta(\mathbf{q})\mu(\mathbf{q}) - \frac{\beta(\mathbf{q}) + \beta_{\text{s}}}{2} \sum_{i'}^{N'} \phi(\mathbf{q} - \mathbf{q}_{i'}) \right\} \right]^N
$$

$$
\Phi_{\text{rest}}[\mu, \beta, \boldsymbol{\lambda}_R, \beta_{\text{s}}] = -\ln \int \prod_{i'}^{N'} \frac{d\mathbf{q}_{i'}}{\Lambda_{\text{s}}^3} \exp\left\{ -\boldsymbol{\lambda}_R \cdot \hat{\mathbf{R}} - \frac{\beta_{\text{s}}}{2} \sum_{i'j'}^{N'} \phi_{i'j'} - \beta_{\text{s}} \sum_{i'}^{N'} \phi_{i'}^{\text{ext}} \right\}
$$

$$
\times \exp\left[\int \frac{d\mathbf{q}}{\Lambda_{\text{f}}^3(\mathbf{q})} \exp\left\{ \mu_0 + m\beta(\mathbf{q})\mu(\mathbf{q}) - \frac{\beta(\mathbf{q}) + \beta_{\text{s}}}{2} \sum_{i'}^{N'} \phi(\mathbf{q} - \mathbf{q}_{i'}) \right\} \right]
$$

$$
= -\ln \int \prod_{i'}^{N'} \frac{d\mathbf{q}_{i'}}{\Lambda_{\text{s}}^3} \exp\left\{ -\boldsymbol{\lambda}_R \cdot \hat{\mathbf{R}} - \frac{\beta_{\text{s}}}{2} \sum_{i'j'}^{N'} \phi_{i'j'} - \beta_{\text{s}} \sum_{i'}^{N'} \phi_{i'}^{\text{ext}} - \beta_{\text{s}} \Phi^{\text{eff}}(q') \right\}
$$

where the effective potential of the fluid on the solid is

$$
\Phi^{\text{eff}}(q') \equiv k_B T_{\text{s}} \int \frac{d\mathbf{q}}{\Lambda_{\text{f}}^3(\mathbf{q})} \exp\left\{ \mu_0 + m\beta(\mathbf{q})\mu(\mathbf{q}) - \frac{\beta(\mathbf{q}) + \beta_{\text{s}}}{2} \sum_{i'}^{N'} \phi(\mathbf{q} - \mathbf{q}_{i'}) \right\}
$$

This is still not very convenient. Note that we may express

$$
\sum_{i'}^{N'} \phi(\mathbf{q} - \mathbf{q}_{i'}) = \int d\mathbf{r}\, \phi(\mathbf{q} - \mathbf{r}) \hat{n}_{\mathbf{r}}^{\text{s}}(q')
$$

We attempt the following approximation

$$
\sum_{i'}^{N'} \phi(\mathbf{q} - \mathbf{q}_{i'}) = \int d\mathbf{r}\, \phi(\mathbf{q} - \mathbf{r}) n_{\text{s}} \theta(|\mathbf{R} - \mathbf{r}| - a)
$$

which is just a constant independent of the coordinates of the solid particle. In this way, we can express

$$\Phi_{\text{rest}}[\mu, \beta, \boldsymbol{\lambda}_R, \beta_{\text{s}}] = \Phi_{\text{res}}^{\text{s}}[\boldsymbol{\lambda}_R, \beta_{\text{s}}] + \int \frac{d\mathbf{q}}{\Lambda_{\text{f}}^3(\mathbf{q})} \exp\left\{\mu_0 + m\beta(\mathbf{q})\mu(\mathbf{q}) - \frac{\beta(\mathbf{q}) + \beta_{\text{s}}}{2} \int d\mathbf{r}\phi(\mathbf{q} - \mathbf{r})n_{\text{s}}\theta(|\mathbf{R} - \mathbf{r}| - a)\right\}$$

The fluid and the solid do interact and the solid is very stiff.

In this case, we may model the solid as an external field acting on the fluid.

11.11   Appendix: Change of variables

Our initial set of variables is denoted generically by a. Assume that we select a different set of variables b which are related functionally to the original set, $b = B(a)$. The entropy in the old variables can be expressed in terms of the entropy in the new variables by $S(a) = \tilde{S}(B(a))$ where $\tilde{S}(b)$ is the entropy expressed in the new variables. The irreversible dynamics of the b variables is given by

$$\partial_t B(a) = \frac{\partial B}{\partial a}^T (B(a))\partial_t a = \frac{\partial B}{\partial a}^T (B(a))D(a)\frac{\partial S}{\partial a}(a) = \frac{\partial B}{\partial a}^T (B(a))D(a)\frac{\partial B}{\partial a}(B(a))\frac{\partial \tilde{S}}{\partial b}(B(a))$$

This is

$$\partial_t b = \tilde{D}(b)\frac{\partial \tilde{S}}{\partial b}(b)$$

with the new dissipative matrix given by

$$\tilde{D}(b) = \frac{\partial B}{\partial a}^T (b)D(B^{-1}(b))\frac{\partial B}{\partial a}(b)$$

In our case, the old and new set of variables are

$$a = \begin{pmatrix} \rho(\mathbf{r}) \\ \mathbf{g}(\mathbf{r}) \\ e(\mathbf{r}) \\ \mathbf{R} \\ \mathbf{P} \\ E \end{pmatrix} \qquad b = \begin{pmatrix} \rho(\mathbf{r}) \\ \mathbf{g}(\mathbf{r}) \\ \epsilon(\mathbf{r}) \\ \mathbf{R} \\ \mathbf{P} \\ U \end{pmatrix} \qquad B(a) = \begin{pmatrix} \rho(\mathbf{r}) \\ \mathbf{g}(\mathbf{r}) \\ e(\mathbf{r}) - \frac{\mathbf{g}^2(\mathbf{r})}{2\rho(\mathbf{r})} \\ \mathbf{R} \\ \mathbf{P} \\ E - \frac{\mathbf{P}^2}{2M} \end{pmatrix}$$

The Jacobian of the transformation is

$$\frac{\partial B}{\partial a}(a) = \begin{pmatrix} \frac{\delta\rho(\mathbf{r})}{\delta\rho(\mathbf{r}')} & \frac{\delta\mathbf{g}(\mathbf{r})}{\delta\rho(\mathbf{r}')} & \frac{\delta e(\mathbf{r})-\frac{\mathbf{g}^2(\mathbf{r})}{2\rho(\mathbf{r})}}{\delta\rho(\mathbf{r}')} & \frac{\delta\mathbf{R}}{\delta\rho(\mathbf{r}')} & \frac{\delta\mathbf{P}}{\delta\rho(\mathbf{r}')} & \frac{\delta E-\frac{\mathbf{P}^2}{2M}}{\delta\rho(\mathbf{r}')} \\[6pt] \frac{\delta\rho(\mathbf{r})}{\delta\mathbf{g}(\mathbf{r}')} & \frac{\delta\mathbf{g}(\mathbf{r})}{\delta\mathbf{g}(\mathbf{r}')} & \frac{\delta e(\mathbf{r})-\frac{\mathbf{g}^2(\mathbf{r})}{2\rho(\mathbf{r})}}{\delta\mathbf{g}(\mathbf{r}')} & \frac{\delta\mathbf{R}}{\delta\mathbf{g}(\mathbf{r}')} & \frac{\delta\mathbf{P}}{\delta\mathbf{g}(\mathbf{r}')} & \frac{\delta E-\frac{\mathbf{P}^2}{2M}}{\delta\mathbf{g}(\mathbf{r}')} \\[6pt] \frac{\delta\rho(\mathbf{r})}{\delta e(\mathbf{r}')} & \frac{\delta\mathbf{g}(\mathbf{r})}{\delta e(\mathbf{r}')} & \frac{\delta e(\mathbf{r})-\frac{\mathbf{g}^2(\mathbf{r})}{2\rho(\mathbf{r})}}{\delta e(\mathbf{r}')} & \frac{\delta\mathbf{R}}{\delta e(\mathbf{r}')} & \frac{\delta\mathbf{P}}{\delta e(\mathbf{r}')} & \frac{\delta E-\frac{\mathbf{P}^2}{2M}}{\delta e(\mathbf{r}')} \\[6pt] \frac{\partial\rho(\mathbf{r})}{\partial\mathbf{R}} & \frac{\partial\mathbf{g}(\mathbf{r})}{\partial\mathbf{R}} & \frac{\partial e(\mathbf{r})-\frac{\mathbf{g}^2(\mathbf{r})}{2\rho(\mathbf{r})}}{\partial\mathbf{R}} & \frac{\partial\mathbf{R}}{\partial\mathbf{R}} & \frac{\partial\mathbf{P}}{\partial\mathbf{R}} & \frac{\partial E-\frac{\mathbf{P}^2}{2M}}{\partial\mathbf{R}} \\[6pt] \frac{\partial\rho(\mathbf{r})}{\partial\mathbf{P}} & \frac{\partial\mathbf{g}(\mathbf{r})}{\partial\mathbf{P}} & \frac{\partial e(\mathbf{r})-\frac{\mathbf{g}^2(\mathbf{r})}{2\rho(\mathbf{r})}}{\partial\mathbf{P}} & \frac{\partial\mathbf{R}}{\partial\mathbf{P}} & \frac{\partial\mathbf{P}}{\partial\mathbf{P}} & \frac{\partial E-\frac{\mathbf{P}^2}{2M}}{\partial\mathbf{P}} \\[6pt] \frac{\partial\rho(\mathbf{r})}{\partial E} & \frac{\partial\mathbf{g}(\mathbf{r})}{\partial E} & \frac{\partial e(\mathbf{r})-\frac{\mathbf{g}^2(\mathbf{r})}{2\rho(\mathbf{r})}}{\partial E} & \frac{\partial\mathbf{R}}{\partial E} & \frac{\partial\mathbf{P}}{\partial E} & \frac{\partial E-\frac{\mathbf{P}^2}{2M}}{\partial E} \end{pmatrix} = \begin{pmatrix} \delta_{\mathbf{rr}'} & 0 & \frac{\mathbf{v}^2(\mathbf{r})}{2}\delta_{\mathbf{rr}'} & 0 & 0 & 0 \\ 0 & \mathbf{1}\delta_{\mathbf{rr}'} & -\mathbf{v}(\mathbf{r})\delta_{\mathbf{rr}'} & 0 & 0 & 0 \\ 0 & 0 & \delta_{\mathbf{rr}'} & 0 & 0 & 0 \\ 0 & 0 & 0 & \mathbf{1} & 0 & 0 \\ 0 & 0 & 0 & 0 & \mathbf{1} & -\mathbf{V} \\ 0 & 0 & 0 & 0 & 0 & 1 \end{pmatrix}$$

The dissipation matrix in the variables is the result of multiplying the old dissipation matrix with the Jacobians

$$\begin{pmatrix} \delta_{\mathbf{rr}'} & 0 & 0 & 0 & 0 & 0 \\ 0 & \mathbf{1}\delta_{\mathbf{rr}'} & 0 & 0 & 0 & 0 \\ \frac{\mathbf{v}_{\mathbf{r}}^2}{2}\delta_{\mathbf{rr}'} & -\mathbf{v}_{\mathbf{r}}\delta_{\mathbf{rr}'} & \delta_{\mathbf{rr}'} & 0 & 0 & 0 \\ 0 & 0 & 0 & \mathbf{1} & 0 & 0 \\ 0 & 0 & 0 & 0 & \mathbf{1} & 0 \\ 0 & 0 & 0 & 0 & -\mathbf{V} & 1 \end{pmatrix} \begin{pmatrix} 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & \langle\dot{\mathbf{g}}_{\mathbf{r}'}\|\dot{\mathbf{g}}_{\mathbf{r}''}\rangle & \langle\dot{\mathbf{g}}_{\mathbf{r}'}\|\dot{e}_{\mathbf{r}''}\rangle & 0 & \langle\dot{\mathbf{g}}_{\mathbf{r}'}\|\dot{\mathbf{P}}\rangle & \langle\dot{\mathbf{g}}_{\mathbf{r}'}\|\dot{E}\rangle \\ 0 & \langle\dot{e}_{\mathbf{r}'}\|\dot{\mathbf{g}}_{\mathbf{r}''}\rangle & \langle\dot{e}_{\mathbf{r}'}\|\dot{e}_{\mathbf{r}''}\rangle & 0 & \langle\dot{e}_{\mathbf{r}'}\|\dot{\mathbf{P}}\rangle & \langle\dot{e}_{\mathbf{r}'}\|\dot{E}\rangle \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & \langle\dot{\mathbf{P}}\|\dot{\mathbf{g}}_{\mathbf{r}''}\rangle & \langle\dot{\mathbf{P}}\|\dot{e}_{\mathbf{r}''}\rangle & 0 & \langle\dot{\mathbf{P}}\|\dot{\mathbf{P}}\rangle & \langle\dot{\mathbf{P}}\|\dot{E}\rangle \\ 0 & \langle\dot{E}\|\dot{\mathbf{g}}_{\mathbf{r}''}\rangle & \langle\dot{E}\|\dot{e}_{\mathbf{r}''}\rangle & 0 & \langle\dot{E}\|\dot{\mathbf{P}}\rangle & \langle\dot{E}\|\dot{E}\rangle \end{pmatrix} \begin{pmatrix} \delta_{\mathbf{rr}'} & 0 & \frac{\mathbf{v}_{\mathbf{r}}^2}{2}\delta_{\mathbf{rr}'} & \\ 0 & \mathbf{1}\delta_{\mathbf{rr}'} & -\mathbf{v}_{\mathbf{r}}\delta_{\mathbf{rr}'} & \\ 0 & 0 & \delta_{\mathbf{rr}'} & \\ 0 & 0 & 0 & \mathbf{1} \\ 0 & 0 & 0 & \\ 0 & 0 & 0 & \end{pmatrix}$$

The matrix multiplication involves "sums over the continuum indices $\mathbf{r}$" (i.e. integrals) when appropriate. The result gives the following dissipation matrix

$$\begin{pmatrix} 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & \langle\dot{\mathbf{g}}_{\mathbf{r}}\|\dot{\mathbf{g}}_{\mathbf{r}'}\rangle & \langle\dot{\mathbf{g}}_{\mathbf{r}}\|\dot{\epsilon}_{\mathbf{r}'}\rangle & 0 & \langle\dot{\mathbf{g}}_{\mathbf{r}}\|\dot{\mathbf{P}}\rangle & \langle\dot{\mathbf{g}}_{\mathbf{r}}\|\dot{U}\rangle \\ 0 & \langle\dot{\epsilon}_{\mathbf{r}}\|\dot{\mathbf{g}}_{\mathbf{r}'}\rangle & \langle\dot{\epsilon}_{\mathbf{r}}\|\dot{\epsilon}_{\mathbf{r}'}\rangle & 0 & \langle\dot{\epsilon}_{\mathbf{r}}\|\dot{\mathbf{P}}\rangle & \langle\dot{\epsilon}_{\mathbf{r}}\|\dot{U}\rangle \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & \langle\dot{\mathbf{P}}\|\dot{\mathbf{g}}_{\mathbf{r}'}\rangle & \langle\dot{\mathbf{P}}\|\dot{\epsilon}_{\mathbf{r}'}\rangle & 0 & \langle\dot{\mathbf{P}}\|\dot{\mathbf{P}}\rangle & \langle\dot{\mathbf{P}}\|\dot{U}\rangle \\ 0 & \langle\dot{U}\|\dot{\mathbf{g}}_{\mathbf{r}'}\rangle & \langle\dot{U}\|\dot{\epsilon}_{\mathbf{r}'}\rangle & 0 & \langle\dot{U}\|\dot{\mathbf{P}}\rangle & \langle\dot{U}\|\dot{U}\rangle \end{pmatrix}$$

where we have introduced the notation

$$\dot{\epsilon}_{\mathbf{r}} = i\mathcal{L}\hat{e}_{\mathbf{r}} - \mathbf{v}_{\mathbf{r}}\cdot i\mathcal{L}\hat{\mathbf{g}}_{\mathbf{r}}$$

$$\dot{U} = i\mathcal{L}\hat{E} - \mathbf{V}\cdot i\mathcal{L}\hat{\mathbf{P}}$$

Note that conservation $i\mathcal{L}\hat{\mathbf{P}}_T = 0, i\mathcal{L}\hat{E}_T = 0$ of total momentum and energy defined in (11.1.2), implies

$$\dot{\mathbf{P}}(z) = -\int d\mathbf{r}\,\dot{\mathbf{g}}_{\mathbf{r}}(z)$$

$$\dot{U}(z) = -\int d\mathbf{r}\,\dot{\epsilon}_{\mathbf{r}}(z) - \int d\mathbf{r}(\mathbf{v}(\mathbf{r}) - \mathbf{V})\dot{\mathbf{g}}_{\mathbf{r}}(z)$$

As we have discussed previously, the entropy expressed in terms of internal energies no longer depends on the momentum variables. Therefore, the dissipative part of the dynamics in terms of the new variables is

$$\partial_t \begin{pmatrix} \rho(\mathbf{r}) \\ \mathbf{g}(\mathbf{r}) \\ \epsilon(\mathbf{r}) \\ \mathbf{R} \\ \mathbf{P} \\ U \end{pmatrix}\Bigg|_{\text{irr}} = \begin{pmatrix} 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & \int d\mathbf{r}'\langle\dot{\mathbf{g}}_{\mathbf{r}}\,\|\,\dot{\mathbf{g}}_{\mathbf{r}'}\rangle & \int d\mathbf{r}'\langle\dot{\mathbf{g}}_{\mathbf{r}}\,\|\,\dot{\epsilon}_{\mathbf{r}'}\rangle & 0 & \langle\dot{\mathbf{g}}_{\mathbf{r}}\,\|\,\dot{\mathbf{P}}\rangle & \langle\dot{\mathbf{g}}_{\mathbf{r}}\,\|\,\dot{U}\rangle \\ 0 & \int d\mathbf{r}'\langle\dot{\epsilon}_{\mathbf{r}}\,\|\,\dot{\mathbf{g}}_{\mathbf{r}'}\rangle & \int d\mathbf{r}'\langle\dot{\epsilon}_{\mathbf{r}}\,\|\,\dot{\epsilon}_{\mathbf{r}'}\rangle & 0 & \langle\dot{\epsilon}_{\mathbf{r}}\,\|\,\dot{\mathbf{P}}\rangle & \langle\dot{\epsilon}_{\mathbf{r}}\,\|\,\dot{U}\rangle \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & \int d\mathbf{r}'\langle\dot{\mathbf{P}}\,\|\,\dot{\mathbf{g}}_{\mathbf{r}'}\rangle & \int d\mathbf{r}'\langle\dot{\mathbf{P}}\,\|\,\dot{\epsilon}_{\mathbf{r}'}\rangle & 0 & \langle\dot{\mathbf{P}}\,\|\,\dot{\mathbf{P}}\rangle & \langle\dot{\mathbf{P}}\,\|\,\dot{U}\rangle \\ 0 & \int d\mathbf{r}'\langle\dot{U}\,\|\,\dot{\mathbf{g}}_{\mathbf{r}'}\rangle & \int d\mathbf{r}'\langle\dot{U}\,\|\,\dot{\epsilon}_{\mathbf{r}'}\rangle & 0 & \langle\dot{U}\,\|\,\dot{\mathbf{P}}\rangle & \langle\dot{U}\,\|\,\dot{U}\rangle \end{pmatrix} \begin{pmatrix} \frac{\delta S}{\delta\rho_{\mathbf{r}'}} \\ \mathbf{0} \\ \beta(\mathbf{r}') \\ \frac{\partial S}{\partial\mathbf{R}} \\ \mathbf{0} \\ \beta_{\text{s}} \end{pmatrix}$$

These gives the following irreversible equations

$$\partial_t\rho(\mathbf{r})|_{\text{irr}} = 0$$

$$\partial_t\mathbf{g}(\mathbf{r})|_{\text{irr}} = \int d\mathbf{r}'\langle\dot{\mathbf{g}}_{\mathbf{r}}\,\|\,\dot{\epsilon}_{\mathbf{r}'}\rangle\beta(\mathbf{r}') + \langle\dot{\mathbf{g}}_{\mathbf{r}}\,\|\,\dot{U}\rangle\beta_{\text{s}}$$

$$\partial_t\epsilon(\mathbf{r})|_{\text{irr}} = \int d\mathbf{r}'\langle\dot{\epsilon}_{\mathbf{r}}\,\|\,\dot{\epsilon}_{\mathbf{r}'}\rangle\beta(\mathbf{r}') + \langle\dot{\epsilon}_{\mathbf{r}}\,\|\,\dot{U}\rangle\beta_{\text{s}}$$

$$\partial_t\mathbf{R}|_{\text{irr}} = 0$$

$$\partial_t\mathbf{P}|_{\text{irr}} = \int d\mathbf{r}'\langle\dot{\mathbf{P}}\,\|\,\dot{\epsilon}_{\mathbf{r}'}\rangle\beta(\mathbf{r}') + \langle\dot{\mathbf{P}}\,\|\,\dot{U}\rangle\beta_{\text{s}}$$

$$\partial_t U|_{\text{irr}} = \int d\mathbf{r}'\langle\dot{U}\,\|\,\dot{\epsilon}_{\mathbf{r}'}\rangle\beta(\mathbf{r}') + \langle\dot{U}\,\|\,\dot{U}\rangle\beta_{\text{s}}$$

We make use now of the conservation laws as expressed in (11.11). The only non-trivial equations are those of the fluid

$$\partial_t\mathbf{g}(\mathbf{r})|_{\text{irr}} = \int d\mathbf{r}'\langle\dot{\mathbf{g}}_{\mathbf{r}}\,\|\,\dot{\epsilon}_{\mathbf{r}'}\rangle(\beta(\mathbf{r}') - \beta_{\text{s}}) - \int d\mathbf{r}'\langle\dot{\mathbf{g}}_{\mathbf{r}}\,\|\,\dot{\mathbf{g}}_{\mathbf{r}'}\rangle\beta_{\text{s}}(\mathbf{v}(\mathbf{r}') - \mathbf{V})$$

$$\partial_t\epsilon(\mathbf{r})|_{\text{irr}} = \int d\mathbf{r}'\langle\dot{\epsilon}_{\mathbf{r}}\,\|\,\dot{\epsilon}_{\mathbf{r}'}\rangle(\beta(\mathbf{r}') - \beta_{\text{s}}) - \int d\mathbf{r}'\langle\dot{\epsilon}_{\mathbf{r}}\,\|\,\dot{\mathbf{g}}_{\mathbf{r}'}\rangle\beta_{\text{s}}(\mathbf{v}(\mathbf{r}') - \mathbf{V})$$

because the solid evolves in order to ensure conservation

$$\partial_t \mathbf{P}|_{\mathrm{irr}} = - \int d\mathbf{r}\; \partial_t \mathbf{g}(\mathbf{r})|_{\mathrm{irr}}$$

$$\partial_t U|_{\mathrm{irr}} = - \int d\mathbf{r}\; \partial_t \epsilon(\mathbf{r})|_{\mathrm{irr}} + \int d\mathbf{r}(\mathbf{v}(\mathbf{r}) - \mathbf{V})\; \partial_t \mathbf{g}(\mathbf{r})|_{\mathrm{irr}}$$

Now we transform the Green-Kubo coefficients to comoving Green-Kubo

$$\partial_t \mathbf{g}(\mathbf{r})|_{\mathrm{irr}} = \int d\mathbf{r}' \langle \mathscr{G}^{-1}\dot{\mathbf{g}}_{\mathbf{r}} \| \mathscr{G}^{-1}\dot{\mathbf{g}}_{\mathbf{r}'} \rangle^0 \beta_{\mathrm{s}}(\mathbf{v}(\mathbf{r}') - \mathbf{V}) - \int d\mathbf{r}' \langle \mathscr{G}^{-1}\dot{\mathbf{g}}_{\mathbf{r}} \| \mathscr{G}^{-1}\dot{\epsilon}_{\mathbf{r}'} \rangle^0 (\beta(\mathbf{r}') - \beta_{\mathrm{s}})$$

$$\partial_t \epsilon(\mathbf{r})|_{\mathrm{irr}} = \int d\mathbf{r}' \langle \mathscr{G}^{-1}\dot{\epsilon}_{\mathbf{r}} \| \mathscr{G}^{-1}\dot{\mathbf{g}}_{\mathbf{r}'} \rangle^0 \beta_{\mathrm{s}}(\mathbf{v}(\mathbf{r}') - \mathbf{V}) - \int d\mathbf{r}' \langle \mathscr{G}^{-1}\dot{\epsilon}_{\mathbf{r}} \| \mathscr{G}^{-1}\dot{\epsilon}_{\mathbf{r}'} \rangle^0 (\beta(\mathbf{r}') - \beta_{\mathrm{s}})$$

First consider the time derivative of the internal energy, defined in (11.11)

$$\dot{\epsilon}_{\mathbf{r}} = i\mathcal{L}\hat{e}_{\mathbf{r}} - \mathbf{v_r} \cdot i\mathcal{L}\hat{\mathbf{g}}_{\mathbf{r}} = -\nabla \hat{\mathbf{Q}}_{\mathbf{r}} + \hat{\pi}_{\mathbf{r}} + \mathbf{v_r} \cdot \nabla \hat{\boldsymbol{\sigma}}_{\mathbf{r}} - \mathbf{v_r} \cdot \mathbf{F_r}$$

where we have used (11.1.2). The action of the Galilean operator in this phase function is, by using (11.1.3)

$$\mathscr{G}^{-1}\dot{\epsilon}_{\mathbf{r}} = -\boldsymbol{\nabla} \cdot \left[\hat{\mathbf{Q}}_{\mathbf{r}} + \hat{\boldsymbol{\sigma}}_{\mathbf{r}} \cdot \mathbf{v}(\mathbf{r}) + \frac{1}{2}\mathbf{v}^2(\mathbf{r})\hat{\mathbf{g}}_{\mathbf{r}} + \mathbf{v}(\mathbf{r})\mathscr{G}^{-1}\hat{e}_{\mathbf{r}} \right]$$

$$+ \hat{\pi}_{\mathbf{r}} + \frac{\mathbf{v}(\mathbf{r}) + \mathbf{V}}{2}\hat{\mathbf{F}}_{\mathbf{r}} + \mathbf{v_r} \cdot \boldsymbol{\nabla} \left[\hat{\boldsymbol{\sigma}}_{\mathbf{r}} + \mathbf{v}(\mathbf{r})\hat{\mathbf{g}}_{\mathbf{r}} + \hat{\mathbf{g}}_{\mathbf{r}}\mathbf{v}(\mathbf{r}) + \mathbf{v}(\mathbf{r})\mathbf{v}(\mathbf{r})\hat{\rho}_{\mathbf{r}} \right] - \mathbf{v_r} \cdot \mathbf{F_r}$$

Inside the Green-Kubo expression, the further action of the projection operator $\mathscr{Q}$ on the above phase function will eliminate the terms containing the relevant variables. In summary, the projected currents are

$$\mathscr{Q}\mathscr{G}^{-1}\dot{\mathbf{g}}_{\mathbf{r}} = -\boldsymbol{\nabla} \cdot \mathscr{Q}\hat{\boldsymbol{\sigma}}_{\mathbf{r}} + \mathscr{Q}\hat{\mathbf{F}}_{\mathbf{r}}$$

$$\mathscr{Q}\mathscr{G}^{-1}\dot{\epsilon}_{\mathbf{r}} = -\boldsymbol{\nabla} \cdot \mathscr{Q}\hat{\mathbf{Q}}_{\mathbf{r}} - \mathscr{Q}\hat{\boldsymbol{\sigma}}_{\mathbf{r}} : \boldsymbol{\nabla}\mathbf{v}(\mathbf{r}) + \mathscr{Q}\hat{\pi}_{\mathbf{r}} - \frac{\mathbf{v}(\mathbf{r}) - \mathbf{V}}{2}\mathscr{Q}\hat{\mathbf{F}}_{\mathbf{r}}$$

By substitution of these projected currents into the equations (11.11)

$$\partial_t \mathbf{g_r}|_{\text{irr}} = - \int d\mathbf{r}' \langle \left(-\boldsymbol{\nabla}\!\cdot\!\hat{\boldsymbol{\sigma}}_\mathbf{r} + \hat{\mathbf{F}}_\mathbf{r} \right) \| \left(-\boldsymbol{\nabla}'\!\cdot\!\hat{\boldsymbol{\sigma}}_{\mathbf{r}'} + \hat{\mathbf{F}}_{\mathbf{r}'} \right) \rangle^0 \beta_\text{s} (\mathbf{v}_{\mathbf{r}'} - \mathbf{V})$$

$$+ \int d\mathbf{r}' \langle \left(-\boldsymbol{\nabla}\!\cdot\!\hat{\boldsymbol{\sigma}}_\mathbf{r} + \hat{\mathbf{F}}_\mathbf{r} \right) \| \left(-\boldsymbol{\nabla}'\!\cdot\!\hat{\mathbf{Q}}_{\mathbf{r}'} - \hat{\boldsymbol{\sigma}}_{\mathbf{r}'} : \boldsymbol{\nabla}'\mathbf{v}(\mathbf{r}') + \hat{\pi}_{\mathbf{r}'} - \frac{\mathbf{v}(\mathbf{r}') - \mathbf{V}}{2}\hat{\mathbf{F}}_{\mathbf{r}'} \right) \rangle^0 (\beta(\mathbf{r}') - \beta_\text{s})$$

$$\partial_t \epsilon_\mathbf{r}|_{\text{irr}} = - \int d\mathbf{r}' \langle \left(-\boldsymbol{\nabla}\!\cdot\!\hat{\mathbf{Q}}_\mathbf{r} - \hat{\boldsymbol{\sigma}}_\mathbf{r} : \boldsymbol{\nabla}\mathbf{v_r} + \hat{\pi}_\mathbf{r} - \frac{\mathbf{v_r} - \mathbf{V}}{2}\hat{\mathbf{F}}_\mathbf{r} \right) \| \left(-\boldsymbol{\nabla}'\!\cdot\!\hat{\boldsymbol{\sigma}}_{\mathbf{r}'} + \hat{\mathbf{F}}_{\mathbf{r}'} \right) \rangle^0 \beta_\text{s}(\mathbf{v}_{\mathbf{r}'} - \mathbf{V})$$

$$+ \int d\mathbf{r}' \langle \left(-\boldsymbol{\nabla}\!\cdot\!\hat{\mathbf{Q}}_\mathbf{r} - \hat{\boldsymbol{\sigma}}_\mathbf{r} : \boldsymbol{\nabla}\mathbf{v_r} + \hat{\pi}_\mathbf{r} - \frac{\mathbf{v_r} - \mathbf{V}}{2}\hat{\mathbf{F}}_\mathbf{r} \right) \| \left(-\boldsymbol{\nabla}'\!\cdot\!\hat{\mathbf{Q}}_{\mathbf{r}'} - \hat{\boldsymbol{\sigma}}_{\mathbf{r}'} : \boldsymbol{\nabla}'\mathbf{v}(\mathbf{r}') + \hat{\pi}_{\mathbf{r}'} - \frac{\mathbf{v}(\mathbf{r}') - \mathbf{V}}{2}\hat{\mathbf{F}}_{\mathbf{r}'} \right) \rangle^0 (\beta(\mathbf{r}') - \beta_\text{s})$$

[Finish, but I think it gives the same as before, as it should.]

12

Solid-solid: Heat conduction at the interface between two solids: $e_{\mathbf{r}}^1, e_{\mathbf{r}}^2$

12.1 Introduction

From a mathematical point of view boundary conditions are those requirements on the solutions of a partial differential equation that allow one to select the actual solution for the problem at hand. From a physical point of view, however, boundary conditions are just a way to phenomenologically describe the highly localized interactions occurring at the interface of our system of interest with "the rest of the world".

Our aim is to derive from the original Hamilton's equations that govern the classical dynamics of the atoms the evolution equation of the energy density field. This can be achieved with the technique of projection operators as described in the classical textbook by Grabert [?]. This allows to obtain a *formally exact* set of dynamic equations for the energy density field that are non-local in time and space. In the limit where both non-localities may be neglected, the evolution of the energy density turns out to be governed by Fick's law away from the interface. In this limit, the region of the atoms of different solids that are interacting with each other can be considered as a "surface" and the formalism provides aditional source terms that are localiced at these surface. These source terms can be understood as a way to incorporate "boundary conditions" *within* the partial differential equation that governs the evolution of the energy density field. The framework provides explicit expressions for the boundary conditions in terms of transport coefficients given in terms of Green-Kubo formulae.

12.2 General framework

Let us consider a classical system system made classical particles. At a microscopic level, the system is described with $z = \{\mathbf{q}_i, \mathbf{p}_i\}$ which is the collection of positions and mo-

menta of the particles. The microstate z moves in phase space according to Hamilton's equations. At a coarse-grained level of description, the same system is described by a collection of phase functions $\hat{A}(z)$ referred to as coarse-grained variables or CG variables. The statistical treatment of the system is accounted for with a probability density $\rho_t(z)$ in phase space that obeys the Lioville equation. A crucial object in the theory of coarse-graining is the *relevant ensemble* $\overline{\rho}_t(z)$. This probability density is obtained by maximizing with restrictions the relative entropy functional

$$\mathscr{S}[\rho] = -\mathrm{Tr}\left[\rho(z)\ln\left(\frac{\rho(z)}{\rho_0}\right)\right]$$

where ρ_0 is a uniform distribution function. Usually the Boltzmann constant k_B appears in front of this expression. By not including this factor we are measuring the relative entropy in units of k_B. The trace symbol Tr denotes a summation over the microscopic degrees of freedom z, usually in the form of a (dimensionless) integral over phase space.

The basic idea of the maximum entropy principle is that in order to find the least biased probability density $\rho(z)$ in phase space (i.e. the least biased ensemble) when only partial information is known about $\rho(z)$, one should maximize the entropy functional (12.2) subject to the constraints of this partial information. If no additional information is given, the maximum of (12.2) occurs for the uniform distribution ρ_0 and we have equiprobability of all microstates in phase space.

The ensemble that maximizes the entropy (12.2) subject to the partial information that we have about the system is named the *relevant ensemble* $\overline{\rho}(z)$.

We will consider in this paper that the partial information known about the ensemble $\rho(z)$ is that it gives prescribed values α for the average of the CG variables $\hat{A}(z)$, this is

$$\mathrm{Tr}[\rho(z)\hat{A}(z)] = \alpha$$

Standard maximization of (12.2) with the constraint (12.2) and the normalization of $\rho(z)$ leads to the relevant ensemble

$$\overline{\rho}(z) = \frac{1}{Z[\lambda]}\exp\{-\lambda\hat{A}(z)\}$$

where the **dimensionless partition function** is defined as

$$Z[\lambda] \equiv \mathrm{Tr}[\exp\{-\lambda\hat{A}(z)\}]$$

and λ is a Lagrange multiplier that is obtained by requiring that the generalized canonical ensemble (12.2) fulfills the constraint (12.2). This requirement can be written as

$$\frac{\partial\Phi[\lambda]}{\partial\lambda} = \alpha$$

where we have introduced the *dimensionless potential of the α-level of description*

$$\Phi[\lambda] = -\ln Z[\lambda]$$

The implicit equation (12.2) allows one to obtain $\lambda(\alpha)$. In fact, there is a one to one

correspondence between λ and α, as can be shown by taking the derivative of Eq. (12.2) with respect to λ

$$\frac{\partial^2 \Phi[\lambda]}{\partial \lambda \partial \lambda} = -\langle \delta\hat{A}\delta\hat{A} \rangle^\lambda$$

where $\delta\hat{A} = \hat{A}(z) - \alpha$ and the average $\langle \cdots \rangle^\lambda$ is performed with $\overline{\rho}(z)$. This shows that $\Omega[\lambda]$ is a concave functional of λ because the Hessian matrix of second derivatives is negative definite. Eq. (12.2) means also that

$$\frac{\partial a}{\partial \lambda} = -\langle \delta\hat{A}\delta A \rangle^\lambda$$

The covariance $\langle \delta\hat{A}\delta\hat{A} \rangle^\lambda$ is a definite positive matrix, and therefore, the Jacobian of the change of variables from λ to α can be inverted to provide $\lambda[\alpha]$. Therefore, *there is a one to one connection between the pair of conjugate variables λ and α*. This argument is valid *for any pair* of conjugate variables!

The *entropy* of the given level of description is defined as the result of evaluating the entropy functional (12.2) at the relevant ensemble (12.2), with the result

$$S(\alpha) \equiv \mathscr{S}[\overline{\rho}] = -\Omega[\lambda(\alpha)] + \lambda(\alpha)\alpha$$

We observe that the entropy and the dimensionless potential are the Legendre transform of each other (up to signs). By taking the derivative of (12.2) with respect ot α and using Eq. (12.2) we have the expression conjugate to Eq. (12.2),

$$\frac{\partial S(\alpha)}{\partial \alpha} = \lambda(\alpha)$$

In general it is possible to derive the evolution equation for a given dynamic variable by using the technique of projection operators [**?**]. The projection operator method can be understood, at its most fundamental level as a way to approximate the actual time dependent ensemble which is the solution of the Liouville equation with an approximate *relevant ensemble*. This relevant ensemble, in turn, is obtained by maximizing the entropy functional subject to macroscopic information. We summarize in the rest of this section the time-dependent projection operator technique as presented in the classical textbook by Grabert [**?**]. The aim is to derive equations of motion for the time dependent average $a_i(t)$ of a set of CG variables $A_i(z)$. The time dependent average is

$$a_i(t) = \text{Tr}[\rho_t(z)A_i(z)]$$

where z is the microscopic state of the system and $\rho_t(z)$ is the non-equilibrium solution of the Liouville equation. As it is shown in [**?**], the Liouville equation can be re-written in the following *exact* form

$$\frac{\partial}{\partial t}a_i(t) = v_i(t) + \int_0^t dt' \sum_j K_{ij}(t,t')\frac{\partial S}{\partial \alpha_j}(t)$$

The reversible term is given by

$$v_i(t) = \text{Tr}[\overline{\rho}_t L A_i]$$

where the Liouville operator is

$$L = -\sum_i \left[\frac{\partial \hat{H}}{\partial \mathbf{q}_i} \frac{\partial}{\partial \mathbf{p}_i} - \frac{\partial \hat{H}}{\partial \mathbf{p}_i} \frac{\partial}{\partial \mathbf{q}_i} \right]$$

and the relevant ensemble $\overline{\rho}_t$ is of the form (12.2), with a time dependent conjugate variable $\lambda(t)$. The conjugate variables λ are selected in such a way that the averages of the real and of the relevant ensemble coincide. Note that if only the reversible term $v_i(t)$ would be present in Eq. (12.2), we would be approximating the actual ensemble that it is a solution of the Liouville equation with a relevant ensemble of the form (12.2) where the conjugate field $\lambda(t)$ is now a function of time. The error in this approximation is, in fact, the memory term which describes irreversible behaviour. The irreversible term in Eq. (12.2) involves the memory kernel

$$K_{ij}(t,t') = \text{Tr}[\overline{\rho}_{t'}\left(\mathscr{Q}_{t'} L A_j \right) G_{t't}\left(\mathscr{Q}_t L A_i \right)]$$

where the projection operator $\mathscr{Q}_{t'}$ applied to an arbitrary function $\hat{F}(z)$ is

$$\mathscr{Q}_{t'}\hat{F}(z) = \hat{F}(z) - \text{Tr}[\overline{\rho}_{t'}F]$$
$$-\sum_i (A_i(z) - a_i(t'))\frac{\partial}{\partial a_i(t')}\text{Tr}[\overline{\rho}_{t'}F]$$

Finally, the time ordered projected propagator $G_{t't}$ is given by

$$G_{t't} = 1 + \sum_{n=1}^{\infty} \int_{t'}^{t} dt_1 \cdots \int_{t'}^{t_{n-1}} dt_n L \mathscr{Q}_{t_n} \cdots L \mathscr{Q}_{t_1}$$
$$= T_- \exp\left\{ \int_{t'}^{t} L \mathscr{Q}_{t'} dt' \right\}$$

Eq. (12.2) is a closed equation for $a(t)$. The relevant ensemble is a functional of $a(t)$ through $\lambda(t)$. The kernel becomes a functional of $a(t)$ through the relevant ensemble. Although Eq. (12.2) is a closed equation it is an integro-differential equation which is difficult to treat in general. Nevertheless, the exact transport equation (12.2) can be approximated by a memory-less equation whenever a clear separation of time scales exists between the evolution of the averages and the decay of the memory kernel. Under this assumption and the neglect of terms of order $\mathscr{O}(LA^3)$, assumed to be small due to the slowness of the relevant variables, one obtains the Markovian equation [?]

$$\dot{a}_i(t) = v_i(t) + \sum_j D_{ij}(t)\frac{\partial S}{\partial a_j}(t)$$

where the dissipative matrix is given by the Green-Kubo formula

$$D_{ij}(t) = \int_0^\tau dt' \, \langle \delta LA_j(t) \delta LA_i(t') \rangle^{\lambda(t)}$$

Here, $\delta LA_j(t) = \mathcal{Q}_t LA_j$, $\delta LA_i(t') = \exp\{Lt'\}(\mathcal{Q}_t LA_i)$ and τ is a time large compared to the decay time of the correlation integrand but short in front of the time scale of evolution of the CG variables. The dissipative matrix depends in general on the CG variables through the relevant ensemble and, as such, is a function of time. It can be shown that the dissipative matrix is symmetric and positive definite [**?**].

12.3 The CG variables

We consider two isolated atomic solid systems that interact with each other. In the present work, we are interested in the dynamics of the energy density field in order to describe how the energy flows in the composite system. In this work, we will assume that the solid 2 is an spherical inclusion within solid 1. This simplifies the discussion but does not limit the generality of the results.

The solids are made of N_1 and N_2 atoms respectively. The set of coordinates and momenta of the first solid are denoted with z and those of the second solid with z'. The atoms interact with a Hamiltonian of the form

$$H^{\text{tot}}(z, z') = H^1(z) + H^2(z') + H^{\text{int}}(z, z')$$

where

$$H^1(z) = \sum_i^{N_1} \frac{\mathbf{p}_i^2}{2m} + \frac{1}{2} \sum_{ij}^{N_1} \phi_{ij}$$

$$H^2(z') = \sum_{i'}^{N_2} \frac{\mathbf{p}_{i'}^2}{2m} + \frac{1}{2} \sum_{i'j'}^{N_2} \phi_{i'j'}$$

$$H^{\text{int}}(z, z') = \sum_{ij'}^{N_1 N_2} \phi_{ij'}$$

Here ϕ_{ij} is the pair-wise potential of interaction between atoms i, j of system 1, $\phi_{i'j'}$ is the pair-wise potential of interaction between atoms i', j' of system 2, and $\phi_{ij'}$ is the pair-wise potential of interaction between atoms i of system 1 and j' of system 2.

We select as CG variables to describe the energy transport in the system the following

energy density fields

$$\hat{e}_\mathbf{r}^1(z, z') = \sum_i^{N_1} \left[\frac{\mathbf{p}_i^2}{2m} + \frac{1}{2} \sum_j^{N_1} \phi_{ij} + \frac{1}{2} \sum_{j'}^{N_2} \phi_{ij'} \right] \delta(\mathbf{r} - \mathbf{q}_i)$$

$$= \sum_i^{N_1} e_i \delta(\mathbf{r} - \mathbf{q}_i)$$

$$\hat{e}_\mathbf{r}^2(z, z') = \sum_{i'}^{N_2} \left[\frac{\mathbf{p}_{i'}^2}{2m} + \frac{1}{2} \sum_j^{N_1} \phi_{i'j} + \frac{1}{2} \sum_{j'}^{N_2} \phi_{i'j'} \right] \delta(\mathbf{r} - \mathbf{r}_{i'})$$

$$= \sum_{i'}^{N_2} e_{i'} \delta(\mathbf{r} - \mathbf{r}_{i'})$$

Note that the energy density fields of the solid 1 contains the potential of interaction with solid 2. The rationale for this particular definition of the CG variables is that we would like to obtain a set of dynamic equations that satisfy total energy conservation. Therefore, we need to be able to express the total energy (12.3) of the system in terms of the CG variables selected. In the case of the variables (12.3) the total energy can be obtained from

$$H^{\text{tot}}(z, z') = \int d\mathbf{r} \left[\hat{e}_\mathbf{r}(z, z') + \hat{e}_\mathbf{r}(z, z') \right]$$

In the definitions of the CG variables the point $\mathbf{r}$ is any point of the unbounded domain $\mathbb{R}^3$. Obviously, for the points where there is no solid atom the energy density fields vanish. The domain of the integrals $\int d\mathbf{r}$ is understood to be also $\mathbb{R}^3$.

A second selection of variables could be

$$\hat{e}_\mathbf{r}(z) = \sum_i^{N_1} \left[\frac{\mathbf{p}_i^2}{2m} + \frac{1}{2} \sum_j^{N_1} \phi_{ij} + \frac{1}{2} \sum_{j'}^{N_2} \phi_{ij'} \right] \delta(\mathbf{r} - \mathbf{q}_i)$$

$$\hat{E}'(z') = \sum_{i'}^{N_2} \left[\frac{\mathbf{p}_{i'}^2}{2m} + \frac{1}{2} \sum_j^{N_1} \phi_{i'j} + \frac{1}{2} \sum_{j'}^{N_2} \phi_{i'j'} \right]$$

where the total energy of the second system is used instead of its energy density field. We expect that this selection of variables will be appropriate when the dynamics of the energy in the solid 2 is much faster than that of the solid 1, in such a way that in the time scale in which the energy density of the solid 1 changes, the solid 2 is already fully equilibrated with a constant energy density field.

A third selection of variables uses e^1, e^2, e^0 where e^0 is the energy density of interaction **Marc, mira qué sale en estos dos últimos casos**.

12.4   The entropy functional

The averages of these phase functions with respect to the relevant distribution are denoted by

$$e^1(\mathbf{r}) = \text{Tr}[\overline{\rho}\hat{e}_{\mathbf{r}}^1]$$
$$e^2(\mathbf{r}) = \text{Tr}[\overline{\rho}\hat{e}_{\mathbf{r}}^2]$$

The relevant ensemble (12.2) has the form

$$\overline{\rho}(z, z') = \frac{1}{Z[\beta, \beta']} \exp\left\{ -\int d\mathbf{r} \left(\beta^1(\mathbf{r})\hat{e}_{\mathbf{r}}^1(z) + \beta^2(\mathbf{r})\hat{e}_{\mathbf{r}}^2(z) \right) \right\}$$

Here, $\beta^1(\mathbf{r})$ and $\beta^1(\mathbf{r})$ are the Lagrange multipliers associated to each constrain in (22.4). The normalization factor is the dimensionless partition function defined as

$$Z[\beta^1, \beta^2] = \int dz dz' \exp\left\{ -\sum_{i=1}^{N_1} \beta^1(\mathbf{q}_i)e_i + \sum_{i'}^{N_2} \beta^2(\mathbf{r}_{i'})e_{i'} \right\}$$

This partition function is a functional of both fields β^1, β^2 which are the conjugate fields of $e^1(\mathbf{r}), e^2(\mathbf{r})$, respectively. By inserting (12.4) into (22.4) we may find the connection between the Lagrange multipliers $\beta^1(\mathbf{r}), \beta^2(\mathbf{r})$ and the averages $e^1(\mathbf{r}), e^2(\mathbf{r})$. This connections can be expressed as

$$\frac{\delta\Omega[\beta^1, \beta^2]}{\delta\beta^1(\mathbf{r})} = e^1(\mathbf{r})$$
$$\frac{\delta\Omega[\beta^1, \beta^2]}{\delta\beta^2(\mathbf{r})} = e^2(\mathbf{r})$$

where the dimensionless potential is given by

$$\Omega[\beta^1, \beta^2] \equiv -\ln Z[\beta^1, \beta^2]$$

The entropy is defined as the result of evaluating the entropy functional (12.2) at the relevant ensemble (12.4). By inserting the relevant ensemble Eq. (12.4) in (12.2), we obtain the *entropy functional*

$$S[e^1, e^2] = -\Omega[\beta^1, \beta^2] + \int d\mathbf{r} \left[\beta^1(\mathbf{r})e^1(\mathbf{r}) + \beta^2(\mathbf{r})e^2(\mathbf{r}) \right]$$

The functional derivatives of the entropy functional satisfies the following relationships,

$$\frac{\delta S[e^1, e^2]}{\delta e^1(\mathbf{r})} = \beta^1(\mathbf{r})$$

$$\frac{\delta S[e^1, e^2]}{\delta e^2(\mathbf{r})} = \beta^2(\mathbf{r})$$

At this point, it proves convenient to perform the momenta integrals in the partition function (22.4), with the result

$$Z[\beta^1, \beta^2] = \frac{1}{N!N'!} \int \prod_i^{N_1} \frac{d\mathbf{q}_i}{\Lambda_1^3(\mathbf{q}_i)} \int \prod_{i'}^{N_2} \frac{d\mathbf{r}_{i'}}{\Lambda_2{}^3(\mathbf{r}_{i'})} \exp\left\{-\sum_j^N \beta^1(\mathbf{q}_j)\phi_j - \sum_{j'}^{N_2} \beta^2(\mathbf{r}_{j'})\phi_{j'}\right\}$$

where the *local thermal wavelengths* are defined as

$$\Lambda_1(\mathbf{r}) \equiv \left(\frac{h^2 \beta^1(\mathbf{r})}{2m\pi}\right)^{\frac{1}{2}}$$

$$\Lambda_2(\mathbf{r}) \equiv \left(\frac{h^2 \beta^2(\mathbf{r})}{2m\pi}\right)^{\frac{1}{2}}$$

The functional derivative in (22.4) becomes now

$$e^1(\mathbf{r}) = \frac{3n^1(\mathbf{r})}{2\beta^1(\mathbf{r})} + \phi^1(\mathbf{r})$$

where we have introduced the average density field and average potential energy field as

$$n^1(\mathbf{r}) = \text{Tr}\left[\bar{\rho} \sum_i^{N_1} \delta(\mathbf{r} - \mathbf{q}_i)\right]$$

$$\phi^1(\mathbf{r}) = \text{Tr}\left[\bar{\rho} \sum_{i=0}^{N_1} \phi_i \delta(\mathbf{r} - \mathbf{q}_i)\right]$$

It is natural to define the average kinetic energy field as $k^1(\mathbf{r}) = e^1(\mathbf{r}) - \phi^1(\mathbf{r})$, in such a way that the physical meaning of the Lagrange multiplier $\beta^1(\mathbf{r})$ becomes transparent as proportional to the inverse of the kinetic energy field. Note that we may introduce the microscopic kinetic density field as

$$\hat{k}_{\mathbf{r}}^1(z) = \sum_i^{N_1} \frac{\mathbf{p}_i^2}{2m_i} \delta(\mathbf{r} - \mathbf{q}_i)$$

and, therefore,

$$k^1(\mathbf{r}) = \langle \hat{k}_{\mathbf{r}}^1 \rangle^{\beta^1,\beta^2} = \frac{3n^1(\mathbf{r})}{2\beta^1(\mathbf{r})}$$

In order to obtain the explicit functional form of the entropy functional one would need to compute the partition function (22.4), invert the relations (22.4) in order to find β^1, β^2 as functionals of e^1, e^2 and finally compute the Legendre transform (22.4). This is very difficult in general and only for some simple ideal models (like the harmonic solid, for example) this can be fully achieved. **Marc: Calculas la entropía para un sólido armónico?** When the interaction energy between the two solids is negligible, it is possible to show that the entropy functional takes the form $S[e^1, e^2] = S^1[e^1] + S^2[e^2]$ where the entropy functionals of each solid need still to be computed explicitly. A simple model for these functionals is given by the *local approximation* given by

$$S^1[e^1] = \int d\mathbf{r}\, s^1(e^1(\mathbf{r}))$$

where $s^1(e^1) = \frac{1}{V^1} S^1(V^1 e^1)$ is the entropy density, given in terms of the macroscopic thermodynamic entropy $S^1(E)$ of the system. Here V^1 is the volume of solid 1.

12.5   The time derivatives

The time derivatives of the CG variables are a crucial object in the theory. They are obtained by applying the Liouville operator over the CG variables. This gives the result

$$i\mathcal{L}\hat{e}_{\mathbf{r}}^1(z) = -\sum_i^{N_1} \mathbf{v}_i e_i \nabla\delta(\mathbf{r}-\mathbf{q}_i) + \frac{1}{4}\sum_{ij}^{N_1 N_1} \mathbf{F}_{ij}(\mathbf{v}_i+\mathbf{v}_j)\left[\delta(\mathbf{r}-\mathbf{q}_i)-\delta(\mathbf{r}-\mathbf{q}_j)\right]$$

$$+ \frac{1}{2}\sum_i^{N_1} \delta(\mathbf{r}-\mathbf{q}_i)\sum_{j'}^{N_2} \mathbf{F}_{ij'}(\mathbf{v}_i+\mathbf{v}_{j'})$$

$$i\mathcal{L}\hat{e}_{\mathbf{r}}^2(z) = -\sum_{i'}^{N_2} \mathbf{v}_{i'} e_{i'} \nabla\delta(\mathbf{r}-\mathbf{r}_{i'}) + \frac{1}{4}\sum_{i'j'}^{N_2 N_2} \mathbf{F}_{i'j'}(\mathbf{v}_{i'}+\mathbf{v}_{j'})\left[\delta(\mathbf{r}-\mathbf{r}_{i'})-\delta(\mathbf{r}-\mathbf{r}_{j'})\right]$$

$$+ \frac{1}{2}\sum_{i'}^{N_2} \delta(\mathbf{r}-\mathbf{r}_{i'})\sum_j^{N_1} \mathbf{F}_{i'j}(\mathbf{v}_{i'}+\mathbf{v}_j)$$

We use now the well-known trick of Taylor expansion the delta function [?, ?, ?]

$$\delta(\mathbf{r} - \mathbf{q}_i) - \delta(\mathbf{r} - \mathbf{q}_j) = -\nabla \int_0^1 d\epsilon \mathbf{q}_{ij} \delta(\mathbf{r} - \mathbf{q}_j + \epsilon \mathbf{q}_{ij})$$

that allows to express some terms in (18.5) as full divergences

$$i\mathcal{L}\hat{e}_{\mathbf{r}}^1 = -\nabla \hat{\mathbf{Q}}_{\mathbf{r}}^1 + \hat{\sigma}_{\mathbf{r}}^1$$
$$i\mathcal{L}\hat{e}_{\mathbf{r}}^2 = -\nabla \hat{\mathbf{Q}}_{\mathbf{r}}^2 + \hat{\sigma}_{\mathbf{r}}^2$$

where the heat fluxes are defined as

$$\hat{\mathbf{Q}}_{\mathbf{r}}^1 = \sum_i^{N_1} \mathbf{v}_i e_i \delta(\mathbf{r} - \mathbf{q}_i)$$

$$+ \frac{1}{4} \sum_{ij}^{N_1 N_1} (\mathbf{v}_i + \mathbf{v}_j) \cdot \mathbf{F}_{ij} \mathbf{q}_{ij} \int_0^1 d\epsilon \delta(\mathbf{r} - \mathbf{q}_j + \epsilon \mathbf{q}_{ij})$$

$$\hat{\mathbf{Q}}_{\mathbf{r}}^2 = \sum_{i'}^{N_2} \mathbf{v}_{i'} e_{i'} \delta(\mathbf{r} - \mathbf{r}_{i'})$$

$$+ \frac{1}{4} \sum_{i'j'}^{N_2 N_2} (\mathbf{v}_{i'} + \mathbf{v}_{j'}) \cdot \mathbf{F}_{i'j'} \mathbf{r}_{i'j'} \int_0^1 d\epsilon \delta(\mathbf{r} - \mathbf{r}_{j'} + \epsilon \mathbf{r}_{i'j'})$$

and the source terms are

$$\hat{\sigma}_{\mathbf{r}}^1 = \frac{1}{2} \sum_{ij'}^{N_1 N_2} \mathbf{F}_{ij'} \cdot (\mathbf{v}_i + \mathbf{v}_{j'}) \delta(\mathbf{r} - \mathbf{q}_i)$$

$$\hat{\sigma}_{\mathbf{r}}^2 = -\frac{1}{2} \sum_{ij'}^{N_1 N_2} \mathbf{F}_{ij'} \cdot (\mathbf{v}_i + \mathbf{v}_{j'}) \delta(\mathbf{r} - \mathbf{r}_{j'})$$

12.6   The dynamic equations

We first note that the reversible part $v_i(t)$ in Eq. (12.2) vanishes for the case of the relevant functions (12.3) because these terms include a Gaussian momentum integral of a velocity. In the irreversible part, for the same reason, the projected currents are simply $\mathcal{Q}_t i\mathcal{L}A_i = i\mathcal{L}A_i$. The dynamic equations are

$$\partial_t e^a(\mathbf{r}, t) = \int d\mathbf{r}' D_{\mathbf{r}\mathbf{r}'}^{ab} \beta^b(\mathbf{r}', t)$$

where the different elements of the dissipative matrix are defined as (a, b may take the values $1, 2$)

$$D_{\mathbf{rr}'}^{ab} = \int_0^\infty dt' \mathrm{Tr} \left[\overline{\rho}_t \left(\nabla_{\mathbf{r}'} \hat{\mathbf{Q}}_{\mathbf{r}'}^b + \sigma_{\mathbf{r}'}^b \right) \left(\nabla_{\mathbf{r}} \hat{\mathbf{Q}}_{\mathbf{r}}^a + \sigma_{\mathbf{r}}^a \right)(t) \right]$$
$$= \nabla_{\mathbf{r}'} \nabla_{\mathbf{r}} \mathbf{K}_{\mathbf{rr}'}^{ab} + \nabla_{\mathbf{r}'} \mathbf{L}_{\mathbf{rr}'}^{ab} + \nabla_{\mathbf{r}} \mathbf{M}_{\mathbf{rr}'}^{ab} + S_{\mathbf{rr}'}^{ab}$$

where we have introduced the following Green-Kubo non-local transport coefficients

$$\mathbf{K}_{\mathbf{rr}'}^{ab} = \int_0^\infty dt' \mathrm{Tr} \left[\overline{\rho}_t \hat{\mathbf{Q}}_{\mathbf{r}'}^b \hat{\mathbf{Q}}_{\mathbf{r}}^a(t) \right]$$

$$\mathbf{L}_{\mathbf{rr}'}^{ab} = \int_0^\infty dt' \mathrm{Tr} \left[\overline{\rho}_t \hat{\mathbf{Q}}_{\mathbf{r}'}^b \sigma_{\mathbf{r}}^a(t) \right]$$

$$\mathbf{M}_{\mathbf{rr}'}^{ab} = \int_0^\infty dt' \mathrm{Tr} \left[\overline{\rho}_t \sigma_{\mathbf{r}'}^b \hat{\mathbf{Q}}_{\mathbf{r}}^a(t) \right]$$

$$S_{\mathbf{rr}'}^{ab} = \int_0^\infty dt' \mathrm{Tr} \left[\overline{\rho}_t \sigma_{\mathbf{r}'}^b \sigma_{\mathbf{r}}^a(t) \right]$$

With these definitions, the dynamics equations (12.6) become

$$\partial_t e^a(\mathbf{r}, t) = \int d\mathbf{r}' \left[\nabla_{\mathbf{r}'} \nabla_{\mathbf{r}} \mathbf{K}_{\mathbf{rr}'}^{ab} + \nabla_{\mathbf{r}'} \mathbf{L}_{\mathbf{rr}'}^{ab} \right.$$
$$\left. + \nabla_{\mathbf{r}} \mathbf{M}_{\mathbf{rr}'}^{ab} + S_{\mathbf{rr}'}^{ab} \right] \beta^b(\mathbf{r}', t)$$

We may integrate by parts (12.6) to obtain

$$\partial_t e^a(\mathbf{r}, t) = - \nabla_{\mathbf{r}} \int d\mathbf{r}' \mathbf{K}_{\mathbf{rr}'}^{ab} \nabla_{\mathbf{r}'} \beta^b(\mathbf{r}', t)$$
$$+ \nabla_{\mathbf{r}} \int d\mathbf{r}' \mathbf{M}_{\mathbf{rr}'}^{ab} \beta^b(\mathbf{r}', t)$$
$$+ \int d\mathbf{r}' \mathbf{L}_{\mathbf{rr}'}^{ab} \nabla_{\mathbf{r}'} \beta^b(\mathbf{r}', t)$$
$$+ \int d\mathbf{r}' S_{\mathbf{rr}'}^{ab} \beta^b(\mathbf{r}', t)$$

We have neglected the boundary terms emerging from the integration by parts, because those occur at the infinite, where there is no solid.

The symmetry $D_{ij} = D_{ji}$ of the dissipative matrix translates into

$$D_{\mathbf{rr}'}^{ab} = D_{\mathbf{r}'\mathbf{r}}^{ba}$$

This implies

$$
\begin{aligned}
0 &= D_{\mathbf{rr}'}^{ab} - D_{\mathbf{rr}'}^{ab} \\
&= \nabla_{\mathbf{r}'} \nabla_{\mathbf{r}} \mathbf{K}_{\mathbf{rr}'}^{ab} + \nabla_{\mathbf{r}'} \mathbf{L}_{\mathbf{rr}'}^{ab} + \nabla_{\mathbf{r}} \mathbf{M}_{\mathbf{rr}'}^{ab} + S_{\mathbf{rr}'}^{ab} \\
&\quad - \nabla_{\mathbf{r}} \nabla_{\mathbf{r}'} \mathbf{K}_{\mathbf{r}'\mathbf{r}}^{ba} - \nabla_{\mathbf{r}} \mathbf{L}_{\mathbf{r}'\mathbf{r}}^{ba} - \nabla_{\mathbf{r}'} \mathbf{M}_{\mathbf{r}'\mathbf{r}}^{ba} - S_{\mathbf{r}'\mathbf{r}}^{ba} \\
&= \nabla_{\mathbf{r}'} \nabla_{\mathbf{r}} (\mathbf{K}_{\mathbf{rr}'}^{ab} - \mathbf{K}_{\mathbf{r}'\mathbf{r}}^{ba}) \\
&\quad + \nabla_{\mathbf{r}'} (\mathbf{L}_{\mathbf{rr}'}^{ab} - \mathbf{M}_{\mathbf{r}'\mathbf{r}}^{ba}) + \nabla_{\mathbf{r}} (\mathbf{M}_{\mathbf{rr}'}^{ab} - \mathbf{L}_{\mathbf{r}'\mathbf{r}}^{ba}) \\
&\quad + (S_{\mathbf{rr}'}^{ab} - S_{\mathbf{r}'\mathbf{r}}^{ba})
\end{aligned}
$$

suggesting that

$$
\begin{aligned}
\mathbf{K}_{\mathbf{rr}'}^{ab} &= \mathbf{K}_{\mathbf{r}'\mathbf{r}}^{ba} \\
\mathbf{M}_{\mathbf{rr}'}^{ab} &= \mathbf{L}_{\mathbf{r}'\mathbf{r}}^{ba} \\
S_{\mathbf{rr}'}^{ab} &= S_{\mathbf{r}'\mathbf{r}}^{ba}
\end{aligned}
$$

The dynamic equations (**??**) have two distinguishing features. First, the total energy

$$
E = \int d\mathbf{r} (e^1(\mathbf{r}, t) + e^2(\mathbf{r}, t))
$$

is exactly conserved. The first two terms are a full divergence term whereas the last two terms are equal and opposite in both equations **check**.

The second important features is that the entropy functional is striclty increasing in the dynamics. **write down.**

12.7   Singular local model

The two solids are interacting with each other through an "interface". It is obvious that "interface" is not a well defined concept at an atomic level, because the only thing that exist is a collection of point particles that are at certain distances of each other, moving around from its mechanical equilibrium position due to the thermal agitation. We take in this section a "macroscopic" point of view in which we may distinguish three regions (see Fig. 12.1: bulk of solid 1 (which is the region of space occupied by the atoms of solid 1 that interact with atoms of solid 1 only), bulk of solid 2 and interface region (which is the region occupied by those atoms of solid 1 and 2 are interacting with each other). The microscopic heat fluxes (12.5) and source terms (12.5) are defined only where there are particles. In fact, they are "spiky fields" due to the Dirac delta functions. Once averaged with the solution of the Liouville equation, they become smooth functions of space. Its worth noting that the average field $\mathbf{Q}^a(\mathbf{r}, t)$ will only be different from zero only in the region "where the solid a is located" or "within the domain where there is solid a". This, in fact, may be the criteria for defining the domain Ω_1. On the other hand, the average of the source terms $\sigma^1(\mathbf{r}, t), \sigma^2(\mathbf{r}, t)$ will be different from zero only around the region where the solid 1 is interacting with the solid 2 because, otherwise, the force $\mathbf{F}_{ij'}$ vanishes. We also expect that the correlations of these quantities, that appear in the definition of the Green-Kubo transport coefficients (12.6), reflect the fact that the microscopic heat fluxes are only non-zero in the bulk of the solid while the source terms are non-zero at the boundary of interaction. To be more precise, we expect that the heat flux equilibrium correlations $\langle \hat{\mathbf{Q}}_{\mathbf{r}}^a \hat{\mathbf{Q}}_{\mathbf{r}'}^b(t) \rangle$ are non-zero only for distances $|\mathbf{r} - \mathbf{r}'|$ of molecular scale. In addition, the correlation of the heat fluxes of different solids $a \neq b$ is expected to vanish except possibly in a region of $\mathbf{r}, \mathbf{r}'$ at the boundary of interaction. On the other hand, the correlation of a source term with the heat flux or source term as, for example, $\langle \hat{\mathbf{Q}}_{\mathbf{r}}^a \hat{\sigma}_{\mathbf{r}'}^b(t) \rangle$ and $\langle \hat{\sigma}_{\mathbf{r}}^a \hat{\sigma}_{\mathbf{r}'}^b(t) \rangle$ will be expected to be non-zero only in the interfacial region Σ. Because the Green-Kubo kernels are expected to be correlated only on small molecular length scales, if the spatial scale of variation of the fields $\beta(\mathbf{r}, t), \nabla\beta(\mathbf{r}, t)$ is much larger than the molecular length scale, we may approximate the different terms in Eq. (12.9) as follows. For example

$$\int d\mathbf{r}' \ \mathbf{K}_{\mathbf{rr}'}^{ab} \nabla_{\mathbf{r}'} \beta^b(\mathbf{r}', t) \approx \left(\int d\mathbf{r}' \ \mathbf{K}_{\mathbf{rr}'}^{ab} \right) \nabla_{\mathbf{r}} \beta^b(\mathbf{r}, t)$$
$$\equiv \mathbf{K}_{\mathbf{r}}^{ab} \nabla_{\mathbf{r}} \beta^b(\mathbf{r}, t)$$

where the last equality defines the transport coefficient $\mathbf{K}_{\mathbf{r}}^{ab}$. In fact, this approximation is equivalent to approximate the non-local kernel with a Dirac delta function, this is

$$\mathbf{K}_{\mathbf{rr}'}^{ab} \approx \mathbf{K}_{\mathbf{r}}^{ab} \delta(\mathbf{r} - \mathbf{r}')$$
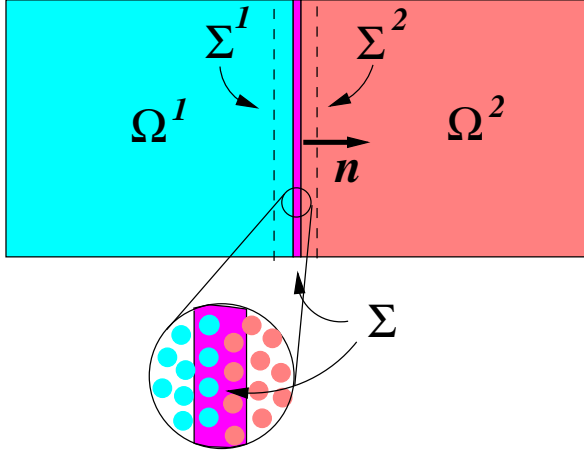
Figure 12.1: In this schematic picture, solid 1 and solid 2 are interacting through a planar interface. The domain ocupied with atoms of solid 1 that only interact with atoms of solid 1 is Ω_1 and similarly for solid 2. The molecularly thin domain Σ (magenta) contains those atoms of solid 1 and 2 that interact with some atom of the other solid. The zoom shows the atoms of solid 1 and 2. The surfaces Σ^1, Σ^2 are slightly outside the boundary region Σ.

In a similar way, the rest of the kernels in Eq. (12.9) may be approximated by

$$\mathbf{M}^{ab}_{\mathbf{rr}'} \approx \mathbf{M}^{ab}_{\mathbf{r}}\delta(\mathbf{r}-\mathbf{r}')$$
$$\mathbf{L}^{ab}_{\mathbf{rr}'} \approx \mathbf{L}_{\mathbf{r}}\delta(\mathbf{r}-\mathbf{r}')$$
$$S^{ab}_{\mathbf{rr}'} \approx S^{ab}_{\mathbf{r}}\delta(\mathbf{r}-\mathbf{r}')$$

where we have introduced

$$\mathbf{K}^{ab}_{\mathbf{r}} \equiv \int d\mathbf{r}'\mathbf{K}^{ab}_{\mathbf{rr}'} = \int_0^\infty dt'\mathrm{Tr}\left[\overline{\rho}_t\hat{\mathbf{Q}}^b\hat{\mathbf{Q}}^a_{\mathbf{r}}(t)\right]$$

$$\mathbf{M}^{ab}_{\mathbf{r}} \equiv \int d\mathbf{r}'\mathbf{M}^{ab}_{\mathbf{rr}'} = \int_0^\infty dt'\mathrm{Tr}\left[\overline{\rho}_t\sigma^b\hat{\mathbf{Q}}^a_{\mathbf{r}}(t)\right]$$

$$\mathbf{L}^{ab}_{\mathbf{r}} \equiv \int d\mathbf{r}'\mathbf{L}_{\mathbf{rr}'} = \int_0^\infty dt'\mathrm{Tr}\left[\overline{\rho}_t\hat{\mathbf{Q}}^b\sigma^a_{\mathbf{r}}(t)\right]$$

$$S^{ab}_{\mathbf{r}} \equiv \int d\mathbf{r}'S_{\mathbf{rr}'} = \int_0^\infty dt'\mathrm{Tr}\left[\overline{\rho}_t\sigma^b\sigma^a_{\mathbf{r}}(t)\right]$$

Here we have introduced the total heat flux $\mathbf{Q}^a$ and total source σ^a

$$\mathbf{Q}^a \equiv \sum_i^{N_a} \mathbf{v}_i e_i + \frac{1}{4} \sum_{ij}^{N_a N_a} (\mathbf{v}_i + \mathbf{v}_j) \cdot \mathbf{F}_{ij} \mathbf{q}_{ij}$$

$$\hat{\sigma}^1 = -\hat{\sigma}^2 = \frac{1}{2} \sum_{ij',b\neq a}^{N_1 N_1} \mathbf{F}_{ij'} \cdot (\mathbf{v}_i + \mathbf{v}_{j'})$$

The transport coefficients (12.7) are given in terms of correlations of phase functions, where the temporal evolution is due to a projected dynamics and the ensemble average is done with the relevant ensemble. As such, they are very complex formal objects and some assumptions need to be taken in order to have tractable expressions for them that can be computed through numerical simulations. The first approximation consists on assuming that the projected dynamics can be substituted with the real Hamiltonian dynamics. The second assumption, discussed in the appendix, approximates the relevant ensemble, which depends on the energy density fields with the equilibrium ensemble of the system matched with the local value of the temperature. We consider these approximations now for the Green-Kubo transport coefficients.

We begin with the second order tensor $\mathbf{K}_{\mathbf{r}}^{ab}$ defined in (12.7)

$$\mathbf{K}_{\mathbf{r}}^{ab} = \int_0^\infty dt' \mathrm{Tr}\left[\rho_{(\mathbf{r},t)}^{\mathrm{eq}} \hat{\mathbf{Q}}^b \hat{\mathbf{Q}}_{\mathbf{r}}^a(t')\right]$$

here $\rho_{(\mathbf{r},t)}^{\mathrm{eq}}$ is an equilibrium ensemble with the intensive parameters matched to local values. Because the equilibrium ensemble is translationally invariant (obviate momentarily the fact that the global intensive parameters are matched with the local values), $\mathbf{K}_{\mathbf{r}}^{ab}$ can be expressed as

$$\mathbf{K}_{\mathbf{r}}^{ab} = \frac{1}{V_a} \int d\mathbf{r}' \int_0^\infty dt' \mathrm{Tr}\left[\rho_{(\mathbf{r},t)}^{\mathrm{eq}} \hat{\mathbf{Q}}^b \hat{\mathbf{Q}}_{\mathbf{r}'}^a(t')\right]$$

$$= \frac{1}{V_a} \int_0^\infty dt' \mathrm{Tr}\left[\rho_{(\mathbf{r},t)}^{\mathrm{eq}} \hat{\mathbf{Q}}^a \hat{\mathbf{Q}}^b(t')\right]$$

where V_a is the volume of the domain Ω_a. The heat flux $\hat{\mathbf{Q}}^a$ depends only on the coordinates of the solid a and, therefore, we expect that the correlation with $\hat{\mathbf{Q}}^b$ with $b \neq a$ will be proportional to the number of pairs of atoms with one atom of the pair of solid a and the other of solid b. This number is proportional to the surface S of contact between solids and, therefore, $\mathbf{K}_{\mathbf{r}}^{ab} \propto \frac{S}{V}, a \neq b$ and will be neglected. The equilibrium ensemble is isotropic and for this reason, the second order tensor should be also isotropic. In this way, we have

$$\mathbf{K}_{\mathbf{r}}^{ab} = \kappa_{\mathbf{r}}^a T^a(\mathbf{r})^2 \boldsymbol{\delta} \delta^{ab}$$

where $\boldsymbol{\delta}$ is the unit tensor and the thermal conductivity $\kappa_{\mathbf{r}}^a$ of solid a is defined by the

usual Green-Kubo expression [?]

$$\kappa^a = \frac{1}{V_a T_a^2} \int_0^\infty dt' \operatorname{Tr}\left[\rho^{\mathrm{eq}} \hat{\mathbf{Q}}^a \cdot \hat{\mathbf{Q}}^a(t')\right]$$

and the sole dependence on the position $\mathbf{r}$ cames from the local values of the intensive parameters in the equilibrium ensemble.

Now let us consider the vector transport coefficient $\mathbf{L}_{\mathbf{r}}^{ab}$. It involves the correlation of the source term $\sigma_{\mathbf{r}}^a$ with the total heat flux $\mathbf{Q}^b$.

$$\mathbf{L}_{\mathbf{r}}^{ab} \equiv \int d\mathbf{r}' \mathbf{L}_{\mathbf{r}\mathbf{r}'} = \int_0^\infty dt' \operatorname{Tr}\left[\rho_{(\mathbf{r},t)}^{\mathrm{eq}} \hat{\mathbf{Q}}^b \sigma_{\mathbf{r}}^a(t')\right]$$

$$S_{\mathbf{r}}^{ab} \equiv \int d\mathbf{r}' S_{\mathbf{r}\mathbf{r}'} = \int_0^\infty dt' \operatorname{Tr}\left[\rho_{(\mathbf{r},t)}^{\mathrm{eq}} \sigma^b \sigma_{\mathbf{r}}^a(t')\right]$$

We have seen in Eq. (12.7) that $\sigma^1 = -\sigma^2$ and this imposes certain symmetries for the matrices of transport coefficients. They become

$$\mathbf{K}_{\mathbf{r}}^{ab} = \begin{pmatrix} \mathbf{K}_{\mathbf{r}}^{11} & 0 \\ 0 & \mathbf{K}_{\mathbf{r}}^{22} \end{pmatrix}$$

$$\mathbf{L}_{\mathbf{r}}^{ab} = \begin{pmatrix} \mathbf{L}_{\mathbf{r}}^{11} & -\mathbf{L}_{\mathbf{r}}^{22} \\ -\mathbf{L}_{\mathbf{r}}^{11} & \mathbf{L}_{\mathbf{r}}^{22} \end{pmatrix}$$

$$\mathbf{M}_{\mathbf{r}}^{ab} = \begin{pmatrix} \mathbf{M}_{\mathbf{r}}^{11} & -\mathbf{M}_{\mathbf{r}}^{11} \\ -\mathbf{M}_{\mathbf{r}}^{22} & \mathbf{M}_{\mathbf{r}}^{22} \end{pmatrix}$$

$$S_{\mathbf{r}}^{ab} = \begin{pmatrix} S_{\mathbf{r}}^{11} & -S_{\mathbf{r}}^{11} \\ -S_{\mathbf{r}}^{11} & S_{\mathbf{r}}^{11} \end{pmatrix}$$

The additional symmetry $\mathbf{M}_{\mathbf{r}\mathbf{r}'}^{ab} = \mathbf{L}_{\mathbf{r}'\mathbf{r}}^{ba}$ in Eq. (12.6) implies that $\mathbf{M}_{\mathbf{r}}^{11} = \mathbf{L}_{\mathbf{r}}^{11}$ and $\mathbf{M}_{\mathbf{r}}^{22} = \mathbf{L}_{\mathbf{r}}^{22}$. By using the models (12.7) with the symmetries (12.7) into the dynamic equation (12.6)

$$\begin{aligned}
\partial_t e^1(\mathbf{r}, t) = &- \nabla_{\mathbf{r}}\left(\mathbf{K}_{\mathbf{r}}^{11} \nabla_{\mathbf{r}} \beta^1(\mathbf{r}, t) + \mathbf{L}_{\mathbf{r}}^{11}(\beta^1(\mathbf{r}, t) - \beta^2(\mathbf{r}, t))\right) \\
&+ \mathbf{L}_{\mathbf{r}}^{11} \nabla_{\mathbf{r}} \beta^1(\mathbf{r}', t) - \mathbf{L}_{\mathbf{r}}^{22} \nabla_{\mathbf{r}} \beta^2(\mathbf{r}', t) \\
&+ S_{\mathbf{r}}^{11}(\beta^1(\mathbf{r}', t) - \beta^2(\mathbf{r}', t))
\end{aligned}$$

and for the solid 2

$$\begin{aligned}
\partial_t e^2(\mathbf{r}, t) = &- \nabla_{\mathbf{r}}\left(\mathbf{K}_{\mathbf{r}}^{22} \nabla_{\mathbf{r}} \beta^2(\mathbf{r}, t) + \mathbf{L}_{\mathbf{r}}^{22}(\beta^2(\mathbf{r}, t) - \beta^1(\mathbf{r}, t))\right) \\
&- \mathbf{L}_{\mathbf{r}}^{11} \nabla_{\mathbf{r}} \beta^1(\mathbf{r}, t) + \mathbf{L}_{\mathbf{r}}^{22} \nabla_{\mathbf{r}} \beta^2(\mathbf{r}, t) \\
&- S_{\mathbf{r}}^{11}(\beta^1(\mathbf{r}, t) - \beta^2(\mathbf{r}, t))
\end{aligned}$$

We have, therefore, only five non-zero transport coefficients $\kappa_{\mathbf{r}}^1, \kappa_{\mathbf{r}}^2, \mathbf{L}_{\mathbf{r}}^{11}, \mathbf{L}_{\mathbf{r}}^{22}, S_{\mathbf{r}}^{11}$. Because $\sigma_{\mathbf{r}}^1$ vanishes outside the interface region Σ of molecular size around the inteface between the two solids. For this reason, we expect that the transport coefficient $\mathbf{L}_{\mathbf{r}}^{ab}$ will be non-zero only near the boundary of contact between the two solids. The same argument applies to the transport coefficients $\mathbf{M}_{\mathbf{r}}$ and $S_{\mathbf{r}}$. The fact that the boundary transport coefficients $\mathbf{L}_{\mathbf{r}}^{11}, \mathbf{L}_{\mathbf{r}}^{22}, S_{\mathbf{r}}^{11}$ are only non-zero at the boundary allows to model them through the use of a surface Dirac delta function $\delta^{\Sigma}(\mathbf{r})$ which is defined for closed surfaces Σ [?]. Among other properties, this surface delta function satisfies

$$\int d\mathbf{r}\delta^{\Sigma}(\mathbf{r})f(\mathbf{r}) = \int_{\Sigma} dS f(\mathbf{r})$$

$$\int_{\Omega} d\mathbf{r}\nabla f(\mathbf{r}) = \int_{\Omega} d\mathbf{r}\delta^{\Sigma}(\mathbf{r})\mathbf{n}f(\mathbf{r})$$

where the right hand side is the surface integral of the function $f(\mathbf{r})$. For symmetry reasons, we expect that the vector $\mathbf{L}_{\mathbf{r}}$ should be proportional to the normal vector $\mathbf{n}_{\mathbf{r}}$ to the surface. Here $\mathbf{n}$ is the normal to the surface Σ pointing towards the solid 1. In this way, we have the following local (and singular) model for the surface transport coefficients

$$\mathbf{L}_{\mathbf{r}}^{aa} = l_{\mathbf{r}}^{aa}\delta^{\Sigma}(\mathbf{r})\mathbf{n}_{\mathbf{r}}$$

$$S_{\mathbf{r}} = s_{\mathbf{r}}\delta^{\Sigma}(\mathbf{r})$$

where $l_{\mathbf{r}}^{aa}$ and $s_{\mathbf{r}}$ are scalar transport coefficients defined in terms of Green-Kubo formulae that can be obtained as follows. By using (12.7) for $\mathbf{L}_{\mathbf{r}}^{aa}$ in (12.7), taking the scalar product with $\mathbf{n}_{\mathbf{r}}$, and integrating over the whole space we obtain

$$l^{aa} = \frac{1}{S}\int_0^{\infty} dt\,\mathrm{Tr}\left[\rho^{\mathrm{eq}}\mathbf{n}\cdot\hat{\mathbf{Q}}^a\sigma^a(t)\right]$$

$$s = \frac{1}{S}\int_0^{\infty} dt\,\mathrm{Tr}\left[\rho^{\mathrm{eq}}\sigma^a\sigma^a(t)\right]$$

where S is the surface of interaction. We expect that the correlation of the surface source term σ^a with either σ^a or $\mathbf{Q}^a$ will scale as the number of pairs with one atom of solid 1 and the other of solid 2. This number should be proportional to the surface S and, therefore, the resulting transport coefficients $l_{\mathbf{r}}^{aa}, s_{\mathbf{r}}$ are finite and well-defined. The above transport coefficients acquire a dependence on $\mathbf{r}, t$ when we use for the equilibrium ensemble the equilibrium ensemble $\rho_{(\mathbf{r},t)}^{\mathrm{eq}}$ that has the intensive parameters matched with the local ones.

By using the model (12.7) and the surface singular model (12.7) in the dynamic

equations (12.7) we obtain

$$
\begin{aligned}
\partial_t e^1(\mathbf{r}, t) =& \nabla \left(\kappa^1_{\mathbf{r}} \nabla T^1(\mathbf{r}, t) \right) \\
& - \nabla \left(\mathbf{n}_{\mathbf{r}} l^{11}_{\mathbf{r}} \delta^\Sigma(\mathbf{r}) (\beta^1(\mathbf{r}, t) - \beta^2(\mathbf{r}, t)) \right) \\
& + l^{11}_{\mathbf{r}} \delta^\Sigma(\mathbf{r}) \mathbf{n}_{\mathbf{r}} \cdot \nabla \beta^1(\mathbf{r}, t) \\
& - l^{22}_{\mathbf{r}} \delta^\Sigma(\mathbf{r}) \mathbf{n}_{\mathbf{r}} \cdot \nabla \beta^2(\mathbf{r}, t) \\
& + s_{\mathbf{r}} \delta^\Sigma(\mathbf{r}) (\beta^1(\mathbf{r}, t) - \beta^2(\mathbf{r}, t))
\end{aligned}
$$

where we have introduced the temperature field $T^1(\mathbf{r}, t) = \frac{1}{\beta^1(\mathbf{r}, t)}$. The equation for the field $e^2(\mathbf{r}, t)$ is identical to (12.7) with the indices 1 and 2 permuted.

12.8 Boundary conditions

Away from the boundary between solids 1,2, the dynamics is given simply by

$$
\partial_t e^1(\mathbf{r}) = \nabla \left(\kappa^1_{\mathbf{r}} \nabla T^1(\mathbf{r}) \right)
$$

This is just Fick's law for heat conduction. Near the interface of the two solids, the terms containing the surface delta $\delta^\Sigma(\mathbf{r})$ become important. We show in this section that these terms give rise to the appropriate boundary condition.

Let us integrate Eq. (12.7) over the volume Ω^{12} that is enclosed by the surfaces Σ^1, Σ^2 and a tiny strip on the edges of these surfaces, see Fig. 12.1. This strip has negligible area and surface integrals over this strip will be neglected in what follows. The volume contains the interface Σ. We have

$$\underbrace{\partial_t \int_{\Omega^{12}} d\mathbf{r} e^1(\mathbf{r}, t)}_{1} = \int_{\Omega^{12}} d\mathbf{r} \nabla \left(\kappa_{\mathbf{r}}^1 \nabla T^1(\mathbf{r}, t) \right) - \int_{\Omega^{12}} d\mathbf{r} \nabla \left(\mathbf{n_r} l_{\mathbf{r}}^{11} \delta^\Sigma(\mathbf{r}) (\beta^1(\mathbf{r}, t) - \beta^2(\mathbf{r}, t)) \right)$$

$$+ \int_{\Omega^{12}} d\mathbf{r} \delta^\Sigma(\mathbf{r}) \left[l_{\mathbf{r}}^{11} \mathbf{n_r} \cdot \nabla \beta^1(\mathbf{r}, t) - l_{\mathbf{r}}^{22} \mathbf{n_r} \cdot \nabla \beta^2(\mathbf{r}, t) + s_{\mathbf{r}}(\beta^1(\mathbf{r}, t) - \beta^2(\mathbf{r}, t)) \right]$$

$$= - \int_{\Sigma^1} dS \mathbf{n} \left(\kappa_{\mathbf{r}}^1 \nabla T^1(\mathbf{r}, t) \right) + \underbrace{\int_{\Sigma^2} dS \mathbf{n} \left(\kappa_{\mathbf{r}}^1 \nabla T^1(\mathbf{r}, t) \right)}_{2}$$

$$+ \underbrace{\int_{\Sigma^1} dS \mathbf{n} \left(\mathbf{n_r} l_{\mathbf{r}}^{11} \delta^\Sigma(\mathbf{r}) (\beta^1(\mathbf{r}, t) - \beta^2(\mathbf{r}, t)) \right)}_{3}$$

$$+ \underbrace{\int_{\Sigma^2} dS \mathbf{n} \left(\mathbf{n_r} l_{\mathbf{r}}^{11} \delta^\Sigma(\mathbf{r}) (\beta^1(\mathbf{r}, t) - \beta^2(\mathbf{r}, t)) \right)}_{4}$$

$$+ \int_{\Sigma} dS \left[l_{\mathbf{r}}^{11} \mathbf{n_r} \cdot \nabla \beta^1(\mathbf{r}, t) - l_{\mathbf{r}}^{22} \mathbf{n_r} \cdot \nabla \beta^2(\mathbf{r}, t) + s_{\mathbf{r}}(\beta^1(\mathbf{r}, t) - \beta^2(\mathbf{r}, t)) \right]$$

The term 1 is vanishingly small, because it is the energy of the solid 1 that is "within" the interface is negligible when we let the volume Ω^{12} go to zero. In other words, we are assuming that we do not have a singular contribution to the energy density field at the interface. The term 2 is also zero because the temperature of solid 1 at the surface Σ^2 is zero. Note that at Σ^2 the energy density field $e^1(\mathbf{r}, t)$ vanishes and, consequently, also the temperature $T^1(\mathbf{r}, t)$. The terms 3,4 vanish because the surfaces Σ^1, Σ^2 are slightly "off" the surface Σ and the surface delta function $\delta^\Sigma(\mathbf{r})$ vanishes at both Σ^1, Σ^2. Note that we can argue in the terms above also for any "pillbox" volume Ω^{12} and, therefore, we conclude that

$$0 = -\kappa_{\mathbf{r}}^1 \mathbf{n_r} \cdot \nabla T^1(\mathbf{r}, t) + l_{\mathbf{r}}^{11} \mathbf{n_r} \cdot \nabla \beta^1(\mathbf{r}, t) - l_{\mathbf{r}}^{22} \mathbf{n_r} \cdot \nabla \beta^2(\mathbf{r}, t) + s_{\mathbf{r}}(\beta^1(\mathbf{r}, t) - \beta^2(\mathbf{r}, t))$$

Doing the same integration for the dynamic equation of the field $e^2(\mathbf{r}, t)$ we obtain

$$0 = \kappa_{\mathbf{r}}^2 \mathbf{n_r} \cdot \nabla T^2(\mathbf{r}, t) + l_{\mathbf{r}}^{22} \mathbf{n_r} \cdot \nabla \beta^2(\mathbf{r}, t) - l_{\mathbf{r}}^{11} \mathbf{n_r} \cdot \nabla \beta^1(\mathbf{r}, t) + s_{\mathbf{r}}(\beta^2(\mathbf{r}, t) - \beta^1(\mathbf{r}, t))$$

Adding these two equations gives

$$\kappa_{\mathbf{r}}^1 \mathbf{n_r} \cdot \nabla T^1(\mathbf{r}, t) = \kappa_{\mathbf{r}}^2 \mathbf{n_r} \cdot \nabla T^2(\mathbf{r}, t)$$

which simply express that the normal heat flux leaving solid 1 is the same as the normal

heat flux entering solid 2. We next use (12.8) in Eq. (12.8) and obtain

$$0 = -\kappa_{\mathbf{r}}^1 \mathbf{n_r} \cdot \nabla T^1(\mathbf{r}, t) - \frac{l_{\mathbf{r}}^{11}}{(T^1)^2} \mathbf{n_r} \cdot \nabla T^1(\mathbf{r}, t) + \frac{l_{\mathbf{r}}^{22}}{(T^2)^2} \mathbf{n_r} \cdot \nabla T^2(\mathbf{r}, t) + s_{\mathbf{r}}(\beta^1(\mathbf{r}, t) - \beta^2(\mathbf{r}, t))$$

$$= -\kappa_{\mathbf{r}}^1 \mathbf{n_r} \cdot \nabla T^1(\mathbf{r}, t) - \frac{l_{\mathbf{r}}^{11}}{(T^1)^2} \mathbf{n_r} \cdot \nabla T^1(\mathbf{r}, t) + \frac{l_{\mathbf{r}}^{22}}{(T^2)^2} \frac{\kappa_{\mathbf{r}}^1}{\kappa_{\mathbf{r}}^2} \mathbf{n_r} \cdot \nabla T^1(\mathbf{r}, t) + s_{\mathbf{r}}(\beta^1(\mathbf{r}, t) - \beta^2(\mathbf{r}, t))$$

$$= -\left[\kappa_{\mathbf{r}}^1 + \frac{l_{\mathbf{r}}^{11}}{(T^1)^2} - \frac{l_{\mathbf{r}}^{22}}{(T^2)^2} \frac{\kappa_{\mathbf{r}}^1}{\kappa_{\mathbf{r}}^2} \right] \mathbf{n_r} \cdot \nabla T^1(\mathbf{r}, t) + s_{\mathbf{r}}(\beta^1(\mathbf{r}, t) - \beta^2(\mathbf{r}, t))$$

Finally, we obtain for all the points $\mathbf{r} \in \Sigma$ on the interface the following condition

$$\mathbf{n_r} \cdot \nabla T^1(\mathbf{r}, t) = c_{\mathbf{r}}(\beta^1(\mathbf{r}, t) - \beta^2(\mathbf{r}, t))$$

with the coefficient

$$c_{\mathbf{r}} = \frac{s_{\mathbf{r}}}{\left[\kappa_{\mathbf{r}}^1 + \frac{l_{\mathbf{r}}^{11}}{(T^1)^2} - \frac{l_{\mathbf{r}}^{22}}{(T^2)^2} \frac{\kappa_{\mathbf{r}}^1}{\kappa_{\mathbf{r}}^2} \right]}$$

We have a paradox. What happens when solid 1 and 2 are identical? We still can divide the energy density in two fields e^1, e^2 albeit now the way to select the atoms of solid 1 or 2 is arbitrary. All the transport coefficients become identical for each solid.

This condition, valid for the points $\mathbf{r} \in \Sigma^+$ should be understood as a boundary condition to be satisfied by the heat conduction (12.8). The boundary condition (**??**) that has been obtained microscopically has the form of the Kaptiza resistance law in which the temperature jump $\beta^1(\mathbf{r}, t) - \beta^2(\mathbf{r}, t)$ occurring at the interface is proportional to the heat flux through the interface. However, there are some differences too.

In a similar way, we may integrate the equation for $e^2(\mathbf{r}, t)$ outside the region exterior to Σ^-

12.9   The solid 2 has a fast equilibration

In order to understand the role of the different terms in the dynamic equations it proves convenient to consider first the situation in which the system 2 relaxes so fast that $\beta^2(\mathbf{r}, t)$ is always a constant in space $\beta_2(t)$. This limit, I think, it coincides with the selection of

the CG variables as e^1, E^2 (**check**).

$$\partial_t e^1(\mathbf{r}, t) = - \nabla_{\mathbf{r}} \int d\mathbf{r}' \; \mathbf{K}_{\mathbf{rr}'}^{11} \nabla_{\mathbf{r}'} \beta^1(\mathbf{r}', t)$$

$$+ \nabla_{\mathbf{r}} \int d\mathbf{r}' \mathbf{M}_{\mathbf{rr}'}^{11} \beta^1(\mathbf{r}', t)$$

$$+ \int d\mathbf{r}' \mathbf{L}_{\mathbf{rr}'}^{11} \nabla_{\mathbf{r}'} \beta^1(\mathbf{r}', t)$$

$$+ \int d\mathbf{r}' S_{\mathbf{rr}'}^{11} \beta^1(\mathbf{r}', t)$$

$$+ \left[\int d\mathbf{r}' \nabla_{\mathbf{r}} \mathbf{M}_{\mathbf{rr}'}^{12} + \int d\mathbf{r}' S_{\mathbf{rr}'}^{12} \right] \beta_2$$

Note that $\hat{\sigma}_{\mathbf{r}}^1, \hat{\sigma}_{\mathbf{r}}^2$ defined in (12.5) satisfy

$$\int d\mathbf{r} \hat{\sigma}_{\mathbf{r}}^1 = - \int d\mathbf{r} \hat{\sigma}_{\mathbf{r}}^2$$

This property, that reflects the fact that the total energy lost by system 1 goes into system 2, implies the following properties on the transport coefficients

$$\int d\mathbf{r} M_{\mathbf{rr}'}^{12} = - \int d\mathbf{r} M_{\mathbf{rr}'}^{11}$$

$$\int d\mathbf{r} S_{\mathbf{rr}'}^{12} = - \int d\mathbf{r} S_{\mathbf{rr}'}^{11}$$

Therefore, the dynamic equation becomes

$$\partial_t e(\mathbf{r}, t) = - \nabla_{\mathbf{r}} \int d\mathbf{r}' \; \mathbf{K}_{\mathbf{rr}'} \nabla_{\mathbf{r}'} \beta(\mathbf{r}', t)$$

$$+ \nabla_{\mathbf{r}} \int d\mathbf{r}' \mathbf{M}_{\mathbf{rr}'} (\beta(\mathbf{r}', t) - \beta_2)$$

$$+ \int d\mathbf{r}' \mathbf{L}_{\mathbf{rr}'} \nabla_{\mathbf{r}'} \beta(\mathbf{r}', t)$$

$$+ \int d\mathbf{r}' S_{\mathbf{rr}'} (\beta(\mathbf{r}', t) - \beta_2)$$

where we have dropped the superscript 1 referring to solid 1 in order to alleviate the notation. I like this equation because it has the same structure as the one encountered in the hydrodynamic in the presence of a solid sphere case, albeit with reduced tensorial character.

12.10   Appendix: Approximating averages with the relevant ensemble

Consider the relevant ensemble (12.4) that we write compactly as

$$\overline{\rho}_t(z) = \frac{1}{Z[\{\beta^i\}]} \exp\left\{-\int d\mathbf{r}' \sum_i^2 \beta^i(\mathbf{r}',t)\hat{e}_{\mathbf{r}'}^i(z)\right\}$$

with a sum over the repeated index i. The partition function is

$$Z[\{\beta^i\}] = \int dz \exp\left\{-\int d\mathbf{r}' \sum_i^2 \beta^i(\mathbf{r}',t)\hat{e}_{\mathbf{r}'}^i(z)\right\}$$

We may add and substract a term in order to get

$$\overline{\rho}_t(z) = \frac{1}{Z[\{\beta^i\}]} \exp\left\{-\int d\mathbf{r}' \sum_i^2 (\beta^i(\mathbf{r}',t) - \beta^i(\mathbf{r},t))\hat{e}_{\mathbf{r}'}^i(z)\right\} \exp\left\{-\sum_i^2 \beta^i(\mathbf{r},t)\int d\mathbf{r}'\hat{e}_{\mathbf{r}'}^i(z)\right\}$$

and similarly for the partition function

$$Z[\{\beta^i\}] = \int dz \exp\left\{-\int d\mathbf{r}' \sum_i^2 (\beta^i(\mathbf{r}',t) - \beta^i(\mathbf{r},t))\hat{e}_{\mathbf{r}'}^i(z)\right\} \exp\left\{-\sum_i^2 \beta^i(\mathbf{r},t)\int d\mathbf{r}'\hat{e}_{\mathbf{r}'}^i(z)\right\}$$

Note that the term

$$\exp\left\{-\beta^i(\mathbf{r},t)\int d\mathbf{r}'\hat{e}_{\mathbf{r}'}^i(z)\right\} = \exp\left\{-\beta^1(\mathbf{r},t)H^1(z) + \beta^2(\mathbf{r},t)H^2(z) + \frac{1}{2}(\beta^1(\mathbf{r},t) + \beta^2(\mathbf{r},t))H^{\text{int}}(z)\right\}$$

If $\beta^1(\mathbf{r},t) = \beta^2(\mathbf{r},t)$, this term would be precisely proportional to the equilibrium ensemble at a temperature matched with the local temperature $\beta^i(\mathbf{r},t)$. For this reason we introduce the pseudo equilibrium ensemble

$$\rho_{\mathbf{r},t}^{\text{eq}}(z) \equiv \frac{1}{Z_{\mathbf{r},t}} \exp\left\{-\beta^1(\mathbf{r},t)H^1(z) + \beta^2(\mathbf{r},t)H^2(z) + \frac{1}{2}(\beta^1(\mathbf{r},t) + \beta^2(\mathbf{r},t))H^{\text{int}}(z)\right\}$$

where $Z_{\mathbf{r},t}$ is the normalization.

We may formally expand Eq. (12.10) now in terms of $(\beta^i(\mathbf{r}',t) - \beta^i(\mathbf{r},t))$ both the numerator and denominator and obtain

$$\overline{\rho}_t(z) = \rho_{\mathbf{r},t}^{\text{eq}}(z)\left[1 - \sum_i^2 \int d\mathbf{r}' \left(\beta^i(\mathbf{r}',t) - \beta^i(\mathbf{r},t)\right)\left(\hat{e}_{\mathbf{r}'}^i(z) - \langle\hat{e}_{\mathbf{r}'}^i\rangle_{\mathbf{r},t}^{\text{eq}}\right) + \cdots\right]$$

where the local equilibrium average is defined as

$$\langle \hat{e}^i_{\mathbf{r}'} \rangle^{\text{eq}}_{\mathbf{r},t} = \int dz \rho^{\text{eq}}_{\mathbf{r},t}(z) \hat{e}^i_{\mathbf{r}'}(z)$$

Consider now the average with this relevant ensemble of a local function of the form $\hat{a}_{\mathbf{r}} = \sum_i a_i \delta(\mathbf{r} - \mathbf{q}_i)$. By using the expansion (12.10) we obtain

$$\langle \hat{a}_{\mathbf{r}} \rangle^{[\beta^i]} = \int dz \overline{\rho}_t(z) a_{\mathbf{r}}$$

$$= \langle \hat{a}_{\mathbf{r}} \rangle^{\text{eq}}_{\mathbf{r},t} - \sum_i^2 \int d\mathbf{r}' \left(\beta^i(\mathbf{r}',t) - \beta^i(\mathbf{r},t) \right) \left\langle \left[\hat{e}^i_{\mathbf{r}'}(z) - \langle \hat{e}^i_{\mathbf{r}'} \rangle^{\text{eq}}_{\mathbf{r},t} \right] \hat{a}_{\mathbf{r}} \right\rangle^{\text{eq}}_{\mathbf{r},t} + \cdots$$

We expect that the correlation $\left\langle \left[\hat{e}^i_{\mathbf{r}'}(z) - \langle \hat{e}^i_{\mathbf{r}'} \rangle^{\text{eq}}_{\mathbf{r},t} \right] a_{\mathbf{r}} \right\rangle^{\text{eq}}_{\mathbf{r},t}$ will be non-zero only if the distance $|\mathbf{r}' - \mathbf{r}|$ is of molecular size. If the temperature field does not change in these molecular scales, we may neglect in the expansion all the terms except the first one. In this case, the average with the relevant ensemble may be well approximated with the average with the pseudo local equilibrium, this is

$$\text{Tr}[\overline{\rho}_t \hat{a}_{\mathbf{r}}] \approx \text{Tr}[\rho^{\text{eq}}_{\mathbf{r},t} \hat{a}_{\mathbf{r}}]$$

13

Chemical reactions in diffusing systems $\rho_{\mathbf{r}}^1, \rho_{\mathbf{r}}^2$

[Zubarev book deals with chemical reactions, in a Quantum Mechanical Setting]

We show that the theory of Non-Equilibrium Statistical Mechanics accomodates chemical reactions between different species. By defining molecular species through a molecular template, we show that the dynamics of the concentration of different species obeys reaction-diffusion equations. The method gives in a natural way Green-Kubo expressions for the rate of reactions. Therefore, by running simple molecular dynamics simulations it is possible to obtain explicit expressions for the reaction rates.

13.1   Introduction

Individual atoms have the tendency to bind together forming molecules of different substances. A chemical reaction is a process by which atoms change their particular combinations, thus changing the number of molecules of different species in the recombination process. We aim in this paper to present a general theory for chemical kinetics based on the modern formulation of the theory of non-equilibrium statistical mechanics. The attempt to obtain the chemical kinetics from the underlying microscopic dynamics of the atoms is not new. Yamamoto was the first to obtain an expression of the reaction rate in terms of a Green-Kubo formula [?]. However, his theory was based on Kubo's linear theory and therefore, as explicitly mentioned in [?], not of sufficient generality to deal with arbitrarily far from equilibrium situations. Kapral presented a derivation of reaction rates in terms of Green-Kubo expressions [?] by using the techinque of projector operators. However he made use of Mori projector [?] instead of the more general Kawasaki-Gunton projector [?] gives rise to equations that are linear in the concentrations instead of the chemical potentials. This may limit again the framework to near equilibrium situations, i.e. valid for the late states of reactions only. A more recent approach that uses modern concepts of projection operators has been given by Dahler and Qin [?]. However, their use of a Mori like operator gives rise to a rate which is

independent on the affinities and is, therefore, valid for the latest states of the reaction, very close to equilibrium [**?**]. Chandler [**?**] made the connection of the microscopically informed linear theory with the venerable Transtition State Theory [**?**][**?**].

A usual approach in the description of chemical reactions is through the use of master equations. In this approach the population of different species evolves as a consequence of jumps due to "events" that cause a recombination. The recombination is understood as a birth dead process in which molecules dissapear or are created in each event. This approach is phenomenological and the transition rates need to be modelled according to judiciously chosen hypothesis. However, the direct connection with the microscopic dynamics is not apparent in this approach.

Kinetic theory of reacting mixtures is also a different route to study chemical reactions but it is, of course, an approach limited to low density gases [**?**].

13.2 The chemical reaction $A + A \rightleftharpoons A_2$

Before considering the general case we explore in this section a simple chemical reaction, the reversible formation and dissociation of a dimer $A + A \rightleftharpoons A_2$. We have just one kind of atoms and the molecules are defined by a criterium of proximity. In a subsequent section we will consider the general case of a chemical reaction bewteen different molecular species. The system consists on N_A identical atoms of element A that interact with a potential such that it may lead to a bonding of two atoms forming a molecule. For example, Stillinger and Weber use a three body potential for fluorine. The Hamiltonian is denoted as

$$\hat{H}(z) = \sum_i^{N_A} \frac{\mathbf{p}_i^2}{2m} + \phi(q)$$

13.2.1 The CG variables

We want to describe how the concentrations of atoms and molecules evolve in time. While we know how to describe the number density of point particles, through the number density defined as

$$\hat{n}_{\mathbf{r}}^A(z_N) = \sum_i^{N_A} \delta(\mathbf{q}_i - \mathbf{r})$$

this variable does not distinguishes whether in the point of space $\mathbf{r}$ we have a "single atom" or a "an atom forming part of a molecule". To distinguish between the two cases, we introduce the concentration field $[\hat{A}_2]_{\mathbf{r}}$ of A_2 molecules as the following phase function

$$[\hat{A}_2]_{\mathbf{r}} \equiv \frac{1}{2} \sum_{ij}^{N_A} \theta(r_{ij}) \delta\left(\frac{\mathbf{q}_i + \mathbf{q}_j}{2} - \mathbf{r}\right)$$

Here $\theta(r)$ is a *molecular template function*. **[Expand]**

Therefore, (13.2.1) counts the number of molecules at the space point **r**. The specific shape of the function $\theta(r)$ depends on what we believe that a molecule is. Of course, the quality of the predictions do depend on the right guess for the molecular template function. It may be necessary to consider more complicated functions θ that better *recognize* that we have a molecule at **r**. It may be helpful for the sake of intuition and visualization purposes to think of space divided into tiny cells of finite volume and the Dirac delta function as the limit of the characteristic function of that cell divided by its volume. In this way, we may have both, dissociated atoms and molecules, within the little cell (assumed to be large enough to contain many molecules and atoms).

Having defined the concentration of molecules, now we have to define the concentration of dissociated atoms. Dissociated atoms is what is left in the system when we remove the molecules. This suggests to define the concentration $[A]_{\mathbf{r}}$ of dissociated atoms as

$$[\hat{A}]_{\mathbf{r}} = \hat{n}_{\mathbf{r}}^A - 2[\hat{A}_2]_{\mathbf{r}}$$

where the number density $\hat{n}_{\mathbf{r}}^A$ is given by (13.2.1). The factor 2 comes about because if we have a molecule at **r** (i.e. within the little cell volume around **r**), there are, in fact, two atoms of A that we need to substract in order to find out the dissociated atoms in that cell. These definitions of atomic and molecular concentrations ensure, automatically a conservation law for the mass at the microscopic level

$$\int d\mathbf{r} \left([\hat{A}]_{\mathbf{r}} + 2[\hat{A}_2]_{\mathbf{r}}\right) = N_A$$

The CG variables that we will consider in the dynamic description of the system are the two concentration fields $[\hat{A}]_{\mathbf{r}}, [\hat{A}_2]_{\mathbf{r}}$.

13.2.2   The relevant ensemble and the entropy

With the above selection of relevant variables $\hat{\mathscr{H}}(z), [\hat{A}]_{\mathbf{r}}(z), [\hat{A}_2]_{\mathbf{r}}(z)$, the relevant ensemble (12.2) becomes

$$\overline{\rho}(z) = \frac{\rho^0}{Z[\beta, \lambda]} \exp\left\{-\beta\hat{H}(z) - \int d\mathbf{r}' \left[\lambda^A(\mathbf{r}')[\hat{A}]_{\mathbf{r}'}(z) + \lambda^{A_2}(\mathbf{r}')[\hat{A}_2]_{\mathbf{r}'}(z)\right]\right\}$$

with the normalizing dimensionless partition function given by

$$Z[\beta, \lambda] = \text{Tr}\left[\exp\left\{-\beta\hat{H}(z) - \int d\mathbf{r}' \left[\lambda^A(\mathbf{r}')[\hat{A}]_{\mathbf{r}'}(z) + \lambda^{A_2}(\mathbf{r}')[\hat{A}_2]_{\mathbf{r}'}(z)\right]\right\}\right]$$

The conjugate variables $\beta, \lambda^A(\mathbf{r}), \lambda^{A_2}(\mathbf{r})$ have the physical meaning of the inverse temperature and the chemical potentials of the different species. They are adjusted in a way to produce the correct averages $E, [A](\mathbf{r}), [A_2](\mathbf{r})$ for the CG variables, this is

$$\langle \hat{H} \rangle_t = E$$
$$\langle [\hat{A}]_{\mathbf{r}} \rangle_t = [A](\mathbf{r}, t)$$
$$\langle [\hat{A}_2]_{\mathbf{r}} \rangle_t = [A_2](\mathbf{r}, t)$$

The conjugate variables and the average of the CG variables are related by (12.2) that in the present case becomes

$$\frac{\partial \Phi}{\partial \beta}[\beta, \lambda] = E$$

$$\frac{\delta \Phi}{\delta \lambda^{\mathrm{A}}(\mathbf{r})}[\beta, \lambda^{\mathrm{A}}, \lambda^{\mathrm{A}_2}] = [\mathrm{A}](\mathbf{r})$$

$$\frac{\delta \Phi}{\delta \lambda^{\mathrm{A}_2}(\mathbf{r})}[\beta, \lambda^{\mathrm{A}}, \lambda^{\mathrm{A}_2}] = [\mathrm{A}_2](\mathbf{r})$$

The entropy (**??**) for this level of description is given by

$$S[\overline{E}, [\mathrm{A}], [\mathrm{A}_2]] = -\Phi[\beta, \lambda^A, \lambda^{A_2}] + \int d\mathbf{r} \left[\lambda^{\mathrm{A}}(\mathbf{r})[\mathrm{A}](\mathbf{r}) + \lambda^{\mathrm{A}_2}(\mathbf{r})[\mathrm{A}_2](\mathbf{r}) \right]$$

In this expression, $\beta, \lambda^{\mathrm{A}}(\mathbf{r}), \lambda^{\mathrm{A}_2}(\mathbf{r})$ are understood as functions of the averages $E, [\mathrm{A}](\mathbf{r}), [\mathrm{A}_2](\mathbf{r})$. The conjugate variables are given in terms of the derivatives of the entropy functional

$$\frac{\partial S}{\partial E} = \beta$$

$$\frac{\delta S}{\delta [\mathrm{A}](\mathbf{r})}[E, [\mathrm{A}], [\mathrm{A}_2]] = \lambda^{\mathrm{A}}(\mathbf{r})$$

$$\frac{\delta S}{\delta [\mathrm{A}_2](\mathbf{r})}[E, [\mathrm{A}], [\mathrm{A}_2]] = \lambda^{\mathrm{A}_2}(\mathbf{r})$$

13.2.3   The reversible drift

The time derivative of the CG variables is given by

$$i\mathcal{L}[\mathrm{A}_2]_{\mathbf{r}} = P_{\mathbf{r}} - \nabla \mathbf{J}_{\mathbf{r}}^{\mathrm{A}_2}$$

$$i\mathcal{L}[\mathrm{A}]_{\mathbf{r}} = -2P_{\mathbf{r}} - \nabla \mathbf{J}_{\mathbf{r}}^{\mathrm{A}}$$

where we have defined the production term $P_{\mathbf{r}}$ and the two currents as

$$P_{\mathbf{r}} = \frac{1}{2} \sum_{ij}^{N_A} \theta'(r_{ij}) \mathbf{e}_{ij} \cdot \mathbf{v}_{ij} \delta \left(\frac{\mathbf{q}_i + \mathbf{q}_j}{2} - \mathbf{r} \right)$$

$$\mathbf{J}_{\mathbf{r}}^{\mathrm{A}_2} = \frac{1}{2} \sum_{ij}^{N_A} \theta(r_{ij}) \frac{\mathbf{v}_i + \mathbf{v}_j}{2} \delta \left(\frac{\mathbf{q}_i + \mathbf{q}_j}{2} - \mathbf{r} \right)$$

$$\mathbf{J}_{\mathbf{r}}^{\mathrm{A}} = \sum_{i}^{N_A} \mathbf{v}_i \delta(\mathbf{r} - \mathbf{q}_i) - \frac{1}{2} \sum_{ij}^{N_A} \theta(r_{ij}) \frac{\mathbf{v}_i + \mathbf{v}_j}{2} \delta \left(\frac{\mathbf{q}_i + \mathbf{q}_j}{2} - \mathbf{r} \right)$$

In detail

$$i\mathcal{L}[A_2]_{\mathbf{r}} = \frac{1}{2}\sum_{ij}^{N_A}\theta'(r_{ij})\mathbf{e}_{ij}\cdot\mathbf{v}_{ij}\delta\left(\frac{\mathbf{q}_i + \mathbf{q}_j}{2} - \mathbf{r}\right) - \nabla\frac{1}{2}\sum_{ij}^{N_A}\theta(r_{ij})\frac{\mathbf{v}_i + \mathbf{v}_j}{2}\delta\left(\frac{\mathbf{q}_i + \mathbf{q}_j}{2} - \mathbf{r}\right)$$

$$i\mathcal{L}[A]_{\mathbf{r}} = -\nabla\sum_{i}^{N_A}\mathbf{v}_i\delta(\mathbf{r} - \mathbf{q}_i) - i\mathcal{L}[A_2]_{\mathbf{r}}$$

$$= -\frac{1}{2}\sum_{ij}^{N_A}\theta'(r_{ij})\mathbf{e}_{ij}\cdot\mathbf{v}_{ij}\delta\left(\frac{\mathbf{q}_i + \mathbf{q}_j}{2} - \mathbf{r}\right) - \nabla\left[\sum_{i}^{N_A}\mathbf{v}_i\delta(\mathbf{r} - \mathbf{q}_i) - \frac{1}{2}\sum_{ij}^{N_A}\theta(r_{ij})\frac{\mathbf{v}_i + \mathbf{v}_j}{2}\delta\left(\frac{\mathbf{q}_i + \mathbf{q}_j}{2} - \mathbf{r}\right)\right]$$

Let us have a look at the form of the term $P_{\mathbf{r}}$. Note that $\mathbf{e}_{ij} = \frac{\mathbf{q}_i - \mathbf{q}_j}{|\mathbf{q}_i - \mathbf{q}_j|}$ is a unit vector that goes from atom j to atom i. The relative velocity is $\mathbf{v}_{ij} = \mathbf{v}_i - \mathbf{v}_j$. Therefore, the term $\mathbf{e}_{ij}\cdot\mathbf{v}_{ij}$ is positive when particle i is moving away from particle j. On the other hand, the function $\theta'(r)$ is negative and different from zero in a "halo" around the origin. This means that $\theta(r_{ij})\mathbf{e}_{ij}\cdot\mathbf{v}_{ij}$ is positive when the particles of the pair are approaching and cross the halo. In this way, $P_{\mathbf{r}}$ gives the number of molecules that are being formed per unit time.

The drift term $v_\mu(t)$ in Eq. (12.2) vanishes now, as it involves a Gaussian momentum integral of a velocity. Alternatively, note that all the CG variables are even under time reversal. Microscopic reversibility implies then that the resulting drift term should vanish.

13.2.4 The dissipative matrix

Because the drift vanishes, the projected current (**??**) is equal to the unprojected current, this is $\mathcal{Q}_t i\mathcal{L}A_\mu = i\mathcal{L}A_\mu$. The dissipative matrix (12.2) becomes now

$$\mathcal{D}_{\mu\nu} \rightarrow \begin{pmatrix} 0 & 0 & 0 \\ 0 & \mathcal{D}_{\mathbf{r}\mathbf{r}'}^{11} & \mathcal{D}_{\mathbf{r}\mathbf{r}'}^{12} \\ 0 & \mathcal{D}_{\mathbf{r}\mathbf{r}'}^{21} & \mathcal{D}_{\mathbf{r}\mathbf{r}'}^{22} \end{pmatrix}$$

where $\nabla_{\mathbf{r}} = \frac{\partial}{\partial\mathbf{r}}$ and the diffusion tensor is given by the Green-Kubo formula

$$\mathcal{D}^{\alpha\beta}(\mathbf{r}, \mathbf{r}', t) = \int_0^{\Delta t} dt' \mathrm{Tr}[\overline{\rho}_t i\mathcal{L}[\hat{A}]_{\mathbf{r}'}^{\beta} i\mathcal{L}[\hat{A}]_{\mathbf{r}}^{\alpha}(t')]$$

where $[\hat{A}]^\alpha = [\hat{A}], [A_2]$ for $\alpha = 1, 2$. Explicitly, after use of Eqs. (13.2.3) we obtain

$$\mathscr{D}^{11}(\mathbf{r}, \mathbf{r}', t) = \int_0^{\Delta t} dt' \text{Tr}[\overline{\rho}_t \left(-2P_{\mathbf{r}'} - \nabla \mathbf{J}_{\mathbf{r}'}^A\right) \exp\{i\mathcal{L}t'\} \left(-2P_{\mathbf{r}} - \nabla \mathbf{J}_{\mathbf{r}}^A\right)]$$

$$\mathscr{D}^{12}(\mathbf{r}, \mathbf{r}', t) = \int_0^{\Delta t} dt' \text{Tr}[\overline{\rho}_t \left(P_{\mathbf{r}'} - \nabla \mathbf{J}_{\mathbf{r}'}^{A_2}\right) \exp\{i\mathcal{L}t'\} \left(-2P_{\mathbf{r}} - \nabla \mathbf{J}_{\mathbf{r}}^A\right)]$$

$$\mathscr{D}^{21}(\mathbf{r}, \mathbf{r}', t) = \int_0^{\Delta t} dt' \text{Tr}[\overline{\rho}_t \left(-2P_{\mathbf{r}'} - \nabla \mathbf{J}_{\mathbf{r}'}^A\right) \exp\{i\mathcal{L}t'\} \left(P_{\mathbf{r}} - \nabla \mathbf{J}_{\mathbf{r}}^{A_2}\right)]$$

$$\mathscr{D}^{22}(\mathbf{r}, \mathbf{r}', t) = \int_0^{\Delta t} dt' \text{Tr}[\overline{\rho}_t \left(P_{\mathbf{r}'} - \nabla \mathbf{J}_{\mathbf{r}'}^{A_2}\right) \exp\{i\mathcal{L}t'\} \left(P_{\mathbf{r}} - \nabla \mathbf{J}_{\mathbf{r}}^{A_2}\right)]$$

By expanding the different terms we have

$$\mathscr{D}^{11}(\mathbf{r}, \mathbf{r}', t) = 4\mathscr{R}(\mathbf{r}, \mathbf{r}') + \nabla_{\mathbf{r}} \nabla_{\mathbf{r}'} \mathbf{D}^{11}(\mathbf{r}, \mathbf{r}')$$
$$\mathscr{D}^{12}(\mathbf{r}, \mathbf{r}', t) = -2\mathscr{R}(\mathbf{r}, \mathbf{r}') + \nabla_{\mathbf{r}} \nabla_{\mathbf{r}'} \mathbf{D}^{12}(\mathbf{r}, \mathbf{r}')$$
$$\mathscr{D}^{21}(\mathbf{r}, \mathbf{r}', t) = -2\mathscr{R}(\mathbf{r}, \mathbf{r}') + \nabla_{\mathbf{r}} \nabla_{\mathbf{r}'} \mathbf{D}^{21}(\mathbf{r}, \mathbf{r}')$$
$$\mathscr{D}^{22}(\mathbf{r}, \mathbf{r}', t) = \mathscr{R}(\mathbf{r}, \mathbf{r}') + \nabla_{\mathbf{r}} \nabla_{\mathbf{r}'} \mathbf{D}^{22}(\mathbf{r}, \mathbf{r}')$$

where

$$\mathscr{R}(\mathbf{r}, \mathbf{r}') = \int_0^{\Delta t} dt' \text{Tr}[\overline{\rho}_t P_{\mathbf{r}'} \exp\{i\mathcal{L}t'\} P_{\mathbf{r}}]$$

$$\mathbf{D}^{\alpha\beta}(\mathbf{r}, \mathbf{r}') = \nabla_{\mathbf{r}} \nabla_{\mathbf{r}'} \int_0^{\Delta t} dt' \text{Tr}[\overline{\rho}_t \mathbf{J}_{\mathbf{r}'}^{(\beta)} \exp\{i\mathcal{L}t'\} \mathbf{J}_{\mathbf{r}}^{(\alpha)}]$$

In Eq. (13.2.4) we have neglected terms that involve correlations production $P_{\mathbf{r}}$ with a current. These terms correlate functions with different tensorial order. In the equilibrium state we expect that these terms vanish and we neglect them at this point for simplicity. Of course, they may be retained in a more precise description, at the expense of lengthy equations. **Ray Kapral says that the cross terms should be here!**

Note that this non-local transport coefficient depends on time t only through the actual value of $n(\mathbf{r}, t)$ on which it depends functionally (through the conjugate fields β, λ appearing in the relevant ensemble $\overline{\rho}_t$). The CG variables are even under time reversal. As a consequence Onsager reciprocal relations (**??**) ensure that the dissipative matrix $\mathscr{D}(\mathbf{r}, \mathbf{r}', t)$ is symmetric, implying

$$\mathscr{D}^{\alpha\beta}(\mathbf{r}, \mathbf{r}', t) = \mathscr{D}^{\beta\alpha}(\mathbf{r}', \mathbf{r}, t)$$

13.2.5 The transport equation

The final dynamic equations (12.2) for the CG variables are given by

$$\partial_t E = 0$$

$$\partial_t [\mathrm{A}](\mathbf{r}, t) = 2 \int d\mathbf{r} P(\mathbf{r}, \mathbf{r}') \mathscr{A}(\mathbf{r}') - \nabla_{\mathbf{r}} \mathbf{J}^{\mathrm{A}}(\mathbf{r}, t)$$

$$\partial_t [\mathrm{A}_2](\mathbf{r}, t) = - \int d\mathbf{r} P(\mathbf{r}, \mathbf{r}') \mathscr{A}(\mathbf{r}') - \nabla_{\mathbf{r}} \mathbf{J}^{\mathrm{A}_2}(\mathbf{r}, t)$$

where we have introduced the *affinity* as the following combination of chemical potentials

$$\mathscr{A}(\mathbf{r}) \equiv -2\lambda^{\mathrm{H}}(\mathbf{r}) + \lambda^{\mathrm{H}_2}(\mathbf{r})$$

and the average diffusive currents as

$$\mathbf{J}^{\mathrm{A}}(\mathbf{r}, t) \equiv \int d\mathbf{r}' \mathbf{D}^{11}(\mathbf{r}, \mathbf{r}', t) \nabla_{\mathbf{r}'} \lambda^{\mathrm{A}}(\mathbf{r}') + \int d\mathbf{r}' \mathbf{D}^{12}(\mathbf{r}, \mathbf{r}', t) \nabla_{\mathbf{r}'} \lambda^{\mathrm{A}_2}(\mathbf{r}')$$

$$\mathbf{J}^{\mathrm{A}_2}(\mathbf{r}, t) \equiv \int d\mathbf{r}' \mathbf{D}^{21}(\mathbf{r}, \mathbf{r}', t) \nabla_{\mathbf{r}'} \lambda^{\mathrm{A}}(\mathbf{r}') + \int d\mathbf{r}' \mathbf{D}^{22}(\mathbf{r}, \mathbf{r}', t) \nabla_{\mathbf{r}'} \lambda^{\mathrm{A}_2}(\mathbf{r}')$$

where we have performed an integration by parts.

The first equation in (13.2.5) simply expresses the conservation of total energy for this isolated system and it is trivial. The following two equations are closed non-local equations for the concentration of species. They contain a first block involving the affinity that describes the rate of change of the concentration of each specie due to chemical reactions. The second block describes the change of the concentrations due to the diffusive motion of the atoms. These equations satisfy two important requirements (in addition to total energy conservation): they conserve the total number of particles, defined in (13.2.1) and they ensure that the total entropy (13.5.2) is a non-decrasing function of time. These equations are thermodynamically consistent with the First and Second Laws of thermodynamics. For this reason, the dynamic equations (13.2.5) predict that the equilibrium concentration fields are those that maximize the entropy (13.5.2) subject to the constrain (13.2.1) and total energy conservation. It is immediate to show that this equilibrium state is the one that makes the affinitiy (**??**) to vanish.

13.2.6 Models and Approximations

Note that both, the non-local reactive coefficient and diffusion tensors will be different from zero for values of $\mathbf{r}, \mathbf{r}'$ such that $|\mathbf{r} - \mathbf{r}'| < \zeta$ where ζ is a molecular length scale related to the correlation length in the system. If the affinities and chemical potentials vary in macroscopic length scales, much larger that the molecular length scale ζ, then we may approximate the non-local equations with a local version. This is, we approximate terms as follows

$$\int d\mathbf{r} \mathscr{R}_{\mathbf{r}\mathbf{r}'} \mathscr{A}(\mathbf{r}') \approx \mathscr{A}(\mathbf{r}) \int d\mathbf{r} \mathscr{R}_{\mathbf{r}\mathbf{r}'} = \mathscr{A}(\mathbf{r}) \mathscr{R}(\mathbf{r})$$

This is equivalent to assume

$$\mathscr{R}_{\mathbf{rr}'} = \mathscr{R}_{\mathbf{r}} \delta(\mathbf{r} - \mathbf{r}')$$

where the local reaction coefficient $\mathscr{R}(\mathbf{r})$ is given by

$$\mathscr{R}_{\mathbf{r}'} = \int d\mathbf{r} \int_0^{\Delta t} dt' \mathrm{Tr}[\overline{\rho}_t P_{\mathbf{r}'} \exp\{i\mathcal{L}t'\} P_{\mathbf{r}}] = \int_0^{\Delta t} dt' \mathrm{Tr}[\overline{\rho}_t P_{\mathbf{r}'} \exp\{i\mathcal{L}t'\} P]$$

Let us see what is the form of the Green-Kubo coefficient for the transport coefficient R. We know that $P_{\mathbf{r}}$ is given by

$$P_{\mathbf{r}} = \frac{1}{2} \sum_{i_A j_B} \theta'\left(|\mathbf{r}_{i_A} - \mathbf{r}_{j_A}|\right) \mathbf{e}_{i_A j_A} \cdot \mathbf{v}_{i_A j_A} \delta\left(\frac{m_{i_A}\mathbf{r}_{i_A} + m_{i_A}\mathbf{r}_{i_A}}{m_{i_A} + m_{j_A}} - \mathbf{r}\right)$$

The correlation of this phase function gives rise to the non-local form for the "reactive" part dissipative matrix

In the local approximation, the relevant ensemble can be approximated by a local ensemble with the conjugate variables matched to the local values

$$\overline{\rho}_t \approx \rho_{\mathbf{r}'t}^{\mathrm{loc}}$$

where

$$\rho_{\mathbf{r}'t}^{\mathrm{loc}}(z) = \frac{\rho^0}{Z^{\mathrm{loc}}[\beta,\lambda]} \exp\left\{-\beta\hat{H}(z) - \beta\left[\lambda^A(\mathbf{r}',t)N_{[A]} + \lambda^{A_2}(\mathbf{r},t')N_{[A_2]}\right]\right\}$$

with the total number of molecules of each specie given by

$$N_{[A]} = \int d\mathbf{r} n_{\mathbf{r}}^{[A]} = N_A - N_{[A_2]}$$

$$N_{[A_2]} = \int d\mathbf{r} n_{\mathbf{r}}^{[A_2]} = \frac{1}{2} \sum_{i_A j_A} \theta(\mathbf{r}_{i_A} - \mathbf{r}_{j_A})$$

Note that we distinguish with the notation the number of dissociated atoms $N_{[A]}$ from the total number of atoms N_A.

The local ensemble is traslation invariant, i.e. $\rho_{\mathbf{r}}(z) = \rho_{\mathbf{r}}(T_{\mathbf{a}}z)$, where $\mathbf{a}$ is the arbitrary translation vector. Therefore,

$$\mathscr{R}_{\mathbf{r}'} = \int_0^{\Delta t} dt' \mathrm{Tr}[\rho_{\mathbf{r}'t}^{\mathrm{loc}} P_{\mathbf{r}'+\mathbf{a}} \exp\{i\mathcal{L}t'\} P]$$

which means that, as far as the "index" $\mathbf{r}'$ of $P_{\mathbf{r}'+\mathbf{a}}$ is concerned, the rate coefficient does not depend on the $\mathbf{r}'$ (it only depends implicitly through the dependence on the conjugate variables, otherwise is like an ordinary equilibrium ensemble). Therefore, we

may average $\mathbf{r}'$ over the volume and obtain the final Green-Kubo expression

$$\mathscr{R}_\mathbf{r} = \frac{1}{\mathscr{V}} \int_0^{\Delta t} dt' \mathrm{Tr}[\rho_\mathbf{r}^{\mathrm{loc}} \hat{R} \exp\{i\mathcal{L}t'\}\hat{R}]$$

and $\rho_\mathbf{r}^{\mathrm{eq}}$ is the equilibrium ensemble with local values of the conjugate variables. The transport coefficients $\mathscr{R}$ are functions of the space through the dependence of the conjugate variables on space. In general, the reactive transport coefficient is a complicated function of the three variables $\beta, \lambda_\mathrm{A}, \lambda_{\mathrm{A}_2}$.

By using (13.4.1), the equilibrium ensemble (13.4.1) becomes

$$\rho_\mathbf{r}^{\mathrm{loc}}(z) = \frac{\rho^0}{Z[\beta, \lambda]} \exp\left\{ -\beta\hat{H}(z) - \lambda_\mathbf{r}^\mathrm{A} N_\mathrm{A} - \mathscr{A}_\mathbf{r} \frac{1}{2} \sum_{i_\mathrm{A} j_\mathrm{A}} \theta(\mathbf{r}_{i_\mathrm{A}} - \mathbf{r}_{j_\mathrm{A}}) \right\}$$

Note that the role of the conjugate parameter $\lambda_\mathbf{r}^\mathrm{A}$ is slightly different than the role of $\mathscr{A}_\mathbf{r}$ because the latter multiplies a phase function, while the former multiplies just the number of atoms of each type. The parameter $\lambda_\mathbf{r}^\mathrm{A}$ fix the local thermodynamic state. Remember that the conjugate variables $\lambda_\mathbf{r}^\mathrm{A}, \mathscr{A}_\mathbf{r}$ are all dependent on the local values $[\mathrm{A}]_\mathbf{r}, [\mathrm{A}_2]_\mathbf{r}$. Finally, note that the above ensemble is just the grand-canonical equilibrium ensemble of a system of atoms that interact with a modified pair potential.

13.3   Transition State Theory

The Green-Kubo formula (**??**) or (**??**) for the rate coefficient requires the evaluation of the microscopic dynamics and is, therefore, not very explicit. It is very convenient to have an approximate way to compute this rate under a set of well-defined approximations. These approximations fall under the name of Transition State Theory. Transition State Theory (TST) is an important conceptual framework for the treatment of chemical reactions and, in general, situations in which a system goes from one "basin of attraction" to another one. Good presentations are given in the original paper by Chandler [**?**] and in the books [**?**], [**?**]. We reproduce the TST near-equilibrium calculation[**?**] of the rate coefficient in order to we extend the calculation to situations far from equilibrium situations.

We may perform the time integral and obtain

$$\mathscr{R}_\mathbf{r} = \frac{1}{\mathscr{V}} \mathrm{Tr}\left[\rho_\mathbf{r}^{\mathrm{loc}} \left(\frac{1}{2} \sum_{i_\mathrm{A} j_\mathrm{A}} \Delta\left(|\mathbf{r}_{i_\mathrm{A}} - \mathbf{r}_{j_\mathrm{A}}|\right) \mathbf{e}_{i_\mathrm{A} j_\mathrm{A}} \cdot \mathbf{v}_{i_\mathrm{A} j_\mathrm{A}} \right) \left(\frac{1}{2} \sum_{i'_A j'_A} \theta\left(|\mathbf{r}_{i'_\mathrm{A}}(T) - \mathbf{r}_{j'_\mathrm{A}}(T)|\right) \right) \right]$$

This correlates a sum over pairs, with a sum over pairs. If we assume that the pairs are uncorrelated, we have

$$\mathscr{R}_\mathbf{r} = \frac{1}{\mathscr{V}} \mathrm{Tr}\left[\rho_\mathbf{r}^{\mathrm{loc}} \frac{1}{2} \sum_{i_\mathrm{A} j_\mathrm{A}} \Delta\left(|\mathbf{r}_{i_\mathrm{A}} - \mathbf{r}_{j_\mathrm{A}}|\right) \mathbf{e}_{i_\mathrm{A} j_\mathrm{A}} \cdot \mathbf{v}_{i_\mathrm{A} j_\mathrm{A}} \theta\left(|\mathbf{r}_{i_\mathrm{A}}(T) - \mathbf{r}_{j_\mathrm{A}}(T)|\right) \right]$$

While, in principle, there are $\sim N_A^2$ pairs, only a number of order N_A give non-zero contribution to the sum, as they correspond to pairs that are exactly at a typical distance of the order of the barrier r_B. If all these pairs are equivalent, we may approximate

$$\mathscr{R}_{\mathbf{r}} = \frac{N_A}{\mathscr{V}} \mathrm{Tr}\left[\rho_{\mathbf{r}}^{\mathrm{loc}} \Delta\left(d\right) \theta\left(d(T)\right) v\right]$$

where $d = |\mathbf{r}_{i_A} - \mathbf{r}_{j_A}|$ is the distance between two atoms and $v = \dot{d} = \mathbf{e}_{i_A j_A} \cdot \mathbf{v}_{i_A j_A}$ is the approaching velocity of two atoms. We consider the limit in which θ goes to the step function $\Theta(d - r_B)$ and Δ to Dirac delta function $\delta(d - r_B)$, this is

$$\mathscr{R}_T \simeq \langle \delta(d - r_B)\theta(d(T) - r_B)v\rangle_\beta$$

For sufficiently short times we have

$$d(T) \simeq d + vT$$

Then we have that

$$\mathscr{R}_T \simeq \langle \delta(d - r_B)\theta(vT)v\rangle$$

Because $T > 0$, we have that $\theta(\mathbf{e}_{i_A j_A} \cdot \mathbf{v}_{i_A j_A} T) = \theta(\mathbf{e}_{i_A j_A} \cdot \mathbf{v}_{i_A j_A})$ and the above expression becomes

$$\mathscr{R}_T \simeq \langle \delta(r_B - d)\theta(\mathbf{e}_{i_A j_A} \cdot \mathbf{v}_{i_A j_A})\mathbf{e}_{i_A j_A} \cdot \mathbf{v}_{i_A j_A}\rangle$$

Note that $\mathscr{R}_T = 0$ for $T = 0$ while for $T > 0$ takes a value which is independent of T for small T. The rate is obviously discontinuous at $T = 0$. The momentum integral over the Maxwellian distribution can be now performed, where we only integrate over half the velocities, and obtain a non-zero result

$$\mathscr{R}_T \simeq \frac{k_B T}{2\pi} \langle \delta(r_B - d)\rangle$$

By definition, $\langle \delta(r_B - d)\rangle_\beta$ is the probability that at equilibrium a pair of atoms is separated by just the barrier length,, i.e. is the probability that a molecule is on top of the barrier. This probability is usually expressed in terms of the so called potential of mean force

$$\frac{1}{Z}e^{-\beta V^{\mathrm{eff}}(r)} = \int dz \rho_\beta(z)\delta(r - d)$$

The coordinate r receives the name of "reaction coordinate". We have finally,

$$\mathscr{R}_T \simeq \frac{k_B T}{2\pi} \frac{1}{Z} e^{-\beta V^{\mathrm{eff}}(r_B)}$$

Under the assumption that the effective potential is roughly independent on the temperature (which is not, strictu sense), this gives the well-knwon Arrhenius dependence of the reaction rate on the temperature.

In summary, the assumptions made in obtaining the TST expression for the rate are the following:

- The general validity of the Markov description in terms of the relevant variable $\hat{N}_+$.

- The system is near equilibrium.

- The relevant variable $\hat{N}_+(z)$ is defined with a sharp Heaviside step function.

- The dynamics of each molecule is uncorrelated from the dynamics of the rest.

- The Taylor expansion (13.3) is appropriate when computing the correlation function. This implicitly assumes that once a molecule crosses the barrier does not recrosses it back.

In order to have an estimate of the rate in far from equilibrium situations, we follow identical arguments in a situation in which the affinity $\mathscr{A}$ is not zero. All that needs to be done is to replace the canonical ensemble in the previous steps by the relevant ensemble (??) or, in other words, the original Hamiltonian (??) with the modified Hamiltonian (??). Instead of (13.3), we arrive now at

$$\mathscr{R}_T(\beta, \mathscr{A}) \simeq \frac{k_B T}{2\pi} \left\langle \delta(r_B - d_\mu) \right\rangle_{\beta\mathscr{A}}$$

where we have introduced the probability that a molecule has an elongation, when the ensemble is the relevant ensemble

$$\left\langle \delta(r - d_\mu) \right\rangle_{\beta\mathscr{A}} = \int dz \frac{\exp\{-\beta\hat{H}(z) - \mathscr{A}\hat{N}_+(z)\}}{Z(\beta, \mathscr{A})} \delta(r - d_\mu)$$

This is the equilibrium probability distribution of a molecule when the Hamiltonian is given by (??) corresponding to a dumbbell potential that contains the additional term (??). The potential of mean force is expected to be qualitatively similar to the actual potential, with slight modifications due to "solvent effects". However, to get an estimate, we may assume that the dumbells are in a state in which interactions between them and with the solvent are negligible. In this ideal gas approximation the effective potential is the same as the real dumbbell potential. In other words, we assume that the probability that one dumbell has an elongation r is given by

$$\left\langle \delta(r - d_\mu) \right\rangle_{\beta\mathscr{A}} \simeq \frac{1}{z(\beta, \mathscr{A})} \exp\{-\beta W(r) - \mathscr{A}\theta(r)\}$$

where we have introduced the normalization

$$z(\beta, \mathscr{A}) = \int_0^\infty dr \exp\{-\beta W(r) - \mathscr{A}\theta(r)\}$$

This normalization can be further expressed as

$$z(\beta, \mathscr{A}) = p_1 + p_2 e^{-\mathscr{A}}$$

$$p_1 = \int_0^{r_B} dr \exp\{-\beta W(r)\}$$

$$p_2 = \int_{r_B}^{\infty} dr \exp\{-\beta W(r)\} = p_1$$

This gives the final explicit answer for the *non-equilibrium* rate of reaction in the TST approximation

$$\mathscr{R}_T(\beta, \mathscr{A}) \simeq \mathscr{R}_T(\beta, 0) \frac{2e^{-\frac{1}{2}\mathscr{A}}}{1 + e^{-\mathscr{A}}}$$

In Fig. **??** we show the graph of the normalized rate as a function of the affinity. The assymptotic behaviour of the rate at large values of the affinity $\mathscr{A}$ is

$$\frac{\mathscr{R}_T(\beta, \mathscr{A})}{\mathscr{R}_T(\beta, 0)} \simeq e^{-\frac{1}{2}|\mathscr{A}| + \ln(2)}$$

which is shown in Fig. **??**. Note that this assymptotice regime is reached at $\mathscr{A} \simeq \pm 3$.

The resulting rate of change, i.e. the right hand side of the evolution equation (**??**), is displayed in Fig. **??**

The calculation of the non-equilibrium rate $\mathscr{R}(\beta, \mathscr{A})$ in this section is made with a number of approximations that will not be accurate in realistic situations. However, the present calculation is valuable because it offers a qualitative picture that should help in discussing these realistic situations. In particular, we expect that the assymptotic exponential behaviour $\sim \exp\left\{-\frac{1}{2}|\mathscr{A}|\right\}$ of the rate at large affinities will be a general feature.

13.4 The reaction $\mathrm{A} + \mathrm{B} \rightleftharpoons \mathrm{AB}$

We consider now a chemical reaction of the form

$$\mathrm{A} + \mathrm{B} \rightleftharpoons \mathrm{AB}$$

We have two types of atoms A, B that react to form a diatomic molecule AB. To select the CG variables we start with the number density of molecule AB

$$\hat{n}_{\mathbf{r}}^{\mathrm{AB}}(z) = \sum_{i_\mathrm{A} i_\mathrm{B}}^{N_\mathrm{A} N_\mathrm{B}} \theta(\mathbf{r}_{i_\mathrm{A}} - \mathbf{r}_{i_\mathrm{B}}) \delta\left(\frac{\mathbf{r}_{i_\mathrm{A}} + \mathbf{r}_{i_\mathrm{B}}}{2} - \mathbf{r}\right)$$

No factor $1/2$ now because atoms A, B are distinct. The number density of atoms of type A (B) (irrespective of the fact that they may form part of an AB molecule) are

$$\hat{n}_{\mathbf{r}}^{\mathrm{A}} = \sum_{i_\mathrm{A}}^{N_\mathrm{B}} \delta(\mathbf{r} - \mathbf{r}_{i_\mathrm{A}})$$

$$\hat{n}_{\mathbf{r}}^{\mathrm{B}} = \sum_{i_\mathrm{B}}^{N_\mathrm{B}} \delta(\mathbf{r} - \mathbf{r}_{i_\mathrm{B}})$$

So we have three species. We define, therefore the following density number of different species **[Remove hats]**

$$[\hat{\mathrm{A}}]_{\mathbf{r}} = \hat{n}_{\mathbf{r}}^{\mathrm{A}} - \hat{n}_{\mathbf{r}}^{\mathrm{AB}}$$
$$[\hat{\mathrm{B}}]_{\mathbf{r}} = \hat{n}_{\mathbf{r}}^{\mathrm{B}} - \hat{n}_{\mathbf{r}}^{\mathrm{AB}}$$
$$[\hat{\mathrm{A}}\hat{\mathrm{B}}]_{\mathbf{r}} = \hat{n}_{\mathbf{r}}^{\mathrm{AB}}$$

$[\hat{\mathrm{A}}]_{\mathbf{r}}$ is the number of atoms A that are not associated with B forming a molecule. Note that

$$[\hat{\mathrm{A}}]_{\mathbf{r}} + [\hat{\mathrm{A}\mathrm{B}}]_{\mathbf{r}} = \sum_{i_\mathrm{A}}^{N_\mathrm{A}} \delta(\mathbf{r} - \mathbf{r}_{i_\mathrm{A}})$$

$$[\hat{\mathrm{B}}]_{\mathbf{r}} + [\hat{\mathrm{A}\mathrm{B}}]_{\mathbf{r}} = \sum_{i_\mathrm{B}}^{N_\mathrm{B}} \delta(\mathbf{r} - \mathbf{r}_{i_\mathrm{B}})$$

and, therefore,

$$\int d\mathbf{r} \left([\hat{\mathrm{A}}]_{\mathbf{r}} + [\hat{\mathrm{A}\mathrm{B}}]_{\mathbf{r}}\right) = N_\mathrm{A}$$

$$\int d\mathbf{r} \left([\hat{\mathrm{B}}]_{\mathbf{r}} + [\hat{\mathrm{A}\mathrm{B}}]_{\mathbf{r}}\right) = N_\mathrm{B}$$

13.4.1   The relevant ensemble and the entropy

In the present level of description the relevant ensemble (1.11.3) becomes

$$\overline{\rho}(z) = \frac{1}{Z[\beta,\lambda]} \exp\left\{ -\beta \hat{H}(z) - \int d\mathbf{r}' \left[\lambda^{\mathrm{A}}(\mathbf{r}')[\mathrm{A}]_{\mathbf{r}'}(z) + \lambda^{\mathrm{B}}(\mathbf{r}')[\mathrm{B}]_{\mathbf{r}'}(z) + \lambda^{\mathrm{AB}}(\mathbf{r}')[\mathrm{AB}]_{\mathbf{r}'}(z) \right] \right\}$$

$$Z[\beta,\lambda] = \int dz \exp\left\{ -\beta \hat{H}(z) - \int d\mathbf{r}' \left[\lambda^{\mathrm{A}}(\mathbf{r}')[\mathrm{A}]_{\mathbf{r}'}(z) + \lambda^{\mathrm{B}}(\mathbf{r}')[\mathrm{B}]_{\mathbf{r}'}(z) + \lambda^{\mathrm{AB}}(\mathbf{r}')[\mathrm{AB}]_{\mathbf{r}'}(z) \right] \right\}$$

The conjugate variables and the average of the CG variables are related by (1.11.7) that in the present case becomes

$$\frac{\partial \Phi}{\partial \beta}[\beta, \lambda^{\mathrm{A}}, \lambda^{\mathrm{B}}, \lambda^{\mathrm{AB}}] = E$$

$$\frac{\delta \Phi}{\delta \lambda^{\mathrm{A}}(\mathbf{r})}[\beta, \lambda^{\mathrm{A}}, \lambda^{\mathrm{B}}, \lambda^{\mathrm{AB}}] = [\mathrm{A}](\mathbf{r})$$

$$\frac{\delta \Phi}{\delta \lambda^{\mathrm{B}}(\mathbf{r})}[\beta, \lambda^{\mathrm{A}}, \lambda^{\mathrm{B}}, \lambda^{\mathrm{AB}}] = [\mathrm{B}](\mathbf{r})$$

$$\frac{\delta \Phi}{\delta \lambda^{\mathrm{AB}}(\mathbf{r})}[\beta, \lambda^{\mathrm{A}}, \lambda^{\mathrm{B}}, \lambda^{\mathrm{AB}}] = [\mathrm{AB}](\mathbf{r})$$

where the dimensionless thermodynamic potential is

$$\Phi[\beta, \lambda^{\mathrm{A}}, \lambda^{\mathrm{B}}, \lambda^{\mathrm{AB}}] = -\ln Z[\beta, \lambda^{\mathrm{A}}, \lambda^{\mathrm{B}}, \lambda^{\mathrm{AB}}]$$

The entropy (**??**) for this level of description is given by

$$S[E, n] = -\Phi[\beta, \lambda] + \int d\mathbf{r} \left[\lambda^{\mathrm{A}}(\mathbf{r})[\mathrm{A}](\mathbf{r}) + \lambda^{\mathrm{B}}(\mathbf{r})[\mathrm{B}](\mathbf{r}) + \lambda^{\mathrm{AB}}(\mathbf{r})[\mathrm{AB}](\mathbf{r}) \right]$$

In Eq. (13.5.2), $\beta, \lambda^{\mathrm{A}}(\mathbf{r}), \lambda^{\mathrm{B}}(\mathbf{r}), \lambda^{\mathrm{AB}}(\mathbf{r})$ are understood as functions of the averages $E, [\mathrm{A}](\mathbf{r}), [\mathrm{B}](\mathbf{r}), [\mathrm{AB}](\mathbf{r})$.

The conjugate variables are given in terms of the derivatives of the entropy functional

$$\frac{\partial S}{\partial E} = \beta$$

$$\frac{\delta S}{\delta [\mathrm{A}](\mathbf{r})}[E, [\mathrm{A}], [\mathrm{B}]] = \lambda^{\mathrm{A}}(\mathbf{r})$$

$$\frac{\delta S}{\delta [\mathrm{B}](\mathbf{r})}[E, [\mathrm{A}], [\mathrm{B}]] = \lambda^{\mathrm{B}}(\mathbf{r})$$

$$\frac{\delta S}{\delta [\mathrm{AB}](\mathbf{r})}[E, [\mathrm{A}], [\mathrm{B}]] = \lambda^{\mathrm{AB}}(\mathbf{r})$$

The time derivatives of the CG variables now take the form

$$i\mathcal{L}[\text{A}]_{\mathbf{r}}(z) = -P_{\mathbf{r}} - \nabla \mathbf{J}_{\mathbf{r}}^{\text{A}}$$
$$i\mathcal{L}[\text{B}]_{\mathbf{r}}(z) = -P_{\mathbf{r}} - \nabla \mathbf{J}_{\mathbf{r}}^{\text{B}}$$
$$i\mathcal{L}[\text{AB}]_{\mathbf{r}}(z) = P_{\mathbf{r}} - \nabla \mathbf{J}_{\mathbf{r}}^{\text{AB}}$$

with obvious definition for the production term $P_{\mathbf{r}}$ and diffusion fluxes $\mathbf{J}_{\mathbf{r}}^{\alpha}$. We focus now only on the reaction bit of the transport equation, because the dissipative part is similar to the previous section. The dissipative matrix will have the following structure

$$\mathcal{D}_{\mu\nu} \rightarrow \begin{pmatrix} 0 & 0 & 0 & 0 \\ 0 & \mathcal{R}_{\mathbf{rr'}} & \mathcal{R}_{\mathbf{rr'}} & -\mathcal{R}_{\mathbf{rr'}} \\ 0 & \mathcal{R}_{\mathbf{rr'}} & \mathcal{R}_{\mathbf{rr'}} & -\mathcal{R}_{\mathbf{rr'}} \\ 0 & -\mathcal{R}_{\mathbf{rr'}} & -\mathcal{R}_{\mathbf{rr'}} & \mathcal{R}_{\mathbf{rr'}} \end{pmatrix}$$

The vanishing first row and column correspond to the total energy variable. The chemical reaction bit of the transport equations will be

$$\partial_t [\text{A}](\mathbf{r}, t) = -\int d\mathbf{r'} \mathcal{R}_{\mathbf{rr'}} \mathscr{A}(\mathbf{r'})$$

$$\partial_t [\text{B}](\mathbf{r}, t) = -\int d\mathbf{r'} \mathcal{R}_{\mathbf{rr'}} \mathscr{A}(\mathbf{r'})$$

$$\partial_t [AB](\mathbf{r}, t) = \int d\mathbf{r'} \mathcal{R}_{\mathbf{rr'}} \mathscr{A}(\mathbf{r'})$$

where the affinity is now

$$\mathscr{A}(\mathbf{r'}) \equiv -\lambda^{\text{A}}(\mathbf{r'}) - \lambda^{\text{B}}(\mathbf{r'}) + \lambda^{\text{AB}}(\mathbf{r'})$$

Note that the structure of the affinity is

$$\mathscr{A} = \sum_{\alpha} \nu_{\alpha} \lambda^{\alpha}$$

where $\alpha = \text{A, B, AB}$ is the index of specie and ν_{α} are the *stoichiometric coefficients* for the reaction

$$\text{A} + \text{B} \rightleftharpoons \text{AB}$$
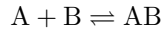
which are $\nu_{\text{A}} = -1, \nu_{\text{B}} = -1, \nu_{\text{AB}} = 1$. The stochiometric coefficients are conventionally taken as positive for products, negative for reactants. Note that the emergence of the affinity as that particular linear combination of chemical potentials is a result of the formalism. Of course, this is rooted on the conservation of the number of atoms (**??**) and in the definition of the CG variables (**??**) in order to account properly for such a

conservation.

In local form, $\mathscr{R}_{\mathbf{rr}'} = R\delta(\mathbf{r} - \mathbf{r}')$

$$\partial_t[\mathrm{A}](\mathbf{r}, t) = -R\mathscr{A}(\mathbf{r}')$$
$$\partial_t[\mathrm{B}](\mathbf{r}, t) = -R\mathscr{A}(\mathbf{r}')$$
$$\partial_t[\mathrm{AB}](\mathbf{r}, t) = R\mathscr{A}(\mathbf{r}')$$

Under the assumption of very fast diffusion as compared with the rate of reaction, the system is homogeneous and we may forget the space dependence

$$\partial_t[\mathrm{A}](t) = -R\mathscr{A}$$
$$\partial_t[\mathrm{B}](t) = -R\mathscr{A}$$
$$\partial_t[\mathrm{AB}](t) = R\mathscr{A}$$

In these equations, *apparently* the rates of change are linear in the affinities. One should understand, however that the transport coefficient R depends, in general, on the state. If R was constant one would obtain that the rate of the reaction would be linear to the affinity, which is known experimentally to be valid only in the late states of the reaction, close to equilibrium.

Let us see what is the form of the Green-Kubo coefficient for the transport coefficient R. We know that $P_{\mathbf{r}}$ is given by

$$P_{\mathbf{r}} = \sum_{i_{\mathrm{A}}j_{\mathrm{B}}} \theta'\left(|\mathbf{r}_{i_{\mathrm{A}}} - \mathbf{r}_{j_{\mathrm{B}}}|\right) \mathbf{e}_{i_{\mathrm{A}}j_{\mathrm{B}}} \cdot \mathbf{v}_{i_{\mathrm{A}}j_{\mathrm{B}}} \delta\left(\frac{m_{i_{\mathrm{A}}}\mathbf{r}_{i_{\mathrm{A}}} + m_{i_{\mathrm{B}}}\mathbf{r}_{i_{\mathrm{B}}}}{m_{i_{\mathrm{A}}} + m_{j_{\mathrm{B}}}} - \mathbf{r}\right)$$

The correlation of this phase function gives rise to the non-local form for the "reactive" part dissipative matrix

$$\mathscr{R}_{\mathbf{rr}'} = \int_0^{\Delta t} dt' \mathrm{Tr}[\bar{\rho}_t P_{\mathbf{r}'} \exp\{i\mathcal{L}t'\} P_{\mathbf{r}}]$$

In the local approximation

$$\mathscr{R}_{\mathbf{rr}'} = \mathscr{R}_{\mathbf{r}}\delta(\mathbf{r} - \mathbf{r}')$$

where, by definition,

$$\mathscr{R}_{\mathbf{r}'} = \int d\mathbf{r} \int_0^{\Delta t} dt' \mathrm{Tr}[\bar{\rho}_t P_{\mathbf{r}'} \exp\{i\mathcal{L}t'\} P_{\mathbf{r}}] = \int_0^{\Delta t} dt' \mathrm{Tr}[\bar{\rho}_t P_{\mathbf{r}'} \exp\{i\mathcal{L}t'\} P]$$

In the local approximation, the relevant ensemble can be approximated by a local ensemble with the conjugate variables matched to the local values

$$\bar{\rho}_t \approx \rho_{\mathbf{r}'t}^{\mathrm{loc}}$$

where

$$\rho_{\mathbf{r}'t}^{\mathrm{loc}}(z) = \frac{\rho^0}{Z^{\mathrm{loc}}[\beta, \lambda]} \exp\left\{-\beta\hat{H}(z) - \beta\left[\lambda^{\mathrm{A}}(\mathbf{r}', t)N_{[A]} + \lambda^{\mathrm{B}}(\mathbf{r}', t)N_{[B]} + \lambda^{\mathrm{AB}}(\mathbf{r}, t')N_{[AB]}\right]\right\}$$

with the total number of molecules of each specie given by

$$N_{[A]} = \int d\mathbf{r} n_{\mathbf{r}}^{[A]} = N_{\mathrm{A}} - N_{[AB]}$$

$$N_{[B]} = \int d\mathbf{r} n_{\mathbf{r}}^{[B]} = N_{\mathrm{B}} - N_{[AB]}$$

$$N_{[AB]} = \int d\mathbf{r} n_{\mathbf{r}}^{[AB]} = \sum_{i_{\mathrm{A}} i_{\mathrm{B}}} \theta(\mathbf{r}_{i_{\mathrm{A}}} - \mathbf{r}_{i_{\mathrm{B}}})$$

Note that we distinguish with the notation the number of dissociated atoms $N_{[A]}$ from the total number of atoms N_A.

The local ensemble is traslation invariant, i.e. $\rho_{\mathbf{r}}(z) = \rho_{\mathbf{r}}(T_{\mathbf{a}}z)$, where $\mathbf{a}$ is the arbitrary translation vector. Therefore,

$$\mathscr{R}_{\mathbf{r}'} = \int_0^{\Delta t} dt' \mathrm{Tr}[\rho_{\mathbf{r}'t}^{\mathrm{loc}} P_{\mathbf{r}'+\mathbf{a}} \exp\{i\mathcal{L}t'\}P]$$

which means that, as far as the "index" $\mathbf{r}'$ of $P_{\mathbf{r}'+\mathbf{a}}$ is concerned, the rate coefficient does not depend on the $\mathbf{r}'$ (it only depends implicitly through the dependence on the conjugate variables, otherwise is like an ordinary equilibrium ensemble). Therefore, we may average $\mathbf{r}'$ over the volume and obtain the final Green-Kubo expression

$$\mathscr{R}_{\mathbf{r}} = \frac{1}{\mathscr{V}} \int_0^{\Delta t} dt' \mathrm{Tr}[\rho_{\mathbf{r}}^{\mathrm{loc}} \hat{R} \exp\{i\mathcal{L}t'\}\hat{R}]$$

where the function that we autocorrelate is

$$\hat{R} = \sum_{i_{\mathrm{A}} j_{\mathrm{B}}} \theta'\left(|\mathbf{r}_{i_{\mathrm{A}}} - \mathbf{r}_{j_{\mathrm{B}}}|\right) \mathbf{e}_{i_{\mathrm{A}} j_{\mathrm{B}}} \cdot \mathbf{v}_{i_{\mathrm{A}} j_{\mathrm{B}}}$$

and $\rho_{\mathbf{r}}^{\mathrm{eq}}$ is the equilibrium ensemble with local values of the conjugate variables. The transport coefficients $\mathscr{R}$ are functions of the space through the dependence of the conjugate variables on space. In general, the reactive transport coefficient is a complicated function of the three variables $\beta, \lambda^{\mathrm{A}}, \lambda^{\mathrm{B}}, \lambda^{\mathrm{AB}}$. Can we assume that it only depends on $\beta, \mathscr{A}$? This would be great because it reduces enormously the problem.

We need to consider some consequences of the local approximation(13.4.1). Note that the averages of the CG variables $[A]_{\mathbf{r}}, [B]_{\mathbf{r}}, [AB]_{\mathbf{r}}$ are given correctly with the relevant

ensemble. This implies that

$$[A](\mathbf{r}) = \mathrm{Tr}\left[\overline{\rho}[A]_{\mathbf{r}}\right] = \frac{\delta}{\delta\lambda_{\mathbf{r}}^{[A]}}\ln Z[\beta,\lambda] = \quad \simeq \mathrm{Tr}\left[\rho_{\mathbf{r}}^{\mathrm{loc}}[A]_{\mathbf{r}}\right]$$

$$[B](\mathbf{r}) = \mathrm{Tr}\left[\overline{\rho}[B]_{\mathbf{r}}\right] \quad \simeq \mathrm{Tr}\left[\rho_{\mathbf{r}}^{\mathrm{loc}}[B]_{\mathbf{r}}\right]$$

$$[AB](\mathbf{r}) = \mathrm{Tr}\left[\overline{\rho}[AB]_{\mathbf{r}}\right] \simeq \mathrm{Tr}\left[\rho_{\mathbf{r}}^{\mathrm{loc}}[AB]_{\mathbf{r}}\right]$$

Let us obtain the entropy function under the local approximation (13.4.1). As we know that the entropy is just the result of evaluating the Gibbs-Jaynes entropy at the relevant ensemble, when the relevant ensemble is approximated by the local ensemble, the entropy becomes

$$S^{\mathrm{loc}} = -\mathrm{Tr}\left[\overline{\rho}\ln\frac{\overline{\rho}}{\rho_0}\right] = -\mathrm{Tr}\left[\rho_{\mathbf{r}'}^{\mathrm{loc}}\ln\frac{\rho_{\mathbf{r}'}^{\mathrm{loc}}}{\rho_0}\right]$$

$$= \ln Z^{\mathrm{loc}}[\beta,\lambda] + \beta\mathrm{Tr}\left[\rho_{\mathbf{r}'}^{\mathrm{loc}}\hat{H}\right] + \lambda^{\mathrm{A}}(\mathbf{r}')\mathrm{Tr}\left[\rho_{\mathbf{r}'}^{\mathrm{loc}}N_{[A]}\right] + \lambda^{\mathrm{B}}(\mathbf{r}')\mathrm{Tr}\left[\rho_{\mathbf{r}'}^{\mathrm{loc}}N_{[B]}\right] + \lambda^{\mathrm{AB}}(\mathbf{r})\mathrm{Tr}\left[\rho_{\mathbf{r}'}^{\mathrm{loc}}N_{[AB]}\right]$$

By using (13.4.1), the equilibrium ensemble (13.4.1) becomes

$$\rho_{\mathbf{r}}^{\mathrm{loc}}(z) = \frac{\rho^0}{Z[\beta,\lambda]}\exp\left\{-\beta\hat{H}(z) - \lambda_{\mathbf{r}}^{\mathrm{A}}N_{\mathrm{A}} - \lambda_{\mathbf{r}}^{\mathrm{B}}N_{\mathrm{B}} - \mathscr{A}_{\mathbf{r}}\sum_{i_{\mathrm{A}}i_{\mathrm{B}}}\theta(\mathbf{r}_{i_{\mathrm{A}}} - \mathbf{r}_{i_{\mathrm{B}}})\right\}$$

Note that the role of the conjugate parameters $\lambda_{\mathbf{r}}^{\mathrm{A}}, \lambda_{\mathbf{r}}^{\mathrm{B}}$ is slightly different than the role of $\mathscr{A}_{\mathbf{r}}$ because the latter multiplies a phase function, while the former multiplies just the number of atoms of each type. The parameters $\lambda_{\mathbf{r}}^{\mathrm{A}}, \lambda_{\mathbf{r}}^{\mathrm{B}}$ fix the local thermodynamic state. Remember that all the conjugate variables $\lambda_{\mathbf{r}}^{\mathrm{A}}, \lambda_{\mathbf{r}}^{\mathrm{B}}, \mathscr{A}_{\mathbf{r}}$ are all dependent on the local values $[A]_{\mathbf{r}}, [B]_{\mathbf{r}}, [AB]_{\mathbf{r}}$.

We may, of course, take a further approximation in which we assume that we may substitute the bit

$$\exp\left\{-\beta\hat{H}(z) - \lambda_{\mathbf{r}}^{\mathrm{A}}N_{\mathrm{A}} - \lambda_{\mathbf{r}}^{\mathrm{B}}N_{\mathrm{B}}\right\}$$

with the real equilibrium ensemble of the system. This is we take $\lambda^{\mathrm{A}}(\mathbf{r},t) \approx \lambda^{\mathrm{Aeq}}$, $\lambda^{\mathrm{B}}(\mathbf{r},t) \approx \lambda^{\mathrm{Beq}}$, but only in this bit. In this way, we approximate

$$\rho_{\mathbf{r}}^{\mathrm{eq}}(z) \approx \rho^{\mathrm{eq}}(z)\frac{Z^{\mathrm{eq}}[\beta,\lambda]}{Z[\beta,\lambda]}\exp\left\{-\mathscr{A}_{\mathbf{r}}\sum_{i_{\mathrm{A}}i_{\mathrm{B}}}\theta(\mathbf{r}_{i_{\mathrm{A}}} - \mathbf{r}_{i_{\mathrm{B}}})\right\}$$

$$= \frac{\rho^{\mathrm{eq}}(z)\exp\left\{-\mathscr{A}_{\mathbf{r}}\sum_{i_{\mathrm{A}}i_{\mathrm{B}}}\theta(\mathbf{r}_{i_{\mathrm{A}}} - \mathbf{r}_{i_{\mathrm{B}}})\right\}}{\mathrm{Tr}\left[\rho^{\mathrm{eq}}\exp\left\{-\mathscr{A}_{\mathbf{r}}\sum_{i_{\mathrm{A}}i_{\mathrm{B}}}\theta(\mathbf{r}_{i_{\mathrm{A}}} - \mathbf{r}_{i_{\mathrm{B}}})\right\}\right]}$$

Therefore, the reaction transport coefficient $\mathscr{R}_{\mathbf{r}}$ depends in a natural way on the local affinity $\mathscr{A}_{\mathbf{r}}$. Of course, the transport coefficient still depends on the overall parameters

$\beta, \lambda^A, \lambda^B$ that fix the equilibrium state. However, due to the particular form of the term
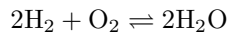
$$\mathscr{A}_\mathbf{r} \sum_{i_A i_B} \theta(\mathbf{r}_{i_A} - \mathbf{r}_{i_B})$$

we expect a very non-trivial dependence of the reaction transport coefficient on the affinity.

13.5 The reaction $2H_2 + O_2 \rightleftharpoons 2H_2O$

We consider as a specific example of a chemical reaction the combustion of hydrogen

$$2H_2 + O_2 \rightleftharpoons 2H_2O$$

In real life, this is a very complex chemical reaction that involves 19 elementary reversible reactions involving eight different species $H, O, OH, H_2, O_2, H_2O, HO_2, H_2O_2$ [?]. We will consider an oversimplified version with just only five species H, O, H_2, O_2, H_2O. The objective here is not to achieve realism but rather to illustrate the general mechanism by which the different affinities arise in the framework, reflecting the different chemical reactions that occur simultaneously in the system.

13.5.1 The CG variables

We start by introducing the atomic density fields

$$\hat{n}_{\mathbf{r}}^H = \sum_{i_H}^{N_H} \delta\left(\mathbf{r}_{i_H} - \mathbf{r}\right)$$

$$\hat{n}_{\mathbf{r}}^O = \sum_{i_O}^{N_O} \delta\left(\mathbf{r}_{i_O} - \mathbf{r}\right)$$

These fields describe the location of each single atom irrespectively of their state of association, i.e. whether they are a dissociated single atoms or forming part of a molecule. Next, we define the following molecular densities

$$\hat{n}_{\mathbf{r}}^{H_2} \equiv \frac{1}{2} \sum_{i_H \neq j_H}^{N_H} \theta^{H_2}\left(z_{i_H}, z_{j_H}\right) \delta\left(\frac{\mathbf{r}_{i_H} + \mathbf{r}_{j_H}}{2} - \mathbf{r}\right)$$

$$\hat{n}_{\mathbf{r}}^{O_2} \equiv \frac{1}{2} \sum_{i_O \neq j_O}^{N_O} \theta^{O_2}\left(z_{i_O}, z_{j_O}\right) \delta\left(\frac{\mathbf{r}_{i_O} + \mathbf{r}_{j_O}}{2} - \mathbf{r}\right)$$

$$\hat{n}_{\mathbf{r}}^{H_2O} \equiv \sum_{i_O}^{N_O} \frac{1}{2} \sum_{i_H \neq j_H}^{N_H} \theta^{H_2O}\left(z_{i_O}, z_{i_H}, z_{j_H}\right) \delta\left(\frac{m_O \mathbf{r}_{i_O} + m_H \mathbf{r}_{i_H} + m_H \mathbf{r}_{j_H}}{m_O + 2m_H} - \mathbf{r}\right)$$

Here, z_{i_H} are the position and momentum of the i-th Hydrogen atom, with analogous meaning for z_{i_O}. The functions $\theta^{H_2}\left(z_{i_H}, z_{j_H}\right)$, $\theta^{O_2}\left(z_{i_O}, z_{j_O}\right)$, $\theta^{H_2O}\left(z_{i_O}, z_{i_H}, z_{j_H}\right)$ are the *molecular template functions* of each molecular species. These functions take the value 1 (or close to 1) if the coordinates of the atoms are such that we may call such a microscopic configuration a "molecule". Once a given microscopic configuration of the atoms is considered a molecule, we consider that that molecule is located at the center of mass. Therefore, the Dirac delta functions in Eq. (13.5.1) "count" the number of molecules that are in the vicinity of $\mathbf{r}$. To fix ideas, a possible realization of the molecular template
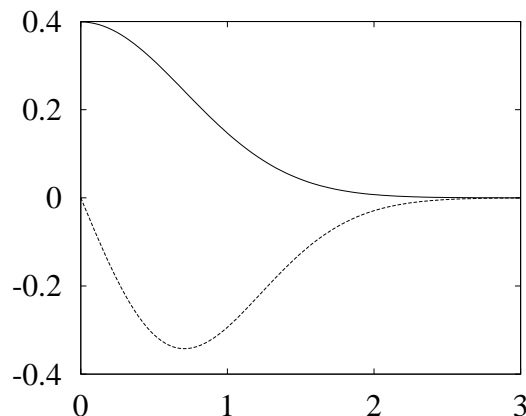
Figure 13.1: The function $\theta(r) = \frac{1}{\sqrt{2\pi}} \exp\{-r^2/r_c^2\}$ and its derivative.

$\theta^{H_2}(z_{i_H}, z_{j_H})$ could be

$$\theta^{H_2}(z_{i_H}, z_{j_H}) = \theta\left(|\mathbf{r}_{i_H} - \mathbf{r}_{j_H}|\right)$$

where the function $\theta(x)$ is a bell shaped function like, for example, a Gaussian of width r_c, see Fig. 13.1. This function ensures that when two atoms are close enough, they are counted as a "molecule" with position given at the center of mass of the two atoms. Of course, this way of characterizing an hydrogen molecule may be too simplistic because, we may also require that in order to be called a "molecule" two hydrogen atoms need to be in a bonded state, this is its energy should be smaller than the potential well of the interaction potential. Such a criteria necesarily involves the momentum of the atoms. Nevertheless, in this paper we do not address the problem of defining the molecular templates that are assumed to be given.

In this way, Eq. (13.5.1), $\hat{n}_{\mathbf{r}}^{H_2}$ count the pairs of atoms of H that are forming an H_2 molecule in a little volume around $\mathbf{r}$. The factor $1/2$ avoids double counting a molecule at $\mathbf{r}$ as we run over all pairs of atoms. The phase functions (13.5.1) do not still give the actual number density fields, denoted with $[H]_{\mathbf{r}}, [O]_{\mathbf{r}}, [H_2]_{\mathbf{r}}, [O_2]_{\mathbf{r}}, [H_2O]_{\mathbf{r}}$ of the different *species*. These number density fields satisfy the following conditions

$$[H]_{\mathbf{r}} + 2[H_2]_{\mathbf{r}} + 2[H_2O]_{\mathbf{r}} = \hat{n}_{\mathbf{r}}^{H}$$
$$[O]_{\mathbf{r}} + 2[O_2]_{\mathbf{r}} + [H_2O]_{\mathbf{r}} = \hat{n}_{\mathbf{r}}^{O}$$

In words, the number of H atoms that are at $\mathbf{r}$ (i.e. in a tiny cell around $\mathbf{r}$) is the sum of the dissociated H atoms, plus two atoms for every H_2 molecules that happen to be in the cell, plus 2 atoms for every water molecule in the cell. A similar interpretation holds for the second equation. These conditions allow to define the densities of dissociated atomic species [H],[O] in terms of the molecular densities $[H_2]$, $[O_2]$ and H_2O. The latter are

given by

$$[\text{H}_2\text{O}] = \hat{n}^{\text{H}_2\text{O}}$$
$$[\text{H}_2] = \hat{n}^{\text{H}_2}$$
$$[\text{O}_2] = \hat{n}^{\text{O}_2}$$

Note that we are assuming that the molecular template functions for each molecular specie is sufficiently elaborated to distinguish between species and not overcounting the presence of molecules. For example, if the template functions do not distinguish between the case that two atoms of hydrogen are forming an H_2 molecules or the case that they are part of a water molecule, then we would run into problems. Eqs. (13.5.1) reflect the fundamental law of conservation of the number of atoms of different kind. They will encode the stoichiometry of the chemical reactions.

In summary, we have the following definitions for the number density fields of the different species this is

$$[\text{H}_2\text{O}]_{\mathbf{r}} = \hat{n}_{\mathbf{r}}^{\text{H}_2\text{O}}$$
$$[\text{H}_2]_{\mathbf{r}} = \hat{n}_{\mathbf{r}}^{\text{H}_2}$$
$$[\text{O}_2]_{\mathbf{r}} = \hat{n}_{\mathbf{r}}^{\text{O}_2}$$
$$[\text{H}]_{\mathbf{r}} = \hat{n}_{\mathbf{r}}^{\text{H}} - 2\hat{n}_{\mathbf{r}}^{\text{H}_2} - 2\hat{n}_{\mathbf{r}}^{\text{H}_2\text{O}}$$
$$[\text{O}]_{\mathbf{r}} = \hat{n}_{\mathbf{r}}^{\text{O}} - 2\hat{n}_{\mathbf{r}}^{\text{O}_2} - \hat{n}_{\mathbf{r}}^{\text{H}_2\text{O}}$$

These fields are the CG variables of our system. Given the relevant variables, the theory of non-equilibrium statistical mechanics explicitly tells us how these variables will evolve, under the sole assumption that these are the only slow variables in the system.

In the present model of hydrogen combustion, we have only five different species. By the very fact that we consider these species and no others, we are limiting the possible kinetic paths in the combustion of hydrogen. Of course, the real reaction of combustion of hydrogen is very complex, involving 19 elementary reaction and, in addition to the above species, also the species HO and HO_2 participate [?]. We consider only five species for pedagogical purposes, in order to illustrate the general mechanism.

Chemical reactions may involve important temperature changes that affect the rate of the reaction. Some times these changes are so important that they lead to explosive behaviour with massive fluid movement. For these reasons, in addition to the CG variables (13.5.1) we would need to consider in general the momentum density field and the energy density field. However, in the present paper, we assume that the reaction takes place at such an slow rate that the fluid is at rest and the local energy inhomogeneities relax sufficiently fast that they can be ignored in the description. Therefore, we take as the only *additional* relevant variable the total energy of the system. We do not consider the energy density *field* as it is required when non-isothermal effects are important.

13.5.2   The relevant ensemble

With the above selection of CG variables $\hat{H}(z), [\hat{A}]_{\mathbf{r}}(z), [\hat{A}_2]_{\mathbf{r}}(z)$, the relevant ensemble (12.2) becomes

$$\overline{\rho}(z) = \frac{\rho^0}{Z[\beta, \lambda]} \exp\left\{-\beta\hat{H}(z)\right\} \exp\left\{-\int d\mathbf{r}' \left[\lambda^A(\mathbf{r}')[A]_{\mathbf{r}'}(z) + \lambda^{A_2}(\mathbf{r}')[A_2]_{\mathbf{r}'}(z)\right]\right\}$$

with the normalizing dimensionless partition function given by

$$Z[\beta, \lambda] = \mathrm{Tr}\left[\exp\left\{-\beta\hat{H}(z)\right\} \exp\left\{-\int d\mathbf{r}' \left[\lambda^A(\mathbf{r}')[A]_{\mathbf{r}'}(z) + \lambda^{A_2}(\mathbf{r}')[A_2]_{\mathbf{r}'}(z)\right]\right\}\right]$$

The conjugate variables $\beta, \lambda^A(\mathbf{r}), \lambda^{A_2}(\mathbf{r})$ have the physical meaning of the inverse temperature and the chemical potentials of the different species. They are adjusted in a way to produce the correct averages $E, [\hat{A}](\mathbf{r}), [A_2](\mathbf{r})$ for the CG variables, this is

$$\langle \hat{H} \rangle_t = E$$
$$\langle [\hat{A}]_{\mathbf{r}} \rangle_t = [A](\mathbf{r})$$
$$\langle [\hat{A}_2]_{\mathbf{r}} \rangle_t = [A_2](\mathbf{r})$$

The conjugate variables and the average of the CG variables are related by (12.2) that in the present case becomes

$$\frac{\partial \Phi}{\partial \beta}[\beta, \lambda] = E$$
$$\frac{\delta \Phi}{\delta \lambda^A(\mathbf{r})}[\beta, \lambda^A, \lambda^{A_2}] = [A](\mathbf{r})$$
$$\frac{\delta \Phi}{\delta \lambda^{A_2}(\mathbf{r})}[\beta, \lambda^A, \lambda^{A_2}] = [A_2](\mathbf{r})$$

The entropy (**??**) for this level of description is given by

$$S[E, [A], [A_2]] = -\Phi[\beta, \lambda^A, \lambda^{A_2}] + \int d\mathbf{r} \left[\lambda^A(\mathbf{r})[A](\mathbf{r}) + \lambda^{A_2}(\mathbf{r})[A_2](\mathbf{r})\right]$$

In this expression, $\beta, \lambda^A(\mathbf{r}), \lambda^{A_2}(\mathbf{r})$ are understood as functions of the averages $E, [A](\mathbf{r}), [A_2](\mathbf{r})$. The conjugate variables are given in terms of the derivatives of the entropy functional

$$\frac{\partial S}{\partial E} = \beta$$
$$\frac{\delta S}{\delta [A](\mathbf{r})}[E, [A], [A_2]] = \lambda^A(\mathbf{r})$$
$$\frac{\delta S}{\delta [A_2](\mathbf{r})}[E, [A], [A_2]] = \lambda^{A_2}(\mathbf{r})$$
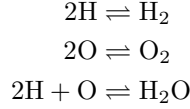
The relevant ensemble is given by (12.2) where the exponent term $\lambda \hat{A}(z)$ is given by the following expression

$$
\begin{aligned}
\lambda \hat{A}(z) &= \lambda^{\mathrm{H}}[\mathrm{H}]_{\mathbf{r}} + \lambda^{\mathrm{O}}[\mathrm{O}]_{\mathbf{r}} + \lambda^{\mathrm{H_2O}}[\mathrm{H_2O}]_{\mathbf{r}} + \lambda^{\mathrm{H_2}}[\mathrm{H_2}]_{\mathbf{r}} + \lambda^{\mathrm{O_2}}[\mathrm{O_2}]_{\mathbf{r}} \\
&= \lambda^{\mathrm{H_2O}}\hat{n}_{\mathbf{r}}^{\mathrm{H_2O}} + \lambda^{\mathrm{H_2}}\hat{n}_{\mathbf{r}}^{\mathrm{H_2}} + \lambda^{\mathrm{O_2}}\hat{n}_{\mathbf{r}}^{\mathrm{O_2}} + \lambda^{\mathrm{H}}(\hat{n}_{\mathbf{r}}^{\mathrm{H}} - 2\hat{n}_{\mathbf{r}}^{\mathrm{H_2}} - 2\hat{n}_{\mathbf{r}}^{\mathrm{H_2O}}) + \lambda^{\mathrm{O}}(\hat{n}_{\mathbf{r}}^{\mathrm{O}} - 2\hat{n}_{\mathbf{r}}^{\mathrm{O_2}} - \hat{n}_{\mathbf{r}}^{\mathrm{H_2O}}) \\
&= \lambda^{\mathrm{H}}\hat{n}_{\mathbf{r}}^{\mathrm{H}} + \lambda^{\mathrm{O}}\hat{n}_{\mathbf{r}}^{\mathrm{O}} + (\lambda^{\mathrm{H_2}} - 2\lambda^{\mathrm{H}})\hat{n}_{\mathbf{r}}^{\mathrm{H_2}} + (\lambda^{\mathrm{O_2}} - 2\lambda^{\mathrm{O}})\hat{n}_{\mathbf{r}}^{\mathrm{O_2}} + (\lambda^{\mathrm{H_2O}} - 2\lambda^{\mathrm{H}} - \lambda^{\mathrm{O}})\hat{n}_{\mathbf{r}}^{\mathrm{H_2O}} \\
&= \lambda^{\mathrm{H}}\hat{n}_{\mathbf{r}}^{\mathrm{H}} + \lambda^{\mathrm{O}}\hat{n}_{\mathbf{r}}^{\mathrm{O}} + \mathscr{A}^{\mathrm{H_2}}\hat{n}_{\mathbf{r}}^{\mathrm{H_2}} + \mathscr{A}^{\mathrm{O_2}}\hat{n}_{\mathbf{r}}^{\mathrm{O_2}} + \mathscr{A}^{\mathrm{H_2O}}\hat{n}_{\mathbf{r}}^{\mathrm{H_2O}}
\end{aligned}
$$

where we have introduced the following **afinities**

$$
\begin{aligned}
\mathscr{A}^{\mathrm{H_2}} &\equiv -2\lambda^{\mathrm{H}} + \lambda^{\mathrm{H_2}} \\
\mathscr{A}^{\mathrm{O_2}} &\equiv -2\lambda^{\mathrm{O}} + \lambda^{\mathrm{O_2}} \\
\mathscr{A}^{\mathrm{H_2O}} &\equiv -2\lambda^{\mathrm{H}} - \lambda^{\mathrm{O}} + \lambda^{\mathrm{H_2O}}
\end{aligned}
$$

These affinities do actually correspond to the usually defined affinities of the following three reactions

$$
\begin{aligned}
2\mathrm{H} &\rightleftharpoons \mathrm{H_2} \\
2\mathrm{O} &\rightleftharpoons \mathrm{O_2} \\
2\mathrm{H} + \mathrm{O} &\rightleftharpoons \mathrm{H_2O}
\end{aligned}
$$

13.5.3 Time derivatives

We observe that the concentration of each specie at point $\mathbf{r}$ in space changes in time at a microscopic level due to two different effects. One is the flow of matter because it is moving, captured with the diffusive flux $\mathbf{J}_{\mathbf{r}}^{M}$. The second effect is because atoms are moving and may "break" the molecule, this is, they may stop fullfilling the template condition that says that they form a molecule. This is captured by the production term $P_{\mathbf{r}}^{M}$ that characterizes the rate at which the specie M is being decomposed.

We first compute the time derivatives of the density fields (13.5.1)(13.5.1)

$$
\begin{aligned}
i\mathcal{L}\hat{n}_{\mathbf{r}}^{\mathrm{H}} &= -\nabla \mathbf{J}_{\mathbf{r}}^{\mathrm{H}} \\
i\mathcal{L}\hat{n}_{\mathbf{r}}^{\mathrm{O}} &= -\nabla \mathbf{J}_{\mathbf{r}}^{\mathrm{O}} \\
i\mathcal{L}\hat{n}_{\mathbf{r}}^{\mathrm{H_2}} &= -\nabla \mathbf{J}_{\mathbf{r}}^{\mathrm{H_2}} + P_{\mathbf{r}}^{\mathrm{H_2}} \\
i\mathcal{L}\hat{n}_{\mathbf{r}}^{\mathrm{O_2}} &= -\nabla \mathbf{J}_{\mathbf{r}}^{\mathrm{O_2}} + P_{\mathbf{r}}^{\mathrm{O_2}} \\
i\mathcal{L}\hat{n}_{\mathbf{r}}^{\mathrm{H_2O}} &= -\nabla \mathbf{J}_{\mathbf{r}}^{\mathrm{H_2O}} + P_{\mathbf{r}}^{\mathrm{H_2O}}
\end{aligned}
$$

where we have defined the current and production terms as

$$\mathbf{J}_{\mathbf{r}}^{H} \equiv \sum_{i_H}^{N_H} \mathbf{v}_{i_H} \delta \left(\mathbf{r}_{i_H} - \mathbf{r} \right)$$

$$\mathbf{J}_{\mathbf{r}}^{O} \equiv \sum_{i_O}^{N_O} \mathbf{v}_{i_O} \delta \left(\mathbf{r}_{i_O} - \mathbf{r} \right)$$

$$\mathbf{J}_{\mathbf{r}}^{H_2} \equiv \frac{1}{2} \sum_{i_H, j_H \neq}^{N_H} \theta^{H_2} \left(z_{i_H}, z_{j_H} \right) \frac{\mathbf{v}_{i_H} + \mathbf{v}_{j_H}}{2} \delta \left(\frac{\mathbf{r}_{i_H} + \mathbf{r}_{j_H}}{2} - \mathbf{r} \right)$$

$$\mathbf{J}_{\mathbf{r}}^{O_2} \equiv \frac{1}{2} \sum_{i_O, j_O \neq}^{N_O} \theta^{O_2} \left(z_{i_O}, z_{j_O} \right) \frac{\mathbf{v}_{i_O} + \mathbf{v}_{j_O}}{2} \delta \left(\frac{\mathbf{r}_{i_O} + \mathbf{r}_{j_O}}{2} - \mathbf{r} \right)$$

$$\mathbf{J}_{\mathbf{r}}^{H_2O} \equiv \sum_{i_O}^{N_O} \frac{1}{2} \sum_{i_H, j_H \neq}^{N_H} \theta^{H_2O} \left(z_{i_O}, z_{i_H}, z_{j_H} \right) \frac{m_O \mathbf{v}_{i_O} + m_H \mathbf{v}_{i_H} + m_H \mathbf{v}_{j_H}}{m_O + 2m_H} \delta \left(\frac{m_O \mathbf{r}_{i_O} + m_H \mathbf{r}_{i_H} + m_H \mathbf{r}_{j_H}}{m_O + 2m_H} - \mathbf{r} \right)$$

$$P_{\mathbf{r}}^{H_2} \equiv \frac{1}{2} \sum_{i_H, j_H \neq}^{N_H} i\mathcal{L} \theta^{H_2} \left(z_{i_H}, z_{j_H} \right) \delta \left(\frac{\mathbf{r}_{i_H} + \mathbf{r}_{j_H}}{2} - \mathbf{r} \right)$$

$$P_{\mathbf{r}}^{O_2} \equiv \frac{1}{2} \sum_{i_O, j_O \neq}^{N_O} i\mathcal{L} \theta^{O_2} \left(z_{i_O}, z_{j_O} \right) \delta \left(\frac{\mathbf{r}_{i_O} + \mathbf{r}_{j_O}}{2} - \mathbf{r} \right)$$

$$P_{\mathbf{r}}^{H_2O} \equiv \sum_{i_O}^{N_O} \frac{1}{2} \sum_{i_H, j_H \neq}^{N_H} i\mathcal{L} \theta^{H_2O} \left(z_{i_O}, z_{i_H}, z_{j_H} \right) \delta \left(\frac{m_O \mathbf{r}_{i_O} + m_H \mathbf{r}_{i_H} + m_H \mathbf{r}_{j_H}}{m_O + 2m_H} - \mathbf{r} \right)$$

We are now in position to consider the time derivatives of the concentration of different species (13.5.1)

$$i\mathcal{L}[H_2O]_{\mathbf{r}} = -\nabla \mathbf{J}_{\mathbf{r}}^{H_2O} + P_{\mathbf{r}}^{H_2O}$$
$$i\mathcal{L}[H_2]_{\mathbf{r}} = -\nabla \mathbf{J}_{\mathbf{r}}^{H_2} + P_{\mathbf{r}}^{H_2}$$
$$i\mathcal{L}[O_2]_{\mathbf{r}} = -\nabla \mathbf{J}_{\mathbf{r}}^{O_2} + P_{\mathbf{r}}^{O_2}$$
$$i\mathcal{L}[H]_{\mathbf{r}} = -\nabla \mathbf{J}_{\mathbf{r}}^{H} - 2\left(-\nabla \mathbf{J}_{\mathbf{r}}^{H_2} + P_{\mathbf{r}}^{H_2} - \nabla \mathbf{J}_{\mathbf{r}}^{H_2O} + P_{\mathbf{r}}^{H_2O}\right) \equiv -\nabla \mathbf{J}_{\mathbf{r}}^{[H]} - 2P_{\mathbf{r}}^{H_2} - 2P_{\mathbf{r}}^{H_2O}$$
$$i\mathcal{L}[O]_{\mathbf{r}} = -\nabla \mathbf{J}_{\mathbf{r}}^{O} - 2\left(-\nabla \mathbf{J}_{\mathbf{r}}^{O_2} + P_{\mathbf{r}}^{O_2}\right) - \left(-\nabla \mathbf{J}_{\mathbf{r}}^{H_2O} + P_{\mathbf{r}}^{H_2O}\right) \equiv -\nabla \mathbf{J}_{\mathbf{r}}^{[O]} - 2P_{\mathbf{r}}^{O_2} - P_{\mathbf{r}}^{H_2O}$$

where we have introduced the following molecular species currents

$$\mathbf{J}_{\mathbf{r}}^{[H]} \equiv \mathbf{J}_{\mathbf{r}}^{H} - 2\mathbf{J}_{\mathbf{r}}^{H_2} - 2\mathbf{J}_{\mathbf{r}}^{H_2O}$$
$$\mathbf{J}_{\mathbf{r}}^{[O]} \equiv \mathbf{J}_{\mathbf{r}}^{O} - 2\mathbf{J}_{\mathbf{r}}^{O_2} - \mathbf{J}_{\mathbf{r}}^{H_2O}$$

13.5.4   Reaction terms in the dynamics

If we focus only on the reactive terms and neglect for the time being the diffusive terms we will have

$$i\mathcal{L}[H]_{\mathbf{r}} = -2P_{\mathbf{r}}^{H_2} - 2P_{\mathbf{r}}^{H_2O}$$
$$i\mathcal{L}[O]_{\mathbf{r}} = -2P_{\mathbf{r}}^{O_2} - P_{\mathbf{r}}^{H_2O}$$
$$i\mathcal{L}[H_2]_{\mathbf{r}} = P_{\mathbf{r}}^{H_2}$$
$$i\mathcal{L}[O_2]_{\mathbf{r}} = P_{\mathbf{r}}^{O_2}$$
$$i\mathcal{L}[H_2O]_{\mathbf{r}} = P_{\mathbf{r}}^{H_2O}$$

The dissipative reactive part of the dynamics involves (in red is the Green-Kubo dissipative matrix)

$$
\partial_t \begin{pmatrix} [\mathrm{H}]_{\mathbf{r}} \\ [\mathrm{O}]_{\mathbf{r}} \\ [\mathrm{H}_2]_{\mathbf{r}} \\ [\mathrm{O}_2]_{\mathbf{r}} \\ [\mathrm{H}_2\mathrm{O}]_{\mathbf{r}} \end{pmatrix} = \int d\mathbf{r}' \int_0^{\Delta t} dt \left\langle \begin{pmatrix} \color{red}{-2P_{\mathbf{r}}^{\mathrm{H}_2} - 2P_{\mathbf{r}}^{\mathrm{H}_2\mathrm{O}}} \\ \color{red}{-2P_{\mathbf{r}}^{\mathrm{O}_2} - P_{\mathbf{r}}^{\mathrm{H}_2\mathrm{O}}} \\ \color{red}{P_{\mathbf{r}}^{\mathrm{H}_2}} \\ \color{red}{P_{\mathbf{r}}^{\mathrm{O}_2}} \\ \color{red}{P_{\mathbf{r}}^{\mathrm{H}_2\mathrm{O}}} \end{pmatrix} \color{red}{\left(-2P_{\mathbf{r}'}^{\mathrm{H}_2}(t) - 2P_{\mathbf{r}'}^{\mathrm{H}_2\mathrm{O}}(t), -2P_{\mathbf{r}'}^{\mathrm{O}_2} - P_{\mathbf{r}'}^{\mathrm{H}_2\mathrm{O}}(t), P_{\mathbf{r}'}^{\mathrm{H}_2}(t), P_{\mathbf{r}'}^{\mathrm{O}_2}(t), P^{\mathrm{H}_2\mathrm{O}}(t) \right.}
$$

$$
\times \begin{pmatrix} \lambda_{\mathbf{r}'}^{[\mathrm{H}]} \\ \lambda_{\mathbf{r}'}^{[\mathrm{O}]} \\ \lambda_{\mathbf{r}'}^{[\mathrm{H}_2]} \\ \lambda_{\mathbf{r}'}^{[\mathrm{O}_2]} \\ \lambda_{\mathbf{r}'}^{[\mathrm{H}_2\mathrm{O}]} \end{pmatrix}
$$

This is

$$
\partial_t \begin{pmatrix} [\mathrm{H}]_{\mathbf{r}} \\ [\mathrm{O}]_{\mathbf{r}} \\ [\mathrm{H}_2]_{\mathbf{r}} \\ [\mathrm{O}_2]_{\mathbf{r}} \\ [\mathrm{H}_2\mathrm{O}]_{\mathbf{r}} \end{pmatrix} = \int d\mathbf{r}' \int_0^{\Delta t} dt \left\langle \begin{pmatrix} \color{red}{-2P_{\mathbf{r}}^{\mathrm{H}_2} - 2P_{\mathbf{r}}^{\mathrm{H}_2\mathrm{O}}} \\ \color{red}{-2P_{\mathbf{r}}^{\mathrm{O}_2} - P_{\mathbf{r}}^{\mathrm{H}_2\mathrm{O}}} \\ \color{red}{P_{\mathbf{r}}^{\mathrm{H}_2}} \\ \color{red}{P_{\mathbf{r}}^{\mathrm{O}_2}} \\ \color{red}{P_{\mathbf{r}}^{\mathrm{H}_2\mathrm{O}}} \end{pmatrix} \left(P_{\mathbf{r}'}^{\mathrm{H}_2}(t)\mathscr{A}_{\mathbf{r}'}^{\mathrm{H}_2} + P_{\mathbf{r}'}^{\mathrm{O}_2}(t)\mathscr{A}_{\mathbf{r}'}^{\mathrm{O}_2} + P_{\mathbf{r}'}^{\mathrm{H}_2\mathrm{O}}(t)\mathscr{A}_{\mathbf{r}'}^{\mathrm{H}_2\mathrm{O}} \right) \right\rangle
$$

From Eq. (13.5.4), the final dynamic equations for the kinetics of the chemical reactions are

$$\partial_t [\mathrm{H}]_{\mathbf{r}} = \int d\mathbf{r}' - 2(\mathscr{R}_{\mathbf{rr}'}^{11} + \mathscr{R}_{\mathbf{rr}'}^{31})\mathscr{A}_{\mathbf{r}'}^{\mathrm{H}_2} \quad -2(\mathscr{R}_{\mathbf{rr}'}^{12} + \mathscr{R}_{\mathbf{rr}'}^{32})\mathscr{A}_{\mathbf{r}'}^{\mathrm{O}_2} - 2(\mathscr{R}_{\mathbf{rr}'}^{13} + \mathscr{R}_{\mathbf{rr}'}^{33})\mathscr{A}_{\mathbf{r}'}^{\mathrm{H}_2\mathrm{O}}$$

$$\partial_t [\mathrm{O}]_{\mathbf{r}} = \int d\mathbf{r}' - (2\mathscr{R}_{\mathbf{rr}'}^{21} + \mathscr{R}_{\mathbf{rr}'}^{31})\mathscr{A}_{\mathbf{r}'}^{\mathrm{H}_2} \quad -(2\mathscr{R}_{\mathbf{rr}'}^{22} + \mathscr{R}_{\mathbf{rr}'}^{32})\mathscr{A}_{\mathbf{r}'}^{\mathrm{O}_2} - 2(\mathscr{R}_{\mathbf{rr}'}^{23} + \mathscr{R}_{\mathbf{rr}'}^{33})\mathscr{A}_{\mathbf{r}'}^{\mathrm{H}_2\mathrm{O}}$$

$$\partial_t [\mathrm{H}_2]_{\mathbf{r}} = \int d\mathbf{r}' \mathscr{R}_{\mathbf{rr}'}^{11} \mathscr{A}_{\mathbf{r}'}^{\mathrm{H}_2} \qquad\qquad\qquad +\mathscr{R}_{\mathbf{rr}'}^{12}\mathscr{A}_{\mathbf{r}'}^{\mathrm{O}_2} + \mathscr{R}_{\mathbf{rr}'}^{13}\mathscr{A}_{\mathbf{r}'}^{\mathrm{H}_2\mathrm{O}}$$

$$\partial_t [\mathrm{O}_2]_{\mathbf{r}} = \int d\mathbf{r}' \mathscr{R}_{\mathbf{rr}'}^{21} \mathscr{A}_{\mathbf{r}'}^{\mathrm{H}_2} \qquad\qquad\qquad +\mathscr{R}_{\mathbf{rr}'}^{22}\mathscr{A}_{\mathbf{r}'}^{\mathrm{O}_2} + \mathscr{R}_{\mathbf{rr}'}^{23}\mathscr{A}_{\mathbf{r}'}^{\mathrm{H}_2\mathrm{O}}$$

$$\partial_t [\mathrm{H}_2\mathrm{O}]_{\mathbf{r}} = \int d\mathbf{r}' \mathscr{R}_{\mathbf{rr}'}^{31} \mathscr{A}_{\mathbf{r}'}^{\mathrm{H}_2} \qquad\qquad\qquad +\mathscr{R}_{\mathbf{rr}'}^{32}\mathscr{A}_{\mathbf{r}'}^{\mathrm{O}_2} + \mathscr{R}_{\mathbf{rr}'}^{23}\mathscr{A}_{\mathbf{r}'}^{\mathrm{H}_2\mathrm{O}}$$

where we have introduced the following non-local rate matrix

$$\begin{pmatrix} \mathscr{R}_{\mathbf{rr}'}^{11} & \mathscr{R}_{\mathbf{rr}'}^{12} & \mathscr{R}_{\mathbf{rr}'}^{13} \\ \mathscr{R}_{\mathbf{rr}'}^{21} & \mathscr{R}_{\mathbf{rr}'}^{22} & \mathscr{R}_{\mathbf{rr}'}^{23} \\ \mathscr{R}_{\mathbf{rr}'}^{31} & \mathscr{R}_{\mathbf{rr}'}^{32} & \mathscr{R}_{\mathbf{rr}'}^{23} \end{pmatrix} = \begin{pmatrix} \int_0^{\Delta t} dt \left\langle P_{\mathbf{r}}^{\mathrm{H}_2} P_{\mathbf{r}}^{\mathrm{H}_2}(t) \right\rangle & \int_0^{\Delta t} dt \left\langle P_{\mathbf{r}}^{\mathrm{H}_2} P_{\mathbf{r}}^{\mathrm{O}_2}(t) \right\rangle & \int_0^{\Delta t} dt \left\langle P_{\mathbf{r}}^{\mathrm{H}_2} P_{\mathbf{r}}^{\mathrm{H}_2\mathrm{O}}(t) \right\rangle \\ \int_0^{\Delta t} dt \left\langle P_{\mathbf{r}}^{\mathrm{O}_2} P_{\mathbf{r}}^{\mathrm{H}_2}(t) \right\rangle & \int_0^{\Delta t} dt \left\langle P_{\mathbf{r}}^{\mathrm{O}_2} P_{\mathbf{r}}^{\mathrm{O}_2}(t) \right\rangle & \int_0^{\Delta t} dt \left\langle P_{\mathbf{r}}^{\mathrm{O}_2} P_{\mathbf{r}}^{\mathrm{H}_2\mathrm{O}}(t) \right\rangle \\ \int_0^{\Delta t} dt \left\langle P_{\mathbf{r}}^{\mathrm{H}_2\mathrm{O}} P_{\mathbf{r}}^{\mathrm{H}_2}(t) \right\rangle & \int_0^{\Delta t} dt \left\langle P_{\mathbf{r}}^{\mathrm{H}_2\mathrm{O}} P_{\mathbf{r}}^{\mathrm{O}_2}(t) \right\rangle & \int_0^{\Delta t} dt \left\langle P_{\mathbf{r}}^{\mathrm{H}_2\mathrm{O}} P_{\mathbf{r}}^{\mathrm{H}_2\mathrm{O}}(t) \right\rangle \end{pmatrix}$$

The correlation function here are computed with the relevant ensemble. This is

$$\int_0^{\Delta t} dt \left\langle P_{\mathbf{r}}^{\alpha} P_{\mathbf{r}}^{\beta}(t) \right\rangle = \int_0^{\Delta t} dt \mathrm{Tr}[\overline{\rho}_t P_{\mathbf{r}}^{\alpha} P_{\mathbf{r}}^{\beta}(t)]$$

13.6   Inhibiting some reaction paths

Note that in (13.5.2) we have an elementary chemical reaction for every molecular specie that we have defined. These elementary reactions describe the formation/dissociation of molecules from dissociated atomic species. Of course, the reaction path does not necessarily go from dissociated atoms to molecules. We may have that a molecule breaks into molecules, for example, or other possible processes. We study next how to describe these situations through the concept of *inhibited reaction paths*. It may happen that, for the given conditions of the system, the microscopic states visited by the system are such that they imply that some of the phase functions (13.5.1) take always the value zero. In plain words, certain species are not present in the system. Let us consider first the case that we do not have any dissociated atomic specie, this is $[\mathrm{H}]_{\mathbf{r}} = 0$, and $[\mathrm{O}]_{\mathbf{r}} = 0$. From Eq. (13.5.4), this implies some conditions on the production terms. In particular,

$$P_{\mathbf{r}}^{\mathrm{H}_2} = -P_{\mathbf{r}}^{\mathrm{H}_2\mathrm{O}}$$
$$2P_{\mathbf{r}}^{\mathrm{O}_2} = -P_{\mathbf{r}}^{\mathrm{H}_2\mathrm{O}}$$

The intuitive meaning of these conditions is clear: the rate of creation of molecules of H_2 is exactly equal to the rate of destruction of molecules H_2O and, for every two molecules of O_2 that are created, on molecule of H_2O is destroyed. We should note that the production terms are, in fact, phase functions that depend on the microstate. In fact, using (13.5.3) into (13.6) we have

$$\frac{1}{2}\sum_{i_H,j_H\neq}^{N_H} i\mathcal{L}\theta^{H_2}\left(z_{i_H},z_{j_H}\right)\delta\left(\frac{\mathbf{r}_{i_H}+\mathbf{r}_{j_H}}{2}-\mathbf{r}\right) = -\sum_{i_O}^{N_O}\frac{1}{2}\sum_{i_H,j_H\neq}^{N_H} i\mathcal{L}\theta^{H_2O}\left(z_{i_O},z_{i_H},z_{j_H}\right)\delta\left(\frac{m_O\mathbf{r}_{i_O}+m_H\mathbf{r}_{i_H}+m_H\mathbf{r}_{j_H}}{m_O+2m_H}-\mathbf{r}\right)$$

The phase functions in the right and left of this equation are formally very different (they depend on different variables indeed). The identities (13.6) should be, therefore, understood not as an exact mathematical identity, but rather as an approximate condition.

Substitution of (13.6) into (13.5.4) implies

$$\partial_t\begin{pmatrix}[H]\\[6pt][O]\\[6pt][H_2]\\[6pt][O_2]\\[6pt][H_2O]\end{pmatrix} = \int_0^{\Delta t} dt \begin{pmatrix}0\\[6pt]0\\[6pt]-P_{\mathbf{r}}^{H_2O}\\[6pt]-\frac{1}{2}P_{\mathbf{r}}^{H_2O}\\[6pt]P_{\mathbf{r}}^{H_2O}\end{pmatrix}\left(P_{\mathbf{r}}^{H_2O}(t)\mathscr{A}_{\mathbf{r}}^{H_2O}\right) = \begin{pmatrix}0\\[6pt]0\\[6pt]-2\\[6pt]-1\\[6pt]2\end{pmatrix}\mathscr{R}_{\mathbf{rr}'}\mathscr{A}_{\mathbf{r}}^{H_2O}$$

This is

$$\partial_t[H]_{\mathbf{r}} = 0$$
$$\partial_t[O]_{\mathbf{r}} = 0$$
$$\partial_t[H_2]_{\mathbf{r}} = -2\mathscr{R}_{\mathbf{rr}'}^{33}\mathscr{A}_{\mathbf{r}}^{H_2O}$$
$$\partial_t[O_2]_{\mathbf{r}} = -\mathscr{R}_{\mathbf{rr}'}^{33}\mathscr{A}_{\mathbf{r}}^{H_2O}$$
$$\partial_t[H_2O]_{\mathbf{r}} = \mathscr{R}_{\mathbf{rr}'}^{33}\mathscr{A}_{\mathbf{r}}^{H_2O}$$

This is the reaction kinetics for the reaction

$$2H_2 + O_2 \rightleftharpoons 2H_2O$$
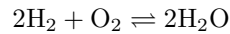
To get more experience now, consider the situation that

$$P_{\mathbf{r}}^{H_2} = -P_{\mathbf{r}}^{H_2O}$$
$$2P_{\mathbf{r}}^{O_2} \neq -P_{\mathbf{r}}^{H_2O}$$

This will imply that there are no dissociated hydrogen atoms but there are dissociated oxigen atoms. What is the reaction kinetics in this case? Clearly, we will have two

chemical reactions. If we go to Eq. (13.5.4) and use (13.6)

$$\partial_t \begin{pmatrix} [\mathrm{H}] \\ [\mathrm{O}] \\ [\mathrm{H}_2] \\ [\mathrm{O}_2] \\ [\mathrm{H}_2\mathrm{O}] \end{pmatrix} = \int_0^{\Delta t} dt \begin{pmatrix} 0 \\ -2P_{\mathbf{r}}^{\mathrm{O}_2} - P_{\mathbf{r}}^{\mathrm{H}_2\mathrm{O}} \\ -P_{\mathbf{r}}^{\mathrm{H}_2\mathrm{O}} \\ P_{\mathbf{r}}^{\mathrm{O}_2} \\ P_{\mathbf{r}}^{\mathrm{H}_2\mathrm{O}} \end{pmatrix} \left(-P_{\mathbf{r}}^{\mathrm{H}_2\mathrm{O}}(t)\mathscr{A}_{\mathbf{r}}^{\mathrm{H}_2} + P_{\mathbf{r}}^{\mathrm{O}_2}(t)\mathscr{A}_{\mathbf{r}}^{\mathrm{O}_2} + P_{\mathbf{r}}^{\mathrm{H}_2\mathrm{O}}(t)\mathscr{A}_{\mathbf{r}}^{\mathrm{H}_2\mathrm{O}} \right)$$

$$= \int_0^{\Delta t} dt \begin{pmatrix} 0 \\ -2P_{\mathbf{r}}^{\mathrm{O}_2} - P_{\mathbf{r}}^{\mathrm{H}_2\mathrm{O}} \\ -P_{\mathbf{r}}^{\mathrm{H}_2\mathrm{O}} \\ P_{\mathbf{r}}^{\mathrm{O}_2} \\ P_{\mathbf{r}}^{\mathrm{H}_2\mathrm{O}} \end{pmatrix} \left(P_{\mathbf{r}}^{\mathrm{O}_2}(t)\mathscr{A}_{\mathbf{r}}^{\mathrm{O}_2} + P_{\mathbf{r}}^{\mathrm{H}_2\mathrm{O}}(t)(\mathscr{A}_{\mathbf{r}}^{\mathrm{H}_2\mathrm{O}} - \mathscr{A}_{\mathbf{r}}^{\mathrm{H}_2}) \right)$$

where we have introduced the following afinities

$$\mathscr{A}_{\mathbf{r}}^{\mathrm{H}_2} \equiv -2\lambda^{\mathrm{H}} + \lambda^{\mathrm{H}_2}$$
$$\mathscr{A}_{\mathbf{r}}^{\mathrm{O}_2} \equiv -2\lambda^{\mathrm{O}} + \lambda^{\mathrm{O}_2}$$
$$\mathscr{A}_{\mathbf{r}}^{\mathrm{H}_2\mathrm{O}} \equiv -2\lambda^{\mathrm{H}} - \lambda^{\mathrm{O}} + \lambda^{\mathrm{H}_2\mathrm{O}}$$
$$\mathscr{B}_{\mathbf{r}}^{\mathrm{H}_2\mathrm{O}} = \mathscr{A}_{\mathbf{r}}^{\mathrm{H}_2\mathrm{O}} - \mathscr{A}_{\mathbf{r}}^{\mathrm{H}_2} \equiv -\lambda^{\mathrm{O}} + \lambda^{\mathrm{H}_2\mathrm{O}} - \lambda^{\mathrm{H}_2}$$

The resulting chemical reaction kinetics is

$$
\partial_t
\begin{pmatrix}
[\text{H}]_{\mathbf{r}} \\
[\text{O}]_{\mathbf{r}} \\
[\text{H}_2]_{\mathbf{r}} \\
[\text{O}_2]_{\mathbf{r}} \\
[\text{H}_2\text{O}]_{\mathbf{r}}
\end{pmatrix}
= \int_0^{\Delta t} dt \left\langle
\begin{pmatrix}
0 \\
-2P_{\mathbf{r}}^{\text{O}_2} - P_{\mathbf{r}}^{\text{H}_2\text{O}} \\
-P_{\mathbf{r}}^{\text{H}_2\text{O}} \\
P_{\mathbf{r}}^{\text{O}_2} \\
P_{\mathbf{r}}^{\text{H}_2\text{O}}
\end{pmatrix}
\left(P_{\mathbf{r}}^{\text{O}_2}(t)\mathscr{A}_{\mathbf{r}}^{\text{O}_2} + P_{\mathbf{r}}^{\text{H}_2\text{O}}(t)\mathscr{B}_{\mathbf{r}}^{\text{H}_2\text{O}} \right) \right\rangle
$$

$$
=
\begin{pmatrix}
0 \\
-2\mathscr{R}_{\mathbf{rr'}}^{2} - \mathscr{R}_{\mathbf{rr'}}^{1} \\
-\mathscr{R}_{\mathbf{rr'}}^{1} \\
\mathscr{R}_{\mathbf{rr'}}^{2} \\
\mathscr{R}_{\mathbf{rr'}}^{1}
\end{pmatrix}
\mathscr{A}_{\mathbf{r}}^{\text{O}_2} +
\begin{pmatrix}
0 \\
-2\mathscr{R}_{\mathbf{rr'}}^{1} - \mathscr{R}_{\mathbf{rr'}}^{3} \\
-\mathscr{R}_{\mathbf{rr'}}^{3} \\
\mathscr{R}_{\mathbf{rr'}}^{1} \\
\mathscr{R}_{\mathbf{rr'}}^{3}
\end{pmatrix}
\mathscr{B}_{\mathbf{r}}^{\text{H}_2\text{O}}
$$

The two affinities appearing here correspond to the two chemical reactions

$$2\text{O} \rightleftharpoons \text{O}_2$$
$$\text{O} + \text{H}_2 \rightleftharpoons \text{H}_2\text{O}$$
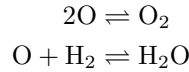
We conclude, therefore, that through **inhibitory conditions** like (13.6) and (13.6), that enforce that some species do not appear in the mixture, we may have different reaction paths as, for example (13.6) or (13.6). The corresponding stoichiometric relations emerge in a natural way from the framework.

13.7   Isomerization and cyclic reactions

Isomerization reactions are those occurring between species in which there is a rearrangement of the atoms within the molecule, but there is no exchange of atoms with other molecules. In the present theory, isomerization reactions involve just using two different molecular templates for each isomer. The dissociated atomic species are inhibited in such a reaction.

13.8   Chemical reactions: the general case

Now that we have considered several examples of chemical reactions, we have the general pattern and can consider an arbitrary number of chemical species that undergo chemical reactions. In all cases, it is important to distinguish between dissociated atomic species and molecular species. This distintion leads naturally to a preferred set of chemical

reactions, those in which molecules are fully dissociated into atoms. Of course, if some dissociated atomic species is inhibited, in the sense that it never occurs in the microscopic evolution of the system, this shows up in the form of further conditions on the type of chemical reactions that may occur in the system.

13.8.1   Selection of CG variables

We consider now the general case in which we have S different species. We need to introduce a notation for labeling the different species. The labeling will be made through vector $\mathbf{m}^\alpha \in \mathbf{R}^Z$ with $\alpha = 1, \cdots, S$ where Z is the number of the different atomic elements that are present in the system. For example, in the case of hydrogen combustion discussed in the previous section, $Z = 2$ because we have only hydrogen and oxygen in the system. In the previous hydrogen combustion example, the vector $\mathbf{m}^\alpha$ for the different species are

$$\mathbf{m}^1 = (1,0) \qquad\qquad \mathrm{H}$$
$$\mathbf{m}^2 = (0,1) \qquad\qquad \mathrm{O}$$
$$\mathbf{m}^3 = (2,0) \qquad\qquad \mathrm{H}_2$$
$$\mathbf{m}^4 = (0,2) \qquad\qquad \mathrm{O}_2$$
$$\mathbf{m}^5 = (2,1) \qquad\qquad \mathrm{H}_2\mathrm{O}$$

We distinguish between *dissociated atomic species* (those corresponding to $\alpha = 1, \cdots, Z$ above, i.e. $\mathbf{m}^1, \mathbf{m}^2$) and *molecular species* (those for $\alpha = Z+1, \cdots, S$ i.e. $\mathbf{m}^3, \mathbf{m}^4, \mathbf{m}^5$). We define the *microscopic concentration field of molecular species* as follows

$$[\mathbf{m}^\alpha]_{\mathbf{r}}(z) = \sum_{\text{tuples of atoms of molecule } \alpha} \theta^\alpha(z)\delta(\mathbf{r}^\alpha - \mathbf{r})$$

where $\mathbf{r}^\alpha$ is the position of the center of mass and $\theta^\alpha(z)$ is the molecular template of the species α. Recall that this template takes the value 1 if a given tuple of atoms are in a configuration that we recognize as a molecule of specie α. The use of a molecular template in the definition of the concentration of a molecular specie is slightly different from the use of a projection operator as in Ref. [?]. Here, the molecular template θ^α is a function in phase space that takes the value 1 for those microstates that we would recognize as a molecule of a given specie. The sum over atoms in (13.8.1) is over all the atoms of different type that may form a molecule of specie α. Examples are given for the case of hydrogen combustion in the previous section in Eqs. (13.5.1). The molecular templates in (13.5.1) are based on proximity criteria alone, but it may be important to characterize what constitutes a molecule through the energy of the group of atoms or, perhaps, the angle that form different bonds between atoms. Be it the case, the molecular template $\theta^\alpha(z)$ depends only on the coordinates of the atoms which are candidates to form a molecule of specie α.

The concentration of molecular species in (13.8.1) has been defined only for those species that are molecules. It is not defined yet for the species of dissociated atoms (like the species $\mathbf{m}^1, \mathbf{m}^2$ above corresponding to dissociated hydrogen and dissociated oxygen).

The concentration of dissociated atomic species is *defined* through the conservation of the number of atoms of different kind gives rise to the following identities

$$\sum_{\alpha}^{S} m_i^{\alpha}[\mathbf{m}^{\alpha}]_{\mathbf{r}} = \hat{n}_{\mathbf{r}}^i \qquad\qquad i = 1, \cdots, Z$$

Here, m_i^{α} is the i-th component of the vector $\mathbf{m}^{\alpha}$. The number density fields $\hat{n}_{\mathbf{r}}^i$ is defined as

$$\hat{n}_{\mathbf{r}}^i = \sum_{k=1}^{N_i} \delta(\mathbf{r} - \mathbf{r}_k)$$

and give the number density of atoms of type i irrespective of their state of association. N_i is the total number of atoms of element i in the system. The above Z equations, allow to *define* the Z fields of *dissociated atomic species* in terms of the molecular species defined in (13.8.1), this is

$$[\mathbf{m}^i]_{\mathbf{r}} \equiv \hat{n}_{\mathbf{r}}^i - \sum_{\alpha=Z+1}^{S} m_i^{\alpha}[\mathbf{m}^{\alpha}]_{\mathbf{r}} \qquad\qquad i = 1, \cdots, Z$$

We will take the first values of the index $\alpha = 1, \cdots, Z$ to correspond to the dissociated atomic species. We may also denote the concentration of the dissociated atomic species by

$$[\text{i}]_{\mathbf{r}} = [\mathbf{m}^i]_{\mathbf{r}} \qquad\qquad i = 1, \cdots, Z$$

13.8.2   The dynamic equation

A direct translation of the general dynamic equation (12.2) for the averages of the relevant functions takes the following form in the present selection of CG variables

$$\partial_t E = 0$$

$$\partial_t [\mathbf{m}^{\alpha}](\mathbf{r}) = v^{\alpha}(\mathbf{r}) + \int d\mathbf{r}' \mathscr{D}_{\mathbf{r}\mathbf{r}'}^{\alpha\beta} \lambda^{\beta}(\mathbf{r}')$$

where the drift term is

$$v^{\alpha}(\mathbf{r}) = \text{Tr}\left[\overline{\rho}_t i\mathcal{L}[\mathbf{m}^{\alpha}]\right],$$

the dissipative matrix is given explicitly by the Green-Kubo formula

$$\mathscr{D}_{\mathbf{r}\mathbf{r}'}^{\alpha\beta} = \int_0^{\Delta t} dt \,\text{Tr}\left[\overline{\rho}_t \left(\mathscr{Q}_t i\mathcal{L}[\mathbf{m}^{\beta}]_{\mathbf{r}'}\right) \exp\{i\mathcal{L}t\} \left(\mathscr{Q}_t i\mathcal{L}[\mathbf{m}^{\alpha}]_{\mathbf{r}}\right)\right]$$

and the chemical potentials $\lambda^\alpha(\mathbf{r})$ are given in terms of the functional derivatives of the entropy function, i.e.

$$\lambda^\alpha(\mathbf{r}) \equiv \frac{\delta S}{\delta[\mathbf{m}^\alpha](\mathbf{r})}[E, [\mathbf{m}]]$$

Let us discuss each bit of this dynamic equation, starting first with the conjugate variable $\lambda^\alpha(\mathbf{r})$. But first we need to discuss the relevant ensemble for this particular selection of CG variables.

13.8.3   The relevant ensemble

The relevant ensemble (12.2) when the CG variables are the total energy $\hat{H}(z)$ and the S concentration fields of the different species $[\mathbf{m}^\alpha]_{\mathbf{r}}(z)$ takes the form

$$\overline{\rho}(z) = \frac{1}{Z} \exp\{-\beta\hat{H}(z)\} \exp\left\{-\int d\mathbf{r} \sum_{\alpha=1}^{S} \lambda^\alpha(\mathbf{r})[\mathbf{m}^\alpha]_{\mathbf{r}}(z)\right\}$$

Let us consider the combination appearing in the argument of the exponential

$$\sum_{\alpha=1}^{S} \int d\mathbf{r}\lambda^\alpha(\mathbf{r})[\mathbf{m}^\alpha]_{\mathbf{r}}$$

$$= \sum_{i=1}^{Z} \int d\mathbf{r}\lambda^i(\mathbf{r})[\mathbf{m}^i]_{\mathbf{r}} + \sum_{\alpha=Z+1}^{S} \int d\mathbf{r}\lambda^\alpha(\mathbf{r})[\mathbf{m}^\alpha]_{\mathbf{r}}+$$

$$= \sum_{i=1}^{Z} \int d\mathbf{r}\lambda^i(\mathbf{r})\hat{n}_{\mathbf{r}}^i - \sum_{i=1}^{Z} \int d\mathbf{r}\lambda^i(\mathbf{r}) \sum_{\alpha=Z+1}^{S} m_i^\alpha[\mathbf{m}^\alpha]_{\mathbf{r}} + \sum_{\alpha=Z+1}^{S} \int d\mathbf{r}\lambda^\alpha(\mathbf{r})[\mathbf{m}^\alpha]_{\mathbf{r}}$$

$$= \sum_{i=1}^{Z} \int d\mathbf{r}\lambda^i(\mathbf{r})\hat{n}_{\mathbf{r}}^i + \sum_{\alpha=Z+1}^{S} \int d\mathbf{r}\mathscr{A}_{\mathbf{r}}^\alpha[\mathbf{m}^\alpha]_{\mathbf{r}}$$

where we have introduced the **affinity of the molecules of specie** α as the following linear combination of chemical potentials $\lambda^\alpha(\mathbf{r})$ of the different species

$$\mathscr{A}_{\mathbf{r}}^\alpha \equiv \lambda^\alpha(\mathbf{r}) - \sum_{i=1}^{Z} m_i^\alpha \lambda^i(\mathbf{r}) \qquad\qquad \alpha = Z+1, \cdots S$$

We have an affinity for each molecular specie α. We may understand this affinity as the one corresponding to the elementary chemical reaction in which a molecule of type α dissociates/associates reversible and completely in terms of its constituent atomic species, this is

$$\sum_{i=1}^{Z} m_i^\alpha[\mathbf{i}] \rightleftharpoons [\mathbf{m}^\alpha] \qquad\qquad \alpha = Z+1, \cdots, S$$

where $[i], i = 1, \cdots, Z$ is the concentration field of dissociated atomic species i.

The entropy function of the selected level of description is given by evaluating the Gibbs-Jaynes entropy (12.2) at the relevant ensemble (13.8.3). The result is

$$S[E, [\mathbf{m}]] = -\ln Z[\beta, \lambda] - \sum_{\alpha=1}^{S} \lambda^{\alpha}(\mathbf{r})[\mathbf{m}^{\alpha}](\mathbf{r})$$

In general, the calculation of the thermodynamic potential $\Phi = -\ln Z$ is imposible to perform exactly, except for ideal non-interacting systems. In this latter case the result is

$$\Phi =$$

and the entropy is

$$S =$$

When interactions are important, one needs to model

13.8.4   The time derivative of the CG variables

The time derivative of the CG variables selected are of the general structure

$$i\mathcal{L}[\mathbf{m}^{\alpha}]_{\mathbf{r}}(z) = P_{\mathbf{r}}^{\alpha}(z) - \nabla \mathbf{J}_{\mathbf{r}}^{\alpha}(z)$$

where

$$P_{\mathbf{r}}^{\alpha}(z) \equiv \sum_{\text{tuples}} i\mathcal{L}\theta^{\alpha}(z)\delta(\mathbf{r}^{\alpha} - \mathbf{r})$$

$$\mathbf{J}_{\mathbf{r}}^{\alpha}(z) \equiv \sum_{\text{tuples}} \theta^{\alpha}(z)\mathbf{v}^{\alpha}\delta(\mathbf{r}^{\alpha} - \mathbf{r})$$

The term $P_{\mathbf{r}}^{\alpha}$ can be named the microscopic rate of production per unit volume of species α whereas $\mathbf{J}_{\mathbf{r}}^{\alpha}$ is the microscopic mass flux of species α, because $\mathbf{v}^{\alpha}$ is the velocity of the center of mass of molecule of specie α.

Now, because the concentration of the dissociated atomic species is defined in Eq. (13.8.1) in terms of the molecular concentrations, the time derivatives of the dissociated atomic species are given in terms of the time derivatives of the rest of molecular species. For example

$$i\mathcal{L}[\mathbf{m}^{i}]_{\mathbf{r}} = -\nabla \left(\mathbf{g}_{\mathbf{r}}^{i} - \sum_{\alpha=Z+1}^{S} m_{i}^{\alpha}\mathbf{J}_{\mathbf{r}}^{\alpha}(z) \right) - \sum_{\alpha=Z+1}^{S} m_{i}^{\alpha}P_{\mathbf{r}}^{\alpha}(z) \quad i = 1, \cdots, Z$$

where we have introduced

$$\mathbf{g}_{\mathbf{r}}^{i}(z) = \sum_{k=1}^{N_{i}} \mathbf{v}_{k}\delta(\mathbf{r} - \mathbf{r}_{k})$$

as the total atomic current of element i. In this way, we have that the for the first Z values of α, corresponding to dissociated atomic species, we have

$$\mathbf{J}_{\mathbf{r}}^i = \mathbf{g}_{\mathbf{r}}^i - \sum_{\alpha=Z+1}^{S} m_i^\alpha \mathbf{J}_{\mathbf{r}}^\alpha(z)$$

$$P_{\mathbf{r}}^i(z) = - \sum_{\alpha=Z+1}^{S} m_i^\alpha P_{\mathbf{r}}^\alpha(z)$$

13.8.5   Drift and dissipative matrix

Note that the selected CG variables are even under time reversal. This implies that the drift term $v^\alpha(\mathbf{r})$ in Eq. (12.2) vanishes due to microscopic reversibility. Another way to see this is that the time derivatives (13.8.4) are linear functions of velocities that will be averaged with the relevant ensemble (13.8.3) which is Gaussian with respect to velocities. As a consequence, the projected currents $\mathcal{Q}_t i\mathcal{L}[\mathbf{m}^\alpha]_{\mathbf{r}}$ entering the dissipative matrix (13.8.2) are given simply by the time derivatives $i\mathcal{L}[\mathbf{m}^\alpha]_{\mathbf{r}}$ of the CG variables. Therefore, the elements of the dissipative matrix are given in terms of the time integral of the time correlation functions of the time derivatives (13.8.4).

By inserting (13.8.4) into (13.8.2), the dissipative matrix decomposes as follows

$$\mathscr{D}_{\mathbf{rr'}}^{\alpha\beta} = \mathscr{R}_{\mathbf{rr'}}^{\alpha\beta} + \nabla_{\mathbf{r}}\mathbf{K}_{\mathbf{rr'}}^{\alpha\beta} + \nabla_{\mathbf{r'}}\mathbf{K}_{\mathbf{rr'}}^{\alpha\beta} + \nabla_{\mathbf{r}}\nabla_{\mathbf{r'}}\mathbf{D}_{\mathbf{rr'}}^{\alpha\beta}$$

The reactive part of the dissipative matrix is given by

$$\mathscr{R}_{\mathbf{rr'}}^{\alpha\beta} = \int_0^{\Delta t} dt \operatorname{Tr}\left[\overline{\rho}_t P_{\mathbf{r'}}^\beta \exp\{i\mathcal{L}t\} P_{\mathbf{r}}^\alpha\right]$$

The reaction-diffusion part of the dissipative matrix is

$$\mathbf{K}_{\mathbf{rr'}}^{\alpha\beta} = \int_0^{\Delta t} dt \operatorname{Tr}\left[\overline{\rho}_t P_{\mathbf{r'}}^\beta \exp\{i\mathcal{L}t\} \mathbf{J}_{\mathbf{r}}^\alpha\right]$$

whereas the purely diffusive part is given by

$$\mathbf{D}_{\mathbf{rr'}}^{\alpha\beta} = \int_0^{\Delta t} dt \operatorname{Tr}\left[\overline{\rho}_t \mathbf{J}_{\mathbf{r'}}^\beta \exp\{i\mathcal{L}t\} \mathbf{J}_{\mathbf{r}}^\alpha\right]$$

The reaction part of the dissipative matrix

Because the production terms of the dissociated atomic species are given in terms of the production terms of the molecular species, Eq. (13.8.4), not all elements of the reaction matrix are independent. If we make explicit the reaction matrix we will have that it

decomposes in four blocks

$$\mathscr{R}_{\mathbf{rr'}} = \int_0^{\Delta t} dt' \begin{pmatrix} \mathrm{Tr}\left[\overline{\rho_t}P^j_{\mathbf{r'}}P^i_{\mathbf{r}}(t')\right] & \mathrm{Tr}\left[\overline{\rho_t}P^\beta_{\mathbf{r'}}P^i_{\mathbf{r}}(t')\right] \\ \\ \mathrm{Tr}\left[\overline{\rho_t}P^j_{\mathbf{r'}}P^\alpha_{\mathbf{r}}(t')\right] & \mathrm{Tr}\left[\overline{\rho_t}P^\beta_{\mathbf{r'}}P^\alpha_{\mathbf{r}}(t')\right] \end{pmatrix}$$

The first block involving $\mathrm{Tr}\left[\overline{\rho_t}P^j_{\mathbf{r'}}P^i_{\mathbf{r}}(t')\right]$ is a square $Z \times Z$ matrix, the block involving $\mathrm{Tr}\left[\overline{\rho_t}P^\beta_{\mathbf{r'}}P^\alpha_{\mathbf{r}}(t')\right]$ is a square $(S-Z-1) \times (S-Z-1)$ matrix. The other two blocks are rectangular matrices. By using (13.8.4) we have that the atomic-atomic block is

$$\mathrm{Tr}\left[\overline{\rho_t}P^j_{\mathbf{r'}}P^i_{\mathbf{r}}(t')\right] = \sum_{\alpha=Z+1}^S \sum_{\beta=Z+1}^S m_i^\alpha m_j^\beta \mathrm{Tr}\left[\overline{\rho_t}P^\beta_{\mathbf{r}}P^\alpha_{\mathbf{r}}(t')\right]$$

In this way,

$$\mathscr{R}_{\mathbf{rr'}} = \begin{pmatrix} \sum_{\alpha,\beta=Z+1}^S m_i^\alpha m_j^\beta R^{\alpha\beta}_{\mathbf{rr'}} & -\sum_{\alpha=Z+1}^S m_i^\alpha R^{\alpha\beta}_{\mathbf{rr'}} \\ \\ -\sum_{\beta=Z+1}^S m_j^\beta R^{\alpha\beta}_{\mathbf{rr'}} & R^{\alpha\beta}_{\mathbf{rr'}} \end{pmatrix}$$

where

$$R^{\alpha\beta}_{\mathbf{rr'}} = \int_0^{\Delta t} dt' \mathrm{Tr}\left[\overline{\rho_t}P^\beta_{\mathbf{r}}P^\alpha_{\mathbf{r}}(t')\right] \qquad \alpha = Z+1,\cdots,S$$

is the matrix of reaction processes arising from the independent molecular production terms $P^\alpha_{\mathbf{r}}$, with $\alpha = Z+1,\cdots,S$.

The chemical kinetics, when diffusion is absent is

$$\partial_t[\mathbf{m}^\alpha](\mathbf{r}) = \int d\mathbf{r'}\, \mathscr{D}^{\alpha\beta}_{\mathbf{rr'}}\lambda^\beta(\mathbf{r'})$$

Explicitly

$$\partial_t \begin{pmatrix} [\mathbf{m}^i](\mathbf{r}) \\ \\ [\mathbf{m}^\alpha](\mathbf{r}) \end{pmatrix} = \int d\mathbf{r'} \begin{pmatrix} m_i^\alpha m_j^\beta R^{\alpha\beta}_{\mathbf{rr'}} & -m_i^\alpha R^{\alpha\beta}_{\mathbf{rr'}} \\ \\ -m_j^\beta R^{\alpha\beta}_{\mathbf{rr'}} & R^{\alpha\beta}_{\mathbf{rr'}} \end{pmatrix} \begin{pmatrix} \lambda^j(\mathbf{r'}) \\ \\ \lambda^\beta(\mathbf{r'}) \end{pmatrix}$$

$$= \int d\mathbf{r'} \begin{pmatrix} m_i^\alpha R^{\alpha\beta}_{\mathbf{rr'}}\left[\sum_j^Z m_j^\beta \lambda^j(\mathbf{r'}) - \lambda^\beta(\mathbf{r'})\right] \\ \\ R^{\alpha\beta}_{\mathbf{rr'}}\left[-\sum_{j=1}^Z m_j^\beta \lambda^j(\mathbf{r'}) + \lambda^\beta(\mathbf{r'})\right] \end{pmatrix} = \int d\mathbf{r'} \begin{pmatrix} -m_i^\alpha R^{\alpha\beta}_{\mathbf{rr'}}\mathscr{A}^\beta(\mathbf{r'}) \\ \\ R^{\alpha\beta}_{\mathbf{rr'}}\mathscr{A}^\beta(\mathbf{r'}) \end{pmatrix}$$

Again, the affinities $\mathscr{A}^\alpha(\mathbf{r})$ of the different reactions

$$dissociated\ atoms \rightleftharpoons molecular\ species$$
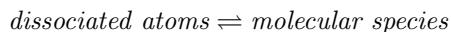
arise in a natural way from the dynamic equation. This is an "explanation" of why the driving force of a chemical reaction is given by the affinity of that chemical reaction.

13.8.6   Inhibited reactions

We consider now the situation in which some of the atomic species *are not present*. This means that for the visited microstates in the system the functions $i\mathcal{L}[\mathbf{m}^i]_{\mathbf{r}}(z) = 0$. This implies that the production rates are necesarily related by

$$\sum_{\alpha=Z+1}^{S} m_i^\alpha P_{\mathbf{r}}^\alpha(z) = 0$$

for those atomic species i that are not in the system.

    To be finished...

13.9   Continuum model

Our starting point are the continuum hydrodynamic equations for a multicomponent reactive mixture [?, ?, ?]. The fluid is described by a set of mass density fields $\rho^\alpha(\mathbf{r}, t)$ where $\alpha = 1, \cdots, r$ labels each chemical species, the velocity field $\mathbf{v}(\mathbf{r}, t)$ of the mixture, and the entropy density field $s(\mathbf{r}, t)$. We do not describe the state of the fluid at the more detailed level in which the velocity fields of each chemical component is considered among the hydrodynamic fields. In our description in which only the velocity field of the whole mixture is included, we are assuming that the time scale of equilibration of the velocity fields of each component towards the overall velocity field is short compared with the rest of time scales of the processes of interest. For the sake of simplicity, only one chemical reaction will be considered, although the generalization to several reactions is straightforward.

The first set of hydrodynamic equations are those for the evolution of the mass densities [?]

$$\frac{d}{dt}\rho^\alpha = -\rho^\alpha \nabla\cdot\mathbf{v} - \nabla\cdot\mathbf{J}^\alpha - \overline{\nu}^\alpha \mathscr{R} \tag{13.9.0}$$

Here, the usual substantial derivative $\frac{d}{dt} = \frac{\partial}{\partial t} - \mathbf{v}\cdot\nabla$ describing the rate of change of a property measured in a frame moving with the local fluid velocity has been introduced. The mass density flux of specie α is denoted by $\mathbf{J}^\alpha$. The usual stochiometric coefficients of the chemical reaction ν^α lead to the modified coefficients $\overline{\nu}^\alpha = \nu^\alpha M^\alpha$ in Eqn. (13.9). Here M^α is the molecular mass of species α. Finally, $\mathscr{R}$ is the reaction rate. The modified stochiometric coefficients satisfy

$$\sum_{\alpha=1}^{r} \overline{\nu}^\alpha = 0 \tag{13.9.0}$$

and the mass density fluxes are subject to the constrain

$$\sum_{\alpha=1}^{r} \mathbf{J}^\alpha = \mathbf{0} \tag{13.9.0}$$

By summing Eqns. (13.9) for each species an using Eqns. (13.9) and (13.9), we obtain the conservation of total mass in the form of the continuity equation

$$\frac{d}{dt}\rho = -\rho\nabla\cdot\mathbf{v} \tag{13.9.0}$$

The momentum balance equation takes the form

$$\rho\frac{d\mathbf{v}}{dt} = -\nabla P - \nabla\mathbf{\Pi} \tag{13.9.0}$$

where P is the pressure and $\mathbf{\Pi}$ is the viscous stress tensor. The balance equation for the entropy density is given by

$$\frac{ds}{dt} = -s\nabla\cdot\mathbf{v} - \nabla\cdot\mathbf{Q} + \sigma \tag{13.9.0}$$

where $\mathbf{Q}$ is a heat flux and σ is the entropy production. The production of entropy is given by [?]

$$T\sigma \;=\; -\mathbf{\Pi} : \nabla\mathbf{v} - \mathbf{Q}\cdot\nabla T - \sum_{\alpha=1}^{r} \mathbf{J}^{\alpha}\cdot\nabla\mu^{\alpha} - \mathscr{A}\mathscr{R} \qquad (13.9.1)$$

Here, T is the temperature field, μ^{α} is the chemical potential of species α and the affinity of the reaction is defined as the weighted average of the chemical potentials

$$\mathscr{A} = \sum_{\alpha=1}^{r} \overline{\nu}^{\alpha}\mu^{\alpha} \qquad (13.9.1)$$

Now the usual strategy in non-equilibrium thermodynamics is to write down linear relations between fluxes and thermodynamic forces in such a way that the entropy production is a positive bilinear form [?, ?]. The first term in the entropy production (13.9.1) is a viscous heating term that produces the usual Newtonian constitutive equation for the viscous stress tensor

$$\begin{aligned}
\overline{\mathbf{\Pi}}^{S} &= -2\eta\left(\overline{\nabla\mathbf{v}}\right) \\
\mathrm{tr}[\mathbf{\Pi}] &= -3\zeta\nabla\cdot\mathbf{v}
\end{aligned} \qquad (13.9.1)$$

where $\overline{\mathbf{\Pi}}^{S}$ is the traceless symmetric part of the viscous stress, $\overline{\nabla\mathbf{v}}$ is the traceless symmetric part of the velocity gradient tensor, and η, ζ are the shear and bulk viscosities, respectivelly. In general, we expect that these transport coefficients depend on the compositions ρ^{α}. A simple model for this dependency is

$$\eta = \sum_{\alpha} \frac{\rho^{\alpha}}{\rho}\eta^{\alpha} \qquad (13.9.1)$$

where η^{α} is the viscosity of a fluid containing only species α.

Let us turn now to the vectorial phenomena in the production of entropy. For the sake of simplicity, we will neglect cross effects like the Duffoir and Soret effects (temperature gradients causing diffusion of mass and viceversa). In this way, the heat flux is given just by the Fourier law

$$\mathbf{Q} = -\frac{\kappa}{T}\nabla T \qquad (13.9.1)$$

where κ is the thermal conductivity. The fact that the diffusion fluxes $\mathbf{J}^{\alpha}$ are not all independent, requires special consideration. Actually, Eqn. (13.9) implies

$$\mathbf{J}^r = -\sum_{\alpha=1}^{r-1} \mathbf{J}^{\alpha} \qquad (13.9.1)$$

and the entropy production term due to mass diffusion becomes simply

$$T\sigma_{\text{diff}} = -\sum_{\alpha=1}^{r-1} \mathbf{J}^\alpha \cdot \nabla(\mu^\alpha - \mu^r) \tag{13.9.1}$$

The assumption of linear dependency between fluxes and thermodynamic forces becomes, in the absence of a coupling with temperature gradients,

$$\mathbf{J}^\alpha = -\sum_{\beta=1}^{r-1} L^{\alpha\beta} \nabla(\mu^\beta - \mu^r) \qquad \alpha = 1, \cdots, r-1 \tag{13.9.1}$$

where $L^{\alpha\beta}$ is a symmetric positive matrix of diffusion coefficients. It is possible to write this equation in the form

$$\mathbf{J}^\alpha = -\sum_{\beta=1}^{r} \overline{L}^{\alpha\beta} \nabla\mu^\beta \qquad \alpha = 1, \cdots, r \tag{13.9.1}$$

where $\overline{L}^{\alpha\beta} = L^{\alpha\beta}$ for $\alpha, \beta = 1, \cdots, r-1$ and $\overline{L}^{\alpha r} = \overline{L}^{r\alpha} = -\sum_{\beta=1}^{r-1} L^{\alpha\beta}$ for $\alpha = 1, \cdots, r-1$, and finally $\overline{L}^{rr} = \sum_{\alpha\beta} L^{\alpha\beta}$. In other words, the conservation of mass expressed in (13.9) is reflected on the fact that the matrix $\overline{L}$ has rank $r-1$. Of course, there are many different ways of writting this matrix and, therefore, many different ways of defining diffusion coefficients [?].

Concerning chemical reactions, it is well-know that a linear relation between the reaction rate $\mathscr{R}$ and the affinity $\mathscr{A}$ is only valid for very late states of the reaction, when the system is close to equilibrium [?]. A more general non-linear rate equation is given by

$$\mathscr{R} = -\frac{P}{k_B T} r(P,T) \left(1 - \exp\{\mathscr{A}/k_B T\}\right) \exp\left\{\sum_{\alpha}^{p} \overline{\nu}^\alpha \mu^\alpha\right\} \tag{13.9.1}$$

Here, $r(T, P)$ is a reciprocal time characterizing the reaction rate, P, T are the pressure and temperature, and the sum in the last exponential runs over the reactants of the reaction only.

Behind the above hydrodynamic equations there is the assumption of local equilibrium, which states that the each fluid element is actually a thermodynamic subsystem that can be described with equilibrium thermodynamic functions. In particular, it is assumed that the internal energy density ϵ of the fluid element is a function of the mass densities and entropy density through the same equilibrium function for the mixture under discussion. In this way, we have that the intensive fields T, μ^α are the equilibrium intensive parameters evaluated at the local values of the hydrodynamic fields. We have the fundamental equation

$$d\epsilon = Tds + \sum_{\alpha=1}^{r} \mu^\alpha d\rho^\alpha \tag{13.9.1}$$

that shows that the intensive parameters are the derivatives of the internal energy with respect to the entropy density or mass densities. The local equilibrium assumption states

that the above relationship is valid for each fluid element, so we have

$$\frac{d\epsilon}{dt} = T\frac{ds}{dt} + \sum_{\alpha=1}^{r} \mu^\alpha \frac{d\rho^\alpha}{dt} \qquad (13.9.1)$$

Let us summarize the continuum hydrodynamic equations

$$
\begin{aligned}
\frac{d}{dt}\rho^\alpha &= -\rho^\alpha \nabla\cdot\mathbf{v} + \nabla\cdot\left(\sum_\beta \overline{L}^{\alpha\beta}\nabla\mu^\beta\right) - \overline{\nu}^\alpha \mathcal{R} \\
\rho\frac{d\mathbf{v}}{dt} &= -\nabla P + \eta\nabla^2\mathbf{v} + \left(\zeta + \frac{\eta}{3}\right)\nabla\nabla\cdot\mathbf{v} \\
T\frac{ds}{dt} &= -Ts\nabla\cdot\mathbf{v} + \kappa\nabla^2 T + \Psi^{\mathrm{vh}} + \Psi^{\mathrm{diff}} - \mathcal{A}\mathcal{R}
\end{aligned}
\qquad (13.9.0)
$$

Here we have introduced the dissipation Ψ^{vh} due to viscous heating and the dissipation Ψ^{diff} due to mass diffusion

$$
\begin{aligned}
\Psi^{\mathrm{vh}} &= 2\eta\overline{\nabla\mathbf{v}} : \overline{\nabla\mathbf{v}} + \zeta(\nabla\cdot\mathbf{v})^2 \\
\Psi^{\mathrm{diff}} &= \sum_{\alpha,\beta}\nabla\mu^\alpha\cdot\left(\overline{L}^{\alpha\beta}\nabla\mu^\beta\right)
\end{aligned}
\qquad (13.9.0)
$$

In order to have a closed set of equations, we need to specify the fundamental equation $\mathcal{E}(m^1, \cdots, m^r, \mathcal{V}, S)$, relating the internal energy $\mathcal{E}$ with the mass m^α of every component, the volume and the entropy. Differentiation of $\mathcal{E}$ with respect to their arguments provides the equations of state (temperature, pressure, and chemical potentials as a function of the mass and entropy densities), the matrix of diffusion coefficients $\overline{L}^{\alpha\beta}$, and the time constant $r(P, T)$ for the chemical reaction.

If we introduce the energy density field $e = \rho\frac{v^2}{2} + \epsilon$, it is possible to derive from Eqns. (13.9), (13.9.0) a balance equation showing that the total energy of the system is conserved by the set of hydrodynamic equations.

14

Solid-liquid: Melting

15

Fluid with spin $\hat{\rho}_{\mathbf{r}}, \hat{\mathbf{g}}_{\mathbf{r}}, \hat{e}_{\mathbf{r}}, \mathbf{s_r}$

Assume that we have a fluid made of molecules labeled with Greek indices $\alpha, \beta, \cdots$ made of atoms labelled with Latin indices $i, j, \cdots$. Space is partitioned into cells labelled with $\mu, \nu, \cdots$. We explore what happens in the discrete version of the fluid dynamics equations. The reason is that I believe that even for point molecules without intrinsic angular momentum, the continuum equations require the use of spin, because the cells themselves have a finite extension.

We introduce the position, momentum, an intrinsic angular momentum of a molecule as follows

$$\mathbf{r}_\alpha = \frac{1}{m_\alpha} \sum_{i_\alpha} m_{i_\alpha} \mathbf{r}_{i_\alpha}$$

$$\mathbf{p}_\alpha = \sum_{i_\alpha} \mathbf{p}_{i_\alpha}$$

$$\mathbf{s}_\alpha = \sum_{i_\alpha} (\mathbf{r}_{i_\alpha} - \mathbf{r}_\alpha) \times \mathbf{p}_{i_\alpha}$$

We define the following discrete hydrodynamic variables are

$$\hat{\rho}_\mu = \sum_\alpha m_\alpha \delta_\mu(\mathbf{r}_\alpha)$$

$$\hat{\mathbf{g}}_\mu = \sum_\alpha \mathbf{p}_\alpha \delta_\mu(\mathbf{r}_\alpha)$$

$$\hat{\boldsymbol{\sigma}}_\mu \equiv \sum_\alpha \mathbf{s}_\alpha \delta_\mu(\mathbf{r}_\alpha)$$

$$\hat{\mathbf{S}}_\mu = \sum_\alpha (\mathbf{r}_\alpha - \mathbf{r}_\mu) \times \mathbf{p}_\alpha \delta_\mu(\mathbf{r}_\alpha)$$

The *intrinsic* angular momentum $\hat{\boldsymbol{\sigma}}_\mu$ vanishes if the molecules are made of a single atom. The *internal* angular momentum $\hat{\mathbf{S}}_\mu$ is present even for monoatomic molecules, and represents the angular momentum with respect to the center of the cell. This contribution

exists due to the finite extension of the cells.

Total mass, momentum, and angular momentum are expressible in terms of the discrete hydrodynamic variables as

$$M_T = \sum_\mu \mathscr{V}_\mu \hat{\rho}_\mu$$

$$\mathbf{P}_T = \sum_\mu \mathscr{V}_\mu \hat{\mathbf{g}}_\mu$$

$$\mathbf{L}_T = \sum_\mu \mathscr{V}_\mu \hat{\boldsymbol{\sigma}}_\mu + \sum_\mu \mathscr{V}_\mu \hat{\mathbf{S}}_\mu + \sum_\mu \mathscr{V}_\mu \left(\mathbf{r}_\mu \times \hat{\mathbf{g}}_\mu \right)$$

The total angular momentum of the system is

$$\mathbf{L}_T = \sum_\alpha \sum_{i_\alpha} \mathbf{r}_{i_\alpha} \times \mathbf{p}_{i_\alpha} = \sum_\alpha \sum_{i_\alpha} (\mathbf{r}_{i_\alpha} - \mathbf{r}_\alpha) \times \mathbf{p}_{i_\alpha} + \sum_\alpha \mathbf{r}_\alpha \times \sum_{i_\alpha} \mathbf{p}_{i_\alpha} = \sum_\alpha \mathbf{s}_\alpha + \sum_\alpha \mathbf{r}_\alpha \times \mathbf{p}_\alpha$$

This shows that total angular momentum is the sum of the intrinsic angular momentum of the molecules plus the angular momentum of the center of mass of the molecules. We now introduce the identity $\sum_\mu \mathscr{V}_\mu \delta_\mu(\mathbf{r}_\alpha) = 1$ to obtain

$$\mathbf{L}_T = \sum_\mu \mathscr{V}_\mu \sum_\alpha \mathbf{s}_\alpha \delta_\mu(\mathbf{r}_\alpha) + \sum_\mu \mathscr{V}_\mu \sum_\alpha \mathbf{r}_\alpha \times \mathbf{p}_\alpha \delta_\mu(\mathbf{r}_\alpha)$$

$$= \sum_\mu \mathscr{V}_\mu \sum_\alpha \mathbf{s}_\alpha \delta_\mu(\mathbf{r}_\alpha) + \sum_\mu \mathscr{V}_\mu \sum_\alpha (\mathbf{r}_\alpha - \mathbf{r}_\mu) \times \mathbf{p}_\alpha \delta_\mu(\mathbf{r}_\alpha) + \sum_\mu \mathscr{V}_\mu \mathbf{r}_\mu \times \sum_\alpha \mathbf{p}_\alpha \delta_\mu(\mathbf{r}_\alpha)$$

$$= \sum_\mu \mathscr{V}_\mu \hat{\boldsymbol{\sigma}}_\mu + \sum_\mu \mathscr{V}_\mu \hat{\mathbf{S}}_\mu + \sum_\mu \mathscr{V}_\mu \left(\mathbf{r}_\mu \times \hat{\mathbf{g}}_\mu \right)$$

16

Non-Isothermal Viscoelasticity: $n_{\mathbf{r}}, \mathbf{g_r}, e_{\mathbf{r}}, \Psi_{\mathbf{r}}(\mathbf{Q})$

This is still for homogeneous systems, but now made of complex molecules, like polymers.

17

Non-Isothermal Viscoelasticity: $\hat{\rho}_{\mathbf{r}}, \hat{\mathbf{g}}_{\mathbf{r}}, \hat{e}_{\mathbf{r}}, \mathbf{c}_{\mathbf{r}}$

[Here $\mathbf{c}_{\mathbf{r}}$ is the conformation tensor]

18

Elasticity of solids: $\hat{\rho}_{\mathbf{r}}, \hat{\mathbf{g}}_{\mathbf{r}}, \hat{e}_{\mathbf{r}}, \hat{\mathbf{d}}_{\mathbf{r}}$

[What I want to do today:]

- Discuss the Goldstone theorem in the light of the restricted ensemble.

- Discuss the definition of the free energy functional, and demonstrate that the stress tensor is the derivative of the free energy with respect to the displacement.

- Introduce the harmonic approximation of the restricted ensemble and discuss the corresponding symmetries.

- Compute the free energy depending on the displacement in the harmonic approximation. This does not allow one to discuss how one looses elasticity when the system fluidices.

- Discuss how Parisi et al. [?] give another restricted ensemble.

- Understand the coarse-grained definition of density and displacement of Hering 2015

[Literature:]

- den Otter et al. [?], that follows also from Schofield and Handerson [?] start from the free energy in the thermodynamic level of description, that depends on the shape of the volume and derive the expression between stress tensor and deformation, through elastic constants. The free energy at the thermodynamic level of description (usually referred to equilibrium thermodynamics) is defined from the partition function

$$Z = \mathrm{tr}\left[e^{-\beta\hat{H} - \mu\hat{N}}\right]$$

This is a function of the inverse temperature β and chemical potential μ and, of course, any parameter appearing in the potential In principle, the Hamiltonian includes information about the container potentials. For a parallepiped box with unit

vectors $\mathbf{H} = (\mathbf{h}_1, \mathbf{h}_2, \mathbf{h}_3)$, the free energy depends on these vectors. The macroscopic pressure tensor is defined from first derivatives while macroscopic elastic constants are defined as second derivatives of these vectors. More specifically, one considers a given reference container $\mathbf{H}$ and deforms it to another shape $\mathbf{H}' = \mathbf{e}\mathbf{H}$ where the matrix $\mathbf{e}$ is expressed as

$$\mathbf{e} = \mathbf{1} + \sum_a^6 \epsilon_a \mathbf{b}_a$$

where $\mathbf{b}_a$ are the independent deformation vectors of the box and ϵ_a are the strain in each direction. The six components of the symmetric pressure tensor are then defined as

$$\pi_a = \lim_{\epsilon_a \to 0} \frac{k_B T V}{m} \frac{Z(\beta, \mu, \mathbf{H}') - Z(\beta, \mu, \mathbf{H})}{\epsilon_a}$$

and the elastic constants are

$$\Gamma_{ab} = \frac{\partial \pi_a}{\partial \epsilon_b}$$

While these are definitions, they must have a physical meaning in terms of forces applied at a boundary of the solid. We would like to promote these quantities to the status of fields.

- Masters [?]: DFT Use Green-Yvon-Kirkwood and Ornstein-Zernicke to show that density gradients imply long range density correlation function $h(\mathbf{r}_1, \mathbf{r}_2)$.

  Then he starts with the free energy density functional and substitute $\rho(\mathbf{r})$ with $\rho(\mathbf{r} + \mathbf{u}(\mathbf{r}))$. Expansion leads to an increase of free energy given in terms of displacement gradients and elastic constants. The elastic constants are defined in terms of the direct correlation function and density gradients. When these are zero due to translation invariance, so the elastic constants! This explains the solid liquid transition (elasticity-hydrodynamics transition).

  For me this is rather strange, because the free energy used in the argument is $F[\rho]$ and not $F[\rho, \mathbf{d}]$.

- Szamel and Ernst [?] seem to repeat Masters with a different definition of the displacement field.

- Waltz and Fuchs consider a non-ideal crystal and use the perfect crystal as reference. They show that the correlation of the Fourier components of the density field are long ranged. Therefore, they use the variables

$$\hat{n}_\mathbf{g}(\mathbf{q}, z) = \frac{1}{V} \sum_i^N e^{-i\mathbf{g}\cdot\mathbf{q}_i}$$

$$\hat{\mathbf{j}}(\mathbf{q}, z) = \sum_i^N \mathbf{p}_i e^{-i\mathbf{g}\cdot\mathbf{q}_i}$$

as slow variables. They obtain a remarkable exact identity for the elastic constants that appear in the wave equation.

- Szamel 1997 Present for the first time the dissipative part of the Goldstone modes. Use $\hat{n}_\mathbf{r}, \mathbf{u_r}, \mathbf{g_r}$ as variables in Mori-Zwanzig.

- Haring 2015 [?] is, by far, **the most important paper to study**. It makes a distinction between the microscopic density field and a coarse-grained density field and coarse-grained displacement fields.

- The following works consider the definition of the displacement field as originating from a Goldstone mode for a crystal [?], [?] and also for disordered systems [?],[?]

[The question that I have is very simply put. What relevance have these objects, which are macroscopic, to the very equations of the elasticity that I have obtained? And also very important: how these quantities relate to the functional derivatives of the free energy functional?]

We all have an intuitive idea of what a solid material is: a brick, a stone, or the flying bone in the famous scene in 2001 Space Odyssey. All these objects share in common that they are more or less rigid. At a microscopic level the material is made of atoms that in the present treatment are just point particles interacting with certain potential energy and whose motion evolves with Hamilton's equations. At this level it is not so obvious how to define "solidness" or "rigidity". What distinguishes a metallic solid sphere from a metallic fluid sphere, at the microscopic level? The question is certainly puzzling when we may think of these two spheres as being made of the same number of identical atoms, and one is in a melted high temperature state while the other is in a crystalline solid state. The only thing that changes in the conditions of both spheres is the total energy of the system. The phenomenological observations that allow us to distinguish both spheres is that one has a crystalline structure and a rigidity, while the other does not. As we will see, both properties are closely related, together with the concept of *broken ergodicity* and *broken symmetry*.

Consider a ruler [?] on top of a table. If we push one of the extremes of the ruler and displace it, the other extreme moves almost instantaneously by the same amount. This property gives the ruler its ability to measure lengths, in fact. This macroscopic effect should have its microscopic counterpart in that if a group of atoms near one of the extremes of the ruler is displaced by a thermal fluctuation, then at the other extreme there should be a highly correlated effect on the displacement of the atoms in the other extreme. We expect that the correlations of the displacements are long ranged in space. Of course, such effects are also present, to some extent in liquids. Consider a tube containing a liquid in between two pistons. If we push one of the pistons, the other will move almost instantaneously because a liquid is not very compressible. The distinguishing feature between a solid and a liquid is that while both are more or less incompressible, only solids can sustain *shear displacements*.

18.1   Introduction

Consider a system of particles interacting with a short range pair-wise potential in a large three dimensional periodic box. In the absence of any external field, total linear momentum is conserved as a result of the invariance of the microscopic Hamiltonian with respect to translations. We choose, therefore, the inertial reference frame of the center of mass in which the system has zero linear momentum.

At high temperatures (i.e. energies) the system is in a fluid state. One way to know that the system is in the fluid state is by looking at the one particle distribution function, which is the thermal average of the microscopic density field

$$\hat{n}_{\mathbf{r}}(z) = \sum_i^N \delta(\mathbf{r}_i - \mathbf{r})$$

In the liquid state, the thermal average of this quantity is strictly constant in space. There are no preferred locations for the particles to be.

[

- **Quenching rate**

  Imagine now that at time intervals t_{rescal} we rescale the velocities of the system by ensuring that total linear momentum is conserved under the rescaling. This allows to reduce the total energy. In every rescaling of velocities we go from a microstate z with energy $E = \hat{H}(z)$ to another microstate z' with a smaller energy $E' = \hat{H}(z')$, both at zero total momentum. Eventually, we will observe that the system starts freezing. How will we notice that? Because the density fields starts developing bumps around certain lattice positions.

- **Freezing**

- **Nucleation**

- **Glass state**

- **Crystal state**

- **Vacancies and defects**

] [**Quasiaverages of Bogoliubov: the density field of a crystal is constant because there is an average over all positions of the center of mass of the crystal. He introduces a pinning potential, take the thermodynamic limit first, and then take the limit of spring constant to zero. The resulting average density is not constant anymore but reflects the lattice structure.**]

Inherent structures

In the presence of vacancies or interstitial **[(see figure)]** or when the system is in a glassy state, it is no longer clear what observable will inform us that the system is in a solid state. In the glass state there is no underlying lattice while in the presence of

interstitial (or vacancies), there are more (or less) particles than lattice points. In these cases, all what we know is that the particles oscillate around fixed positions $\mathbf{q}_i^\alpha$. These fixed positions may eventually move (through jumps!) and become dynamic variables themselves (as in the case of diffusion of interstitial, or in the structural rearrangement that occur in glasses). In a first step, though, we will assume that in the time scales in which we are interested, these reference positions $\mathbf{q}_i^\alpha$ are dynamic invariants of the system and remain fixed. Eventually, in order to capture longer time scales in which vacancies/interstitial move or the glass structure evolves, we will need to promote the reference positions $\mathbf{q}_i^\alpha$ (or, perhaps, coarse-grained representations of these variables) to dynamic variables themselves. But for the time being, the reference positions are assumed to be given.

The strategy in order to find out what is the effective ensemble that will allow us to compute averages and predict statistical information is to first identify the reference positions $\mathbf{q}_i^\alpha$ as functions of the microscopic state of the system. These reference positions are understood as being local minima of the potential energy function $\hat{\Phi}(q)$. Note that the potential energy function (usually termed the energy landscape) will have many local minimum in which the system will display some degree of order, and a global minima that will correspond to a crystalline phase **[Why crystals are the global minima?]** Every local minima is refered to as an **inherent structure** [**?**, **?**, **?**]. One practical way to find out such minima is by solving Newton's equations with a friction force

$$m_i \frac{d^2 \mathbf{q}_i}{dt^2} = -\frac{\partial}{\partial \mathbf{q}_i} \Phi(\mathbf{q}_i) - \gamma \dot{\mathbf{q}}_i$$

The damping will lead the positions to a rest in a minimum of $\hat{\Phi}(q)$. This damping force is a way to model a quench of the system to low energies, because it effectively reduces the kinetic energy of the system. In the large friction limit, the overdamped motion is simply given by

$$\dot{\mathbf{q}}_i = -\frac{1}{\tau} \frac{\partial}{\partial \mathbf{q}_i} \Phi(q)$$

This overdamped equation describes an infinitely rapid quench in which the system is not allowed to move between different local minima. Note that for every initial microscopic configuration q, corresponds a unique solution $q^\alpha = \{\mathbf{q}_1^\alpha, \cdots, \mathbf{q}_N^\alpha\}$ of (18.1). The region of configuration space made of all configurations that reach the same minimum when following the steepest descent dynamics (18.1) is called the basin of attraction $\mathscr{B}^\alpha$ corresponding to the local minimum q^α. In this way, configuration space is divided in disjoint regions corresponding to the basin of attraction of each local minimum or inherent structure. Note that we may sort the different inherent structures according to the value of the potential energy at the minimum $\Phi_0^\alpha = \Phi(q^\alpha)$. The integer index α runs, therefore, from 1 to the total number $\mathscr{N}_{\text{loc}}$ of local minima of the potential function. The value of $\mathscr{N}_{\text{loc}}$ increases in an exponential way as a function of the number of particles [**?**].

The situation we want to describe is one in which, due to a rapid quench, the system becomes trapped in one of these local minima because it does not have enough energy to escape from the well, at least in the time scales of observation. When this happens, the system no longer explores all the energy shell, but only a small part of it, corresponding

to those configurations that are in the basin of attraction $\mathscr{B}^{\alpha}$ of the inherent structure α. If we were to use the microcanonical ensemble in order to compute averages, we would obtain baldy wrong results because we would be given statistical weight to configurations that are never visited by the system in the trapped situation. What ensemble should we use, then, to describe these trapped situations? To answer this, let us introduce the characteristic function of the basin $\mathscr{B}^{\alpha}$, and denote it with $\chi(q, q^{\alpha})$. This function takes the value 1 if q belongs to the basis of attraction of the inherent structure q^{α} and zero otherwise. In the time scales of observation where the particle remains in the basin $\mathscr{B}^{\alpha}$ the characteristic function does not change value, which is always one as far as the microstate does not leave the basin of attraction. Therefore, the phase function $\chi(q, q^{\alpha})$ is a dynamic invariant.

The restricted microcanonical ensemble

Let us construct now what is the appropriate ensemble to describe a situation in which the system is dynamically trapped near a given inherent structure. We first introduce the probability $P(E, \alpha)$ that, if the normalized ensemble is $\rho(z)$, the system has an energy E *and* is in the basin $\mathscr{B}^\alpha$ of attraction of the inherent structure q^α,

$$P(E, \alpha) = \int dz \rho(z) \delta(\hat{H}(z) - E) \chi(q, q^\alpha)$$

$$1 = \int dz \rho(z)$$

Now, let us assume that all what we know about the ensemble $\rho(z)$ is the above information. The maximization of the Gibbs-Jaynes entropy (**??**) subject to these restrictions amounts to maximize the Lagrangian

$$\mathcal{L}[\rho] = -\int dz \rho(z) \ln \frac{\rho(z)}{\rho_0} + \sum_\alpha \int dE \lambda(E, \alpha) \int dz \rho(z) \delta(\hat{H}(z) - E) \chi(q, q^\alpha) + \mu \int dz \rho(z)$$

where $\lambda(E, \alpha), \mu$ are the Lagrange multipliers enforcing the constraints (18.1). The extremum is given by

$$\rho(z) = \rho_0 \exp \left\{ -\sum_\alpha \lambda(\hat{H}(z), \alpha) \chi(q, q^\alpha) - \mu \right\}$$

By inserting this result into the first restriction in (18.1) we have

$$P(E, \alpha) = \int dz \delta(\hat{H}(z) - E) \chi(q, q^\alpha) \rho_0 \exp \left\{ -\sum_{\alpha'} \lambda(\hat{H}(z), \alpha') \chi(q, q^{\alpha'}) - \mu \right\}$$

$$= \rho_0 \int dz \delta(\hat{H}(z) - E) \chi(q, q^\alpha) \exp \left\{ -\sum_{\alpha'} \lambda(E, \alpha') \chi(q, q^{\alpha'}) - \mu \right\}$$

$$= \rho_0 \exp \left\{ -\lambda(E, \alpha') - \mu \right\} \Omega(E, \alpha)$$

where we have introduced the "number of microstates" with energy E that are in the basin α

$$\Omega(E, \alpha) = \int dz \delta(\hat{H}(z) - E) \chi(q, q^\alpha)$$

Therefore, we have an explicit expression for the Lagrange multiplier in terms of the macroscopic information

$$\rho_0 \exp \left\{ -\lambda(E, \alpha') - \mu \right\} = \frac{P(E, \alpha)}{\Omega(E, \alpha)}$$

The ensemble (18.1) can be written as

$$\rho(z) = \prod_\alpha \left[\rho_0 \exp\left\{ -\lambda(\hat{H}(z), \alpha) - \mu \right\} \right]^{\chi(q, q^\alpha)}$$

where use has been made of the property $\sum_\alpha \chi(q, q^\alpha) = 1$. Note that the function $\chi(q, q^\alpha)$ takes only the values $1, 0$. Therefore, for z giving $q \in \mathscr{B}^{\alpha'}$ the above ensemble takes the form

$$\rho(z) = \rho_0 \exp\left\{ -\lambda(\hat{H}(z), \alpha') - \mu \right\} \quad \text{if} \quad q \in \mathscr{B}^{\alpha'}$$

and, therefore, for arbitrary z we have

$$\rho(z) = \sum_\alpha \rho_0 \exp\left\{ -\lambda(\hat{H}(z), \alpha) - \mu \right\} \chi(q, q^\alpha)$$

Finally, by inserting (18.1) in (18.1) we end up with the explicit expression for the restricted ensemble

$$\rho(z) = \sum_\alpha \chi(q, q^\alpha) \frac{P(\hat{H}(z), \alpha)}{\Omega(\hat{H}(z), \alpha)}$$

As usual, the Gibbs-Jaynes least biased ensemble is a formulation of "equiprobability". In the present case, all microstates z that have the same energy and are in the same basin are all equiprobable (have the same value $\rho(z)$). Obviously, for the above expression to make any sense, it is necessary that the function $\Omega(E, \alpha)$ be different from zero. This poses conditions to the possible input probabilities $P(E, \alpha)$. We know that the inherent structure q^{α_0} is a local minimum of the potential function with value $\Phi_0^\alpha = \Phi(q^{\alpha_0})$ and, therefore, any microstate in the basin $\mathscr{B}^{\alpha_0}$ of this inherent structure needs to have, necessarily, an energy larger than Φ_0^α. At the same time, if we know with certainty that the system is in a microstate of the basin $\mathscr{B}^{\alpha_0}$ it has to have an energy smaller than the lowest saddle point in the boundary of the basin, otherwise the microstate could eventually escape from the basin through that saddle point.

Now, let us assume that we know with certainty that the system is in a particular inherent structure α_0 with a precise energy E_0. Under the required physical conditions on the value of the energy E_0, the probability is

$$P(E, \alpha) = \delta(E - E_0) \delta_{\alpha, \alpha_0}$$

where $\delta_{\alpha, \alpha_0}$ is the Kronecker delta. This leads to the following restricted microcanonical ensemble

$$\rho^\alpha(z) = \frac{1}{\Omega(E, \alpha)} \delta(\hat{H}(z) - E) \chi(q, q^\alpha)$$

The restricted canonical ensemble

Let us now turn, because it will be needed later on, to the averages flavor in which we know only the averages of the energy and the probability $P(\alpha)$ of occurrence of the inherent structure q^α. The restrictions are now

$$E = \int dz \rho(z) \hat{H}(z)$$

$$P(\alpha) = \int dz \rho(z) \chi(q, q^\alpha)$$

The usual maximization of the Gibbs-Jaynes entropy now gives

$$\rho^\alpha(z) = \exp\left\{-\beta \hat{H}(z) - \sum_\alpha \lambda(\alpha)\chi(q, q^\alpha) - \mu\right\}$$

where $\lambda(\alpha)$ is the set of Lagrange multipliers enforcing the restriction to give $P(\alpha)$. By substituting this ensemble into the restriction we have

$$P(\alpha) = \int dz \exp\left\{-\beta \hat{H}(z) - \sum_{\alpha'} \lambda(\alpha')\chi(q, q^{\alpha'}) - \mu\right\} \chi(q, q^\alpha)$$

Only for those q in $\mathscr{B}^\alpha$ contribute to the integral and, for those microstates, only the term $\alpha' = \alpha$ survives, leading to

$$P(\alpha) = \exp\{-\lambda(\alpha)\} \int dz \exp\left\{-\beta \hat{H}(z) - \mu\right\} \chi(q, q^\alpha)$$

Note that because the characteristic function takes only the values $1, 0$, we have

$$\exp\left\{-\sum_{\alpha'} \lambda(\alpha')\chi(q, q^{\alpha'})\right\} = \sum_{\alpha'} \chi(q, q^{\alpha'}) \exp\left\{-\lambda(\alpha')\right\}$$

The ensemble (18.1) can be written as

$$\rho^\alpha(z) = \sum_\alpha \chi(q, q^\alpha) \exp\left\{-\beta \hat{H}(z) - \lambda(\alpha) - \mu\right\}$$

and, therefore, we have

$$\rho^\alpha(z) = \sum_\alpha \chi(q, q^\alpha) \frac{P(\alpha)}{Z(\alpha, \beta)} \exp\left\{-\beta \hat{H}(z)\right\}$$

The input information is $P(\alpha)$ and the average energy. If we know with certainty that the system is in *one* particular basin α, then the resulting ensemble is

$$\rho^{\alpha}(z) = \frac{1}{Z_{\alpha}(\beta)} \exp\{-\beta \hat{H}(z)\} \chi(q, q^{\alpha})$$

$$Z_{\alpha}(\beta) = \int dz \exp\{-\beta \hat{H}(z)\} \chi(q, q^{\alpha})$$

Note that the effect of the characteristic function is the same as having a hard wall potential in phase space, because we can always write (18.1) in the form

$$\rho^{\alpha}(z) = \frac{1}{Z_{\alpha}(\beta)} \exp\{-\beta \hat{H}^{\alpha}(z)\}$$

$$\hat{H}^{\alpha}(z) = \hat{H}(z) + \Upsilon^{\alpha}(z)$$

$$\Upsilon^{\alpha}(z) = -k_B T \ln \chi(q, q^{\alpha})$$

The confining potential $\Upsilon^{\alpha}(z)$ takes the value 0 inside the basin $\mathscr{B}^{\alpha}$ and ∞ outside (the temperature prefactor is purely aesthetical and irrelevant). Note that if the energy of the system is small enough for the system to become trapped in the basin $\mathscr{B}^{\alpha}$, then the dynamics generated by $\hat{H}^{\alpha}(z)$ and the dynamics generated by the original Hamiltonian $\hat{H}(z)$ potential is exactly the same. Only if the initial microstate has sufficient energy to eventually overcome some of the potential barrier (which is more probable near saddle points in the energy landscape), the two Hamiltonian would produce different trajectories. The unrestricted Hamiltonian would proceed through the saddle point, whereas the Hamiltonian $\hat{\mathscr{H}}^{\alpha}(z)$ would reflect the microstate back to the basin $\mathscr{B}^{\alpha}$. It should be clear that, as far as we are in a sufficiently low energy/temperature state, these crossings will not occur and both Hamiltonian give identical microscopic trajectories. Therefore, the time averages computed in a long trajectory of any phase function will be the same for both Hamiltonians. However, the Hamiltonians $\hat{\mathscr{H}}(z), H^{\alpha}(z)$ lead to different ensemble averages, as they give different statistical weights to the different microstates in phase space.

Translation invariance in the energy landscape

We want to discuss now interesting effects that occur concerning translation invariance when the system becomes trapped in a basin $\mathscr{B}^{\alpha}$. First, we note that in the absence of external fields and container walls (walls can be modeled, in fact, with of external field, very singular at the wall surface), the potential energy of the system is translation invariant, this is, $\Phi(\mathscr{T}_{\mathbf{c}} q) = \Phi(q)$. The structure of this function is, therefore, canyon-like, in which the potential energy along "diagonal lines" in phase space is the same. See Fig **??** for the potential function of two particles in 1D interacting with a harmonic spring. Note that the bottom of the canyon goes along the direction $(1, 1)$. This is a general feature of translation invariant potential energy functions, as can be seen by taking the derivative of both sides of $\Phi(\mathscr{T}_{\mathbf{c}} q) = \Phi(q)$ with respect to $\mathbf{c}$ and setting at the end $\mathbf{c} = 0$.

This results in the vector identity

$$\sum_i^N \frac{\partial \Phi}{\partial \mathbf{q}_i}(q) = 0 \qquad \forall q$$

Geometrically, this identity says (in 3D) that the gradient of a potential function which is translation invariant is always perpendicular to the three vectors in phase space

$$\mathbf{E}_a = \underbrace{(\mathbf{e}_a, \cdots, \mathbf{e}_a)}_{N} \quad a = 1, 2, 3$$

$$\mathbf{e}_1 = (1, 0, 0)$$
$$\mathbf{e}_2 = (0, 1, 0)$$
$$\mathbf{e}_3 = (0, 0, 1)$$

and is a reflection of the canyon-like structure of the potential landscape. By computing the second derivatives of $\Phi(\mathscr{T}_{\mathbf{c}} q) = \Phi(q)$ we obtain

$$\sum_{ij}^N \frac{\partial^2 \Phi}{\partial \mathbf{q}_i \partial \mathbf{q}_j}(q) = 0 \qquad \forall q$$

that can be written in compact notation as

$$\mathbf{E}_a \cdot \frac{\partial^2 \Phi}{\partial q \partial q} \cdot \mathbf{E}_a = 0$$

that shows that the Hessian matrix is degenerate for all points of phase space, because the vectors $\mathbf{E}_a$ are eigenvectors with null eigenvalue. Intuitively, because the "bottom" of $\Phi(q)$ is not a point but rather a line, if q^α is a local minimum of $\Phi(q)$, then $\mathscr{T}_{\mathbf{c}} q^\alpha$ will also be a minimum. The mathematical proof of this statement goes as follows: q^α satisfies the extremum condition expressed by the set of equations

$$\frac{\partial \Phi}{\partial \mathbf{q}_i}(q^\alpha) = 0 \quad i = 1, \cdots, N$$

The claim is that $\mathscr{T}_{\mathbf{c}} q^\alpha$ is also a solution, this is,

$$\frac{\partial \Phi}{\partial \mathbf{q}_i}(\mathscr{T}_{\mathbf{c}} q^\alpha) = 0 \quad i = 1, \cdots, N$$

By Taylor expanding the left hand side we obtain

$$\frac{\partial \Phi}{\partial \mathbf{q}_i}(\mathscr{T}_{\mathbf{c}} q^\alpha) = \frac{\partial \Phi}{\partial \mathbf{q}_i}(q^\alpha) + \sum_j \frac{\partial^2 \Phi}{\partial \mathbf{q}_i \partial \mathbf{q}_j}(q^\alpha) \cdot \mathbf{c} + \frac{1}{2!} \sum_{jk} \frac{\partial^3 \Phi}{\partial \mathbf{q}_i \partial \mathbf{q}_j \partial \mathbf{q}_k}(q^\alpha) : \mathbf{cc}$$

The first term vanishes because of (18.1). The second term vanishes as a consequence of (18.1). Higher order terms also vanish as can be seen by taking higher derivatives of the

identity $\Phi(\mathscr{T}_{\mathbf{q}}q) = \Phi(q)$.

Broken translation symmetry of the statistical ensemble

Apparently, we could understand all the minima at the bottom of a canyon in the energy landscape as equivalent, but they are not, really. Imagine that we run the steepest descent dynamics (18.1) starting from an initial configuration q_0 leading to the minimum q^α. The collection of all microstates q_0 that land on q^α is what we have called the basin $\mathscr{B}^\alpha$ of the inherent structure q^α. If we now start with an initial microstate $\mathscr{T}_{\mathbf{c}}q_0$ which is translated from q_0, the final state will land on $q^{\alpha'} = \mathscr{T}_{\mathbf{c}}q^\alpha$. The reason is that if $q(t) = \{\mathbf{q}_1(t), \cdots, \mathbf{q}_N(t)\}$ is the unique solution of (18.1) with initial condition $q(0)$, then $\mathscr{T}_{\mathbf{c}}q(t) = \{\mathbf{q}_1(t) + \mathbf{c}, \cdots, \mathbf{q}_N(t) + \mathbf{c}\}$ is also solution with initial condition $\mathscr{T}_{\mathbf{c}}q(0)$. Therefore, the region of phase space $\mathscr{T}_{\mathbf{c}}\mathscr{B}^\alpha$ of the points of the basin $\mathscr{B}^\alpha$ that have been translated by $\mathbf{c}$ is precisely the basin $\mathscr{B}^{\alpha'}$ corresponding to the inherent structure $q^{\alpha'} = \mathscr{T}_{\mathbf{c}}q^\alpha$. Note that the two basis of attraction $\mathscr{B}^\alpha$ and $\mathscr{B}^{\alpha'}$ are disjoint. Therefore, *inherent structures that are simply translated in space, should be regarded as different as far as ergodicity is concerned*. This can be intuitively understood also from a dynamical point of view for the case of a perfect crystal, in which the inherent structure q^α is periodic in space. In that case, configurations in the basin of attraction of the inherent structure q^α describing vibrations around the equilibrium positions q^α can never be understood as vibrations around a translated $\mathscr{T}_{\mathbf{c}}q^\alpha$ (unless, of course, the translation vector $\mathbf{c}$ corresponds to a lattice vector).

The above discussion about translated basins of attraction reflect in the following mathematical property of the characteristic function

$$\chi(q, q^\alpha) = \chi(\mathscr{T}_{\mathbf{c}}q, \mathscr{T}_{\mathbf{c}}q^\alpha)$$

This shows that, in general,

$$\chi(q, q^\alpha) \neq \chi(\mathscr{T}_{\mathbf{c}}q, q^\alpha)$$

and, as far as the argument q is concerned, the characteristic function *is not translation invariant*. This has a strong implication in that the restricted Hamiltonian $\hat{\mathscr{H}}^\alpha(z)$ introduced in (18.1) is not translation invariant neither, and neither is the restricted ensemble (18.1), despite that the original Hamiltonian is. The main conclusion is that when the system experiences a non-ergodic transition due to a deep and fast quenching that traps dynamically the trajectory in phase space near to a local minima of the potential energy, then translation symmetry is lost. This is an example of *symmetry breaking* in which the Hamiltonian is symmetric (in this case under translations) but the statistical description of the system, the ensemble, is not.

Let us consider now the main differences that arise in computing canonical ensemble averages with the original Hamiltonian $\hat{\mathscr{H}}(z)$ and the restricted Hamiltonian $H^\alpha(z)$ of space dependent phase functions like, for example, the microscopic density field. The canonical ensemble ρ^{eq} with the original Hamiltonian $\hat{H}(z)$ gives the following average of the density field

$$n^{\mathrm{eq}}(\mathbf{r}) \equiv \mathrm{Tr}[\rho^{\mathrm{eq}}\hat{n}_{\mathbf{r}}] = \mathrm{Tr}[\mathscr{T}_{\mathbf{c}}(\rho^{\mathrm{eq}}\hat{n}_{\mathbf{r}})] = n^{\mathrm{eq}}(\mathbf{r} - \mathbf{c})$$

In the second identity we have performed a simple change of variables in the positions of all the particles $\mathbf{q}_i \to \mathbf{q}_i + \mathbf{c}$. Then we have used that the Hamiltonian is invariant under translations and so it is the Gibbs ensemble. We have also used the following identity

$$\mathscr{T}_{\mathbf{c}}\hat{n}_{\mathbf{r}}(z) = \mathscr{T}_{\mathbf{c}}\sum_i \delta(\mathbf{r} - \mathbf{q}_i) = \hat{n}_{\mathbf{r}-\mathbf{c}}(z)$$

Eq. (18.1) can only be true for all $\mathbf{c}$ if the average density field is constant in space. In the non-ergodic state characterized by the restricted ensemble $\rho^\alpha(z)$, however, such a translation invariance is broken and the resulting average density is not constant in space, this is

$$n^\alpha(\mathbf{r}) = \mathrm{Tr}[\rho^\alpha \hat{n}_{\mathbf{r}}] \neq n^\alpha(\mathbf{r} + \mathbf{c})$$

This is consistent with the fact that the particles are vibrating near the inherent structure and, therefore, the probability (and hence the value of the density field) of finding a particle near the positions $\mathbf{q}_i^\alpha$ of the inherent structure density should be larger.

Thermodynamics in terms of inherent structures

In passing, we note that due to the disjointness property of the characteristic functions we have the identity

$$\sum_\alpha \chi^\alpha(z) = 1$$

where the sum goes over all the basins of attraction of each inherent structure. Therefore, the thermodynamic free energy of the system can always be written in the form

$$F(\beta, N, V) = \sum_\alpha F^\alpha(\beta, N, V)$$

$$F^\alpha(\beta, N, V) = \int dz \exp\{-\beta\hat{H}(z)\}\chi(q, q^\alpha) = \int \frac{dq}{\Lambda^{3N}} \exp\{-\beta\hat{\Phi}(q)\}\chi_\alpha(q)$$

The free energy $F^\alpha(\beta, N, V)$ of the inherent structure α can be further approximated by expanding the potential of interaction around the minima q^α, $\hat{\Phi}(q) = \hat{\Phi}(q_0^\alpha) + \Delta\hat{\Phi}(q)$

$$F(\beta, N, V) = \sum_\alpha \exp\{-\beta\hat{\Phi}(q_0^\alpha)\}\Delta F^\alpha(\beta, N, V)$$

$$\Delta F^\alpha(\beta, N, V) = \int \frac{dq}{\Lambda^{3N}} \exp\{-\beta\Delta\hat{\Phi}(q)\}\chi_\alpha(q)$$

The free energy $\Delta F^\alpha(\beta, N, V)$ accounts for "vibrations" and a reasonable approximation is to assume that these vibrations are harmonic, thus allowing for an explicit analytical model. In addition, let us introduce the density $g(\phi)$ of inherent structures as

$$g(\phi) = \frac{1}{\mathscr{N}}\sum_\alpha \delta(\hat{\Phi}(q_0^\alpha) - \phi)$$

where $\mathcal{N}$ is the total number of inherent structures. The density of states is normalized to unity

$$\int d\phi g(\phi) = 1$$

This function counts the number of inherent structures that have the energy $\hat{\Phi}(q_0^\alpha)$ between ϕ and $\phi + d\phi$. Then we may express (18.1) in the form

$$F(\beta, N, V) = \int d\phi g(\phi) \exp\{-\beta\phi\} \Delta F^\alpha(\beta, N, V)$$

[What to do with the α index here?] [Cardenas, Franz, and Parisi [?] propose a particular way of restricting by introducing the notion of "overlap" between configurations]

Perfect crystals

For sufficiently low energy, when all the system is in the crystal phase, the i-th atom of the system will be moving around a lattice position $\mathbf{q}_i^0 = n_i^1 \mathbf{a}_1 + n_i^2 \mathbf{a}_2 + n_i^3 \mathbf{a}_2$, where n_i^α are integers and $\mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3$ are the lattice vectors. We will see that the density has developed "bumps" at these lattice location. In other words, in the crystalline state, the observed thermal average will have the functional form

$$n(\mathbf{r}) = \langle \hat{n}_{\mathbf{r}} \rangle^* = \sum_{\mathbf{g}} n_{\mathbf{g}} e^{i\mathbf{g} \cdot \mathbf{r}}$$

which is a superposition of plane waves, with amplitudes given by the *order parameters* $n_{\mathbf{g}}$. Here $\mathbf{g}$ are the reciprocal-lattice vectors defined as

$$\mathbf{g} \cdot \mathbf{L} = 2\pi n$$

where n is an integer and $\mathbf{L} = n_1 \mathbf{a}_1 + n_2 \mathbf{a}_2 + n_3 \mathbf{a}_3$ is the set of discrete translational symmetry operations in real space. If the vectors of the direct lattice are $\mathbf{L} = \mathbf{A} \cdot \mathbf{n}$, where $\mathbf{A}$ is the matrix formed with the column lattice vectors $\mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3$, and $\mathbf{n} = (n_1, n_2, n_3)$ is a vector of integer components, then the reciprocal lattice vectors are of the form $\mathbf{g} = \mathbf{B} \cdot \mathbf{n}$ where the matrix $\mathbf{B}$ satisfies $\mathbf{B}^T \mathbf{A} = 2\pi \mathbf{1}$.

Note that if all the order parameters $n_{\mathbf{g}} = 0$ except for $\mathbf{g} = \mathbf{0}$, then the density field is a constant in space. Therefore, what signals a crystal is that $n_{\mathbf{g}} \neq 0$ for some $\mathbf{g}$. In this case, the density field (18.1) is periodic because it satisfies

$$n(\mathbf{r} + \mathbf{L}) = n(\mathbf{r})$$

By defining the Fourier transform with the convention

$$\hat{n}_{\mathbf{k}}(z) = \int d\mathbf{r} e^{-i\mathbf{k}\cdot\mathbf{r}} \hat{n}_{\mathbf{r}}(z) = \sum_{i}^{N} e^{-i\mathbf{k}\cdot\mathbf{r}_i}$$

$$\hat{n}_{\mathbf{r}}(z) = \int \frac{d\mathbf{k}}{2\pi^3} e^{i\mathbf{k}\cdot\mathbf{r}} \hat{n}_{\mathbf{k}}(z)$$

the order parameters $n_{\mathbf{g}}$ are given by

$$n_{\mathbf{g}} = \langle \hat{n}_{\mathbf{g}} \rangle^*$$

where the microscopic order parameter is given by

$$\hat{n}_{\mathbf{g}}(z) \equiv \frac{1}{V} \sum_{i}^{N} e^{-i\mathbf{g}\cdot\mathbf{r}_i}$$

In (18.1), we have denoted the thermal average with $\langle \cdots \rangle^*$ because this equilibrium average is to be distinguished from the ordinary Gibbs ensemble average $\langle \cdots \rangle^{\text{eq}}$. In fact, we know that if the system has a Hamiltonian which is translation invariant then, necessarily, the Gibbs ensemble average of the density should be constant in space. This is, for an *arbitrary* translation vector $\mathbf{c}$ the Gibbs ensemble average satisfies

$$n^{\text{eq}}(\mathbf{r}) = n^{\text{eq}}(\mathbf{r} + \mathbf{c})$$

This theorem will be proved in the next section. This is true even for the crystalline state! The Hamiltonian in the crystalline state is exactly the same as in the fluid state. This leads to a paradox, because the theorem (18.1) forbids bumps in the density, even in the crystalline state that is defined by having bumps at lattice sites. How do we reconcile these two facts? The origin of this apparent paradox lies on the actual lattice positions $\mathbf{q}_i^0$ which are completely undetermined in the freezing process. When computing the Gibbs average in (18.1) we are somehow integrating also over all possible locations and orientations of the lattice, and this washes out the bumps of the density. In any *particular realization* of the freezing process described above (rescaling of the velocities until the system freezes) we will observe bumps in the density field. What is happening here is that, as the energy is reduced, the system experiences an *ergodic to non-ergodic transition* [?]. In the low energy shell, once the system has selected (by chance) a particular reference lattice spacing $\mathbf{q}_i^0$, then it remains trapped in a very small region of all the energy shell. In fact the system, if sufficiently large, will *never* visit microscopic states for which the density has bumps located in any other lattice $\mathbf{q}_i^1$, even if this lattice is just a simple translation and/or rotation of $\mathbf{q}_i^0$ *with exactly the same energy*. To do that, the system would need to melt by a spontaneous thermal fluctuation and re-crystallize in a lattice with a different orientation and translation, and this is an extremely rare event. Somehow the system has developed spontaneously new dynamic invariants that forbid the system to explore all the energy shell. Therefore, once we are in a crystal phase, it makes no sense to keep performing averages with respect to the equilibrium ensemble in which only the total energy and momenta are conserved, because these ensembles will never

be able to predict the bumpy density fields that are actually observed in the simulation (and in the lab). Does this means that we need to abandon statistical mechanics in this instance? Not really, all we need to do is to account for the new dynamic invariants in the equilibrium ensemble in order to obtain the correct predictions for the observations we see in MD.

In order to construct this restricted ensemble, we may follow the Gibbs-Jaynes route and construct the least biased ensemble that reproduces the known information that we have in the crystalline state, which is the average energy and the average density field. By maximizing the entropy functional subject to the conditions

$$\text{Tr}[\rho\hat{H}] = E$$
$$\text{Tr}[\rho\hat{n}_{\mathbf{g}}] = n_{\mathbf{g}}$$

The resulting ensemble has the form

$$\rho^{\alpha}(z) = \frac{1}{Z(\beta, h)} \exp\left\{-\beta\hat{H}(z) - \beta\sum_{\mathbf{g}} h_{\mathbf{g}}\hat{n}_{\mathbf{g}}(z)\right\}$$

where the partition function is defined as

$$Z(\beta, h) = \int dz \exp\left\{-\beta\hat{H}(z) - \beta\sum_{\mathbf{g}} h_{\mathbf{g}}\hat{n}_{\mathbf{g}}(z)\right\}$$

Here, $h_{\mathbf{g}}$ are the Lagrange multipliers that ensure that the average of $\hat{n}_{\mathbf{g}}(z)$ with the restricted ensemble (18.1) is precisely $n_{\mathbf{g}}$. This is expressed by the condition

$$\frac{\partial}{\partial h_{\mathbf{g}}}\left[-k_B T \ln Z(\beta, h)\right] = n_{\mathbf{g}}$$

that gives the one to one connection between $h_{\mathbf{g}}$ and $n_{\mathbf{g}}$.

Note that the additional term in the restricted ensemble is equivalent to introduce an external potential

$$\sum_{\mathbf{g}} h_{\mathbf{g}}\hat{n}_{\mathbf{g}}(z) = \sum_{i}^{N} \phi^{h}(\mathbf{q}_i)$$

where we have used (18.1) and have introduced the external potential as

$$\phi^{h}(\mathbf{r}) = \frac{1}{V}\sum_{\mathbf{g}} h_{\mathbf{g}} e^{i\mathbf{g}\cdot\mathbf{r}}$$

This is a periodic potential that satisfies $\phi^{h}(\mathbf{r} + \mathbf{L}) = \phi^{h}(\mathbf{r})$ for any direct lattice vector $\mathbf{L}$.

Therefore, in this view of the crystallization process, the transition to a non-ergodic behaviour is represented by the appearance of an effective external potential that leads to an effective ensemble which is no longer translation invariant. The particles move with

the original Hamiltonian but the resulting trajectories do not sample with equiprobability all the energy shell and, therefore, the statistics of the problem is no longer given by Gibbs recipe.

Admittedly, this approach is somewhat unsatisfactory. Ideally, what one would like to obtain is a prediction of the lattice structure through the matrix $\mathbf{A}$ (up to global rotations and translations) out of the Hamiltonian $\hat{H}(z)$ and the thermodynamic state (temperature and number density). For this to make sense, the particular way in which the loss of ergodicity happens would need to be described. This seems to be an extremely difficult task and we take the point of view in which *we know* that the system has become trapped in a particular lattice structure and proceed as usual, according with this information at hand. In this respect, the system is characterized thermodynamically with not only the temperature and number density, but also with the values of the "external fields" $h_{\mathbf{g}}$ that fix univocally the values of the known order parameters $n_{\mathbf{g}}$. Therefore, the actual values of $h_{\mathbf{g}}$ or, equivalently $n_{\mathbf{g}}$, are assumed to be given data of the problem. They are not predicted as one would like in the ideal world. In the picture of Fig. **??**, this procedure is equivalent to specify the effective ensemble by assuming that we know the average energy E_1 and also the value of the average position $\langle q \rangle$. Note that the dynamics in the trapped minima is still given by the Hamiltonian (and not by the effective Hamiltonian, which is used only for the calculation of averages).

As an illustrative example, let us assume that we know that the average density field $n(\mathbf{r})$ has the form of a collection of Gaussian of width σ centered at the lattice points, this is,

$$n(\mathbf{r}) = \frac{1}{N_0} \sum_{\mathbf{L}} \exp\left\{ -\frac{(\mathbf{r} - \mathbf{L})^2}{2\sigma^2} \right\}$$

where $\mathbf{L} = \mathbf{A} \cdot \mathbf{n}$ are the lattice vectors and N_0 ensures the normalization of the density over all volume. At the same time, this density field is given as (18.1).

$$n(\mathbf{r}) = \frac{1}{N_0} \sum_{\mathbf{L}} \exp\left\{ -\frac{(\mathbf{r} - \mathbf{L})^2}{2\sigma^2} \right\} = \sum_{\mathbf{g}} n_{\mathbf{g}} e^{i\mathbf{g} \cdot \mathbf{r}}$$

If we multiply both sides with $e^{-i\mathbf{k} \cdot \mathbf{r}}$ and integrate over all the volume, we obtain

$$\int d\mathbf{r} e^{-i\mathbf{k} \cdot \mathbf{r}} \frac{1}{N_0} \sum_{\mathbf{L}} \exp\left\{ -\frac{(\mathbf{r} - \mathbf{L})^2}{2\sigma^2} \right\} = \sum_{\mathbf{g}} n_{\mathbf{g}} \int d\mathbf{r} e^{-i\mathbf{k} \cdot \mathbf{r}} e^{i\mathbf{g} \cdot \mathbf{r}}$$

this is

$$\frac{1}{N_0} \sum_{\mathbf{L}} e^{-i\mathbf{k} \cdot \mathbf{L}} \int d\mathbf{r}' e^{-i\mathbf{k} \cdot \mathbf{r}'} \exp\left\{ -\frac{(\mathbf{r}')^2}{2\sigma^2} \right\} = \sum_{\mathbf{g}} n_{\mathbf{g}} (2\pi)^3 \delta(\mathbf{g} - \mathbf{k})$$

this is

$$\frac{(2\pi\sigma^2)^{3/2}}{N_0} \sum_{\mathbf{L}} e^{-i\mathbf{k}\cdot\mathbf{L}} e^{-\frac{\sigma^2}{2}\mathbf{k}^2} = \sum_{\mathbf{g}} n_{\mathbf{g}} (2\pi)^3 \delta(\mathbf{g} - \mathbf{k})$$

This equation is valid for any $\mathbf{k}$ in principle. If we choose $\mathbf{k}$ to coincide with a particular reciprocal lattice vector $\mathbf{g}_1$, the above equation becomes

$$\frac{(2\pi\sigma^2)^{3/2}}{N_0} \sum_{\mathbf{L}} e^{-\frac{\sigma^2}{2}\mathbf{g}_1^2} = n_{\mathbf{g}_1} (2\pi)^3 V$$

This is, $n_{\mathbf{g}}$ is, up to a proportionality constant (which is independent on $\mathbf{g}$) equal to $e^{-i\frac{\sigma^2}{2}\mathbf{g}^2}$. The proportionality constant may be computed for $\mathbf{g} = 0$, as we know that in this case, $n_{\mathbf{0}} = N/V$. Therefore, we have

$$n_{\mathbf{g}} = \frac{N}{V} e^{-\frac{\sigma^2}{2}\mathbf{g}^2}$$

Unfortunately, it is not easy to find out what particular values of the conjugate variables $h_{\mathbf{g}}$ would correspond to these particular values of the order parameter, as this would require to compute explicitly the free energy for this particular situation, which is not trivial.

For future reference, we note the effect of the translation operator on the microscopic order parameter. For example, we have

$$\{\hat{\mathbf{P}}, \hat{n}_{\mathbf{g}}\} = i\mathbf{g}\hat{n}_{\mathbf{g}}$$

Therefore, the action of the generator of translations on the restricted ensemble (18.1) is

$$\{\hat{\mathbf{P}}, \rho^\alpha\} = \rho^\alpha \left\{ \hat{\mathbf{P}}, -\beta\hat{H} - \beta \sum_{\mathbf{g}} h_{\mathbf{g}}\hat{n}_{\mathbf{g}} \right\} = -\beta\rho^\alpha \sum_{\mathbf{g}} h_{\mathbf{g}} i\mathbf{g}\hat{n}_{\mathbf{g}}$$

The translation operators have the following action on the microscopic order parameter and the restricted ensemble

$$\mathscr{T}_{\mathbf{t}} \hat{n}_{\mathbf{g}}(z) = e^{-i\mathbf{g}\cdot\mathbf{t}} \hat{n}_{\mathbf{g}}(z)$$

$$\mathscr{T}_{\mathbf{t}} \rho^\alpha(z) = \frac{1}{Z(\beta, h)} \exp\left\{ -\beta\hat{H}(z) - \beta \sum_{\mathbf{g}} h_{\mathbf{g}} e^{-i\mathbf{g}\cdot\mathbf{t}} \hat{n}_{\mathbf{g}}(z) \right\}$$

In counterdistinction to the Gibbs ensemble $e^{-\beta\hat{H}(z)}$, which is invariant under arbitrary translations, the restricted ensemble $\rho^\alpha(z)$ is invariant under *discrete translations* with lattice vectors $\mathbf{L}$. The equilibrium measure has *lost* symmetry and this is what is known as broken symmetry.

Defects

The inherent structure of a perfect crystal has an energy which is not very different from the inherent structure of a crystal that has produced a pair vacancy-interstitial as shown in the Figure. Therefore, it makes sense to look at megabasins of the crystal and study the dynamics of defects. The system is still non-ergodic, but jumps from one basin to another is allowed. This means that we should promote the inherent structure to a dynamic variable. I have to think the way to do this in a coarse-grained way.

18.1.1   Broken symmetries and the Goldstone theorem.

This section is based on the following references: Szamel and Ernst [?], Szamel and Flenner [?], and Walz et al. [?].

As we discussed in ??, Noether's theorem shows the close connection between conservation of total momentum and translation symmetry. We introduce now the *local* version of total momentum which is the momentum density field, defined as

$$\hat{\mathbf{g}}_{\mathbf{r}}(z) = \sum_i^N \mathbf{p}_i \delta(\mathbf{r} - \mathbf{q}_i)$$

We assume that the microscopic state z evolves according to Hamilton's equation with Hamiltonian given by $\hat{H}(z) = \sum_i^N \frac{\mathbf{p}_i^2}{2m_i} + \frac{1}{2}\sum_{ij}\phi_{ij} + \sum_i \phi_i^{\text{ext}}$. Therefore, the evolution of the momentum density is through the balance equation

$$\partial_t \hat{\mathbf{g}}_{\mathbf{r}}(z) = -\{\hat{H}, \hat{\mathbf{g}}_{\mathbf{r}}\} = -\boldsymbol{\nabla}\cdot\hat{\boldsymbol{\sigma}}_{\mathbf{r}}(z) + \mathbf{F}^{\text{ext}}(\mathbf{r})\hat{n}_{\mathbf{r}}(z)$$

where the stress tensor is

$$\hat{\boldsymbol{\sigma}}_{\mathbf{r}} = \hat{\mathbf{K}}_{\mathbf{r}} + \hat{\boldsymbol{\Pi}}_{\mathbf{r}} = \sum_i^N \mathbf{p}_i \mathbf{v}_i \delta(\mathbf{r} - \mathbf{q}_i) + \frac{1}{2}\sum_{ij}^N \mathbf{q}_{ij}\hat{\mathbf{F}}_{ij}\int_0^1 d\epsilon\, \delta(\mathbf{r} - \mathbf{q}_i + \epsilon\mathbf{q}_{ij})$$

and $\mathbf{F}^{\text{ext}}(\mathbf{r})$ is the external force acting on a particle located at $\mathbf{r}$.

Consider a region of space $\mathscr{R}$ with a boundary $\partial\mathscr{R}$. The total momentum of the particles that happen to be in this region is defined as

$$\hat{\mathbf{P}}_{\mathscr{R}}(z) = \int_{\mathbb{R}^3} d\mathbf{r}\, \hat{\mathbf{g}}_{\mathbf{r}}(z)\chi_{\mathscr{R}}(\mathbf{r})$$

where $\chi_{\mathscr{R}}(\mathbf{r})$ is the characteristic function of the region $\mathscr{R}$ that takes the value 1 if $\mathbf{r} \in \mathscr{R}$ and zero otherwise. The time derivative of the momentum of the region $\mathscr{R}$ is given by

$$\partial_t \hat{\mathbf{P}}_{\mathscr{R}} = -\{\hat{H}, \hat{\mathbf{P}}_{\mathscr{R}}\} = -\int_{\mathbb{R}^3} d\mathbf{r}\chi_{\mathscr{R}}(\mathbf{r})\{\hat{H}, \hat{\mathbf{g}}_{\mathbf{r}}\} = \int_{\mathbb{R}^3} d\mathbf{r}\boldsymbol{\nabla}\chi_{\mathscr{R}}(\mathbf{r})\hat{\boldsymbol{\sigma}}_{\mathbf{r}} + \hat{\mathbf{F}}^{\text{ext}}$$

where the total external force on the fluid inside the region $\mathscr{R}$ is

$$\hat{\mathbf{F}}^{\text{ext}} = \sum_i^N \chi_{\mathscr{R}}(\mathbf{q}_i)\mathbf{F}^{\text{ext}}(\mathbf{q}_i)$$

The function $\boldsymbol{\nabla}\chi_{\mathscr{R}}(\mathbf{r})$ is concentrated at the boundary $\partial\mathscr{R}$ of the region $\mathscr{R}$. Note that the integral over the gradient of the characteristic function is another way of writing the surface integral over the boundary $\partial\mathscr{R}$, this is

$$\int_{\mathbb{R}^3} d\mathbf{r}'\boldsymbol{\nabla}'\chi_{\mathscr{R}}(\mathbf{r}')\cdots = \int_{\partial\mathscr{R}} d\mathbf{S}'\cdots$$

When there are no external forces, expression (18.1.1) is just a formulation of the fact that the total momentum in the region $\mathscr{R}$ changes only due to the flow of momentum (represented by the stress tensor) through the surface enclosing the region and it is, in fact, a version of Gauss theorem. Note that is the definition of the momentum in a restricted region of space what brings into the picture the stress tensor of the system.

Consider now the following identity, known as Kubo-Martin-Schwinger (KMS) property []

$$\mathrm{Tr}\left[\rho\{\hat{G},\hat{\mathbf{P}}_{\mathscr{R}}\}\right] = -\mathrm{Tr}\left[\hat{G}\{\rho,\hat{\mathbf{P}}_{\mathscr{R}}\}\right]$$

where $\hat{G}(z)$ is an arbitrary phase function and $\rho(z)$ is an ensemble that satisfies reasonable properties at infinity. This identity is easily proved by considering

$$\left\langle\{\hat{G},\mathbf{P}_{\mathscr{R}}\}\right\rangle = \int dz\rho(z)\{\hat{G},\hat{\mathbf{P}}_{\mathscr{R}}\} = \int dz\rho(z)\sum_{i=1}^{N}\left(\frac{\partial\hat{G}}{\partial\mathbf{q}_i}\frac{\partial\hat{\mathbf{P}}_{\mathscr{R}}}{\partial\mathbf{p}_i} - \frac{\partial\hat{G}}{\partial\mathbf{p}_i}\frac{\partial\hat{\mathbf{P}}_{\mathscr{R}}}{\partial\mathbf{q}_i}\right)$$

Integrate by parts the derivatives acting on the field $\hat{\varphi}_{\mathbf{r}}(z)$

$$\left\langle\{\hat{G},\mathbf{P}_{\mathscr{R}}\}\right\rangle = \sum_{i=1}^{N}\int dz\frac{\partial}{\partial\mathbf{q}_i}\left(\rho(z)\hat{G}\frac{\partial\hat{\mathbf{P}}_{\mathscr{R}}}{\partial\mathbf{p}_i}\right) - \sum_{i=1}^{N}\int dz\frac{\partial}{\partial\mathbf{p}_i}\left(\rho(z)\hat{G}\frac{\partial\hat{\mathbf{P}}_{\mathscr{R}}}{\partial\mathbf{q}_i}\right)$$
$$- \int dz\hat{G}\sum_{i=1}^{N}\left(\frac{\partial\rho(z)}{\partial\mathbf{q}_i}\frac{\partial\hat{\mathbf{P}}_{\mathscr{R}}}{\partial\mathbf{p}_i} - \frac{\partial\rho(z)}{\partial\mathbf{p}_i}\frac{\partial\hat{\mathbf{P}}_{\mathscr{R}}}{\partial\mathbf{q}_i}\right)$$

The first boundary term is zero because

$$\int dz\frac{\partial}{\partial\mathbf{q}_i}\left(\rho(z)\hat{G}\frac{\partial\hat{\mathbf{P}}_{\mathscr{R}}}{\partial\mathbf{p}_i}\right) = \int dz\frac{\partial}{\partial\mathbf{q}_i}\left(\rho(z)\hat{G}\chi_{\mathscr{R}}(\mathbf{q}_i)\right)$$

and the value of $\chi_{\mathscr{R}}(\mathbf{q}_i)$ when $\mathbf{q}_i$ is at the boundary (i.e. $\mathbf{q}_i \to \pm\infty$) is zero. The second boundary term is

$$\int dz\frac{\partial}{\partial\mathbf{p}_i}\left(\rho(z)\hat{G}\sum_{j}\mathbf{p}_j\boldsymbol{\nabla}\chi_{\mathscr{R}}(\mathbf{q}_j)\right)$$

and it can be neglected under the assumption that $\mathbf{p}_i\rho(z)$ vanishes when $\mathbf{p}_i \to \pm\infty$, which is quite reasonable. Once the boundary terms are neglected in (18.1.1) we arrive at (18.1.1).

The KMS identity (18.1.1) may be particularized to the case in which the phase function is

$$\hat{G}(z) = \hat{n}_{\mathbf{r}}(z) - n(\mathbf{r}) = \delta\hat{n}_{\mathbf{r}}(z)$$

and the ensemble is given by the restricted ensemble (18.1), this is

$$\mathrm{Tr}\left[\rho^\alpha\{\delta\hat{n}_\mathbf{r}, \hat{\mathbf{P}}_\mathscr{R}\}\right] = -\mathrm{Tr}\left[\delta\hat{n}_\mathbf{r}\{\rho^\alpha, \hat{\mathbf{P}}_\mathscr{R}\}\right]$$

The two Poisson brackets appearing in this expression are easily computed

$$\{\hat{n}_\mathbf{r}, \hat{\mathbf{P}}_\mathscr{R}\} = \sum_i \frac{\partial\hat{n}_\mathbf{r}}{\partial\mathbf{q}_i}\chi_\mathscr{R}(\mathbf{q}_i) = -\boldsymbol{\nabla}\left(\chi_\mathscr{R}(\mathbf{r})\hat{n}_\mathbf{r}\right)$$

$$\{\rho^\alpha, \hat{\mathbf{P}}_\mathscr{R}\} = -\beta\rho^\alpha\{\hat{H}^\alpha, \hat{\mathbf{P}}_\mathscr{R}\} = \beta\rho^\alpha\left[\int d\mathbf{r}\,\hat{\boldsymbol{\sigma}}_\mathbf{r}\boldsymbol{\nabla}\chi_\mathscr{R}(\mathbf{r}) + \int d\mathbf{r}\hat{n}_\mathbf{r}\mathbf{F}^\mathrm{ext}(\mathbf{r})\chi_\mathscr{R}(\mathbf{r})\right] + \beta\rho^\alpha\left\{\Upsilon^\alpha, \hat{\mathbf{P}}_\mathscr{R}\right\}$$

The last term has the form

$$\rho^\alpha\left\{\Upsilon^\alpha, \hat{\mathbf{P}}_\mathscr{R}\right\} = \rho^\alpha\sum_i \frac{\partial\Upsilon^\alpha}{\partial\mathbf{q}_i}(q)\chi_\mathscr{R}(\mathbf{q}_i)$$

By substituting the two results (18.1.1) into (18.1.1) we obtain

$$-\boldsymbol{\nabla}\left(\chi_\mathscr{R}(\mathbf{r})n^\alpha(\mathbf{r})\right) = -\beta\int d\mathbf{r}'\,\langle\delta\hat{n}_\mathbf{r}\hat{\boldsymbol{\sigma}}_{\mathbf{r}'}\rangle_\alpha\boldsymbol{\nabla}'\chi_\mathscr{R}(\mathbf{r}') + \int d\mathbf{r}'\,\langle\delta\hat{n}_\mathbf{r}\hat{n}_{\mathbf{r}'}\rangle_\alpha\mathbf{F}^\mathrm{ext}(\mathbf{r}')\chi_\mathscr{R}(\mathbf{r}')$$

$$+ \mathrm{Tr}\left[\rho^\alpha\delta\hat{n}_\mathbf{r}\sum_i\frac{\partial\Upsilon^\alpha}{\partial\mathbf{q}_i}(q)\chi_\mathscr{R}(\mathbf{q}_i)\right]$$

The last term is a restricted ensemble average. We assume that this restricted ensemble average coincides with the time average of the microscopic dynamics. By assumption, the microscopic dynamics remains always within the basin $\mathscr{B}^\alpha$ and never touches the boundary of the the basin. For all these interior microstates the confining potential vanishes $\Upsilon^\alpha(q) = 0$ and produces no forces. Therefore, the last term in (18.1.1) vanishes.

From Eq. (18.1.1) in the absence of external forces acting on the system and for a any point $\mathbf{r}$ in the interior of $\mathscr{R}$, one obtains [?]

$$\boldsymbol{\nabla}n^\alpha(\mathbf{r}) = \beta\int_{\partial\mathscr{R}} d\mathbf{S}'\,\langle\delta\hat{n}_\mathbf{r}\hat{\boldsymbol{\sigma}}_{\mathbf{r}'}\rangle_\alpha$$

were we used (18.1.1). This identity shows quite remarkably that the variations on the density at a given point are directly related to the correlations of the density at that point and the stress tensor *at the boundary* of the region. The boundary can be arbitrarily far and this implies necessarily that the correlations of density and stress are long ranged in space in the broken ergodic/broken symmetric state.

Demonstration of the Goldstone theorem

In Fourier space we have that (18.1.1) becomes

$$\partial_t\hat{\mathbf{g}}_\mathbf{k}(z) = -i\mathbf{k}\cdot\hat{\boldsymbol{\sigma}}_\mathbf{k}(z)$$

that shows that the components $\mathbf{k} \sim 0$ of the momentum density field are evolving very slowly. The physical reason is that the time derivative of the field in real space is given in conservative form in Eq. (18.1.1), involving a divergence. According to Gauss theorem, the momentum in a region of space can only change due to its flow through the enclosing surface. The momentum needs to be transported from any point in the interior of the region to the surface. For large volumes (small $\mathbf{k}$) the time it takes the momentum to reach the surface is large, and the time scale of evolution of the total momentum in that region is correspondingly large.

Consider Swartz inequality in the form

$$S_{AA}(q)S_{BB}(q) \geq |S_{AB}(q)|^2$$

where $S_{AB} = \langle AB \rangle$. The averages are computed with some ensemble (either the canonical Gibbs ensemble ρ^{eq} or the restricted ensemble ρ^α apt for broken-ergodic systems). We choose $A = \tilde{\varphi}_{\mathbf{k}}(z)$ and $B = -\{\mathscr{H}, \hat{\mathbf{g}}_{\mathbf{k}}\}$. This implies

$$S_{AA}(\mathbf{k}) = \left\langle |\tilde{\varphi}_{\mathbf{k}}|^2 \right\rangle$$
$$S_{BB}(\mathbf{k}) = \mathbf{k}\mathbf{k} : \langle \hat{\boldsymbol{\sigma}}_{\mathbf{k}} \cdot \hat{\boldsymbol{\sigma}}_{\mathbf{k}} \rangle = k^2 S_{bb}(k)$$
$$S_{AB}(\mathbf{k}) = -\left\langle \tilde{\varphi}_{\mathbf{k}}\{\hat{H}, \hat{\mathbf{g}}_{\mathbf{k}}\} \right\rangle = k_B T \left\langle \{\tilde{\varphi}_{\mathbf{k}}, \hat{\mathbf{g}}_{\mathbf{k}}\} \right\rangle$$

So we start

$$S_{AB}(\mathbf{k}) = -\left\langle \tilde{\varphi}_{\mathbf{k}}\{\hat{H}, \hat{\mathbf{g}}_{\mathbf{k}}\} \right\rangle = -\int dz \rho^\alpha \tilde{\varphi}_{\mathbf{k}}\{\hat{H}, \hat{\mathbf{g}}_{\mathbf{k}}\}$$

$$= k_B T \int dz e^{-\phi} \tilde{\varphi}_{\mathbf{k}}\{e^{-\beta\hat{H}}, \hat{\mathbf{g}}_{\mathbf{k}}\}$$

$$= -k_B T \int dz e^{-\beta\hat{H}}\{e^{-\phi}\tilde{\varphi}_{\mathbf{k}}, \hat{\mathbf{g}}_{\mathbf{k}}\}$$

$$= -k_B T \int dz e^{-\beta\hat{H}-\phi}\{\tilde{\varphi}_{\mathbf{k}}, \hat{\mathbf{g}}_{\mathbf{k}}\} + k_B T \int dz e^{-\beta\hat{H}-\phi}\tilde{\varphi}_{\mathbf{k}}\{\phi, \hat{\mathbf{g}}_{\mathbf{k}}\}$$

$$= -k_B T \left\langle [\{\tilde{\varphi}_{\mathbf{k}}, \hat{\mathbf{g}}_{\mathbf{k}}\} - \tilde{\varphi}_{\mathbf{k}}\{\phi, \hat{\mathbf{g}}_{\mathbf{k}}\}] \right\rangle^{\mathrm{eq}}$$

Note that in the limit $\mathbf{k} \to 0$ the first line shows that

$$\lim_{\mathbf{k} \to 0} S_{AB}(\mathbf{k}) = -\left\langle \tilde{\varphi}_{\mathbf{k}=0}\{\hat{H}, \hat{\mathbf{P}}\} \right\rangle^{\mathrm{eq}} = 0$$

We want to relate

$$\left\langle \tilde{\varphi}_{\mathbf{k}}\{\hat{H}, \hat{\mathbf{g}}_{\mathbf{k}}\} \right\rangle^{\mathrm{eq}}$$

to

$$\langle \tilde{\varphi}_{\mathbf{k}}\{\phi, \hat{\mathbf{g}}_{\mathbf{k}}\} \rangle^{\mathrm{eq}}$$

because we know that

$$\lim_{\mathbf{k}\to 0} \langle \tilde{\varphi}_{\mathbf{k}}\{\phi, \hat{\mathbf{g}}_{\mathbf{k}}\}\rangle^{\mathrm{eq}} = \langle \tilde{\varphi}_{\mathbf{k}=0}\{\phi, \hat{\mathbf{g}}_{\mathbf{k}=0}\}\rangle^{\mathrm{eq}} = \left\langle \int d\mathbf{r}\,\hat{\varphi}_{\mathbf{r}}\{\phi, \hat{\mathbf{P}}\}\right\rangle^{\mathrm{eq}} = \int d\mathbf{r}\,\left\langle \hat{\psi}_{\mathbf{r}}\right\rangle^{\mathrm{eq}}$$

The field $\hat{\psi}_{\mathbf{r}}(z)$ will be called order parameter, the field $\hat{\varphi}_{\mathbf{r}}(z)$ will be called ??.

Note that as $\mathbf{k} \to 0$ we have

$$S_{AB}(\mathbf{k}) \simeq k_B T \left\langle \{\tilde{\varphi}_{\mathbf{k}=0}, \hat{\mathbf{P}}\}\right\rangle^{\mathrm{eq}} = k_B T \int d\mathbf{r}\,\left\langle \{\hat{\varphi}_{\mathbf{r}}, \hat{\mathbf{P}}\}\right\rangle^{\mathrm{eq}} = k_B T \zeta_0 \int d\mathbf{r}\,\left\langle \hat{\psi}_{\mathbf{r}}\right\rangle^{\mathrm{eq}}$$

Therefore, Swartz inequality becomes, for small k

$$\left\langle |\tilde{\varphi}_{\mathbf{k}}|^2\right\rangle^{\mathrm{eq}} \geq \frac{k_B T \zeta_0}{k^2 S_{bb}(0)} \int d\mathbf{r}\,\left\langle \hat{\psi}_{\mathbf{r}}\right\rangle^{\mathrm{eq}}$$

where $S_{bb}(0)$ is a non-vanishing number.

Therefore, we arrive at the conclusion that the covariance of the field $\varphi_{\mathbf{k}}$ scales as k^{-2} if the average of the field $\langle \hat{\psi}_{\mathbf{r}}\rangle^{\mathrm{eq}}$ is not zero. The physical meaning of this scaling is that in real space, according to the Tauberian theorem, at long distances the correlation decays as $\langle \varphi_{\mathbf{r}}\varphi_{\mathbf{r}'}\rangle^{\mathrm{eq}} \simeq |\mathbf{r} - \mathbf{r}'|^{-1}$ i.e. there are long range correlations.

Obviously, if "the symmetry is maintained thermodynamically"

$$\{\rho^{\mathrm{eq}}, \hat{\mathbf{P}}\} = 0$$

and the equilibrium average of $\hat{\psi}_{\mathbf{r}}(z)$ vanishes.

As mentioned in Freezing and beyond, if a mode has a static correlation function in Fourier space $\langle \phi_k \phi_{-k}\rangle \sim k^{-2}$, for small k, i.e. there is long range in real space, then this results in a slow decay of the mode. This is known as the Goldstone theorem.

18.2   Fields with long range correlations are slow

The schematic path of the logic behind this is as follows. Imagine that, for some reason, you have detected that a particular field variable $\phi(\mathbf{r})$ is long ranged in space, meaning that for sufficient long distances $|\mathbf{r} - \mathbf{r}'|$, the equilibrium correlation function decays (in 3D) as

$$\langle \delta\phi(\mathbf{r})\delta\phi(\mathbf{r}')\rangle \sim \frac{1}{|\mathbf{r} - \mathbf{r}'|}$$

We can refer to this long range feature as a kind of *rigidity*, because what is happening in a part of the sample is felt very far away. In 3D the inverse of the distance is the

solution of the Poisson equation, this is,

$$\nabla^2 \frac{1}{|\mathbf{r} - \mathbf{r}'|} = -4\pi\delta(\mathbf{r} - \mathbf{r}')$$

that suggests that in a generalized sense, the Laplacian operator is the inverse of the correlation function.

The prescription is that we should include as CG variables of the description those fields that are long ranged because they are slow. Let us see how this happens. If we consider the entropy functional as depending on the field $\phi(\mathbf{r})$ and assume that we are sufficiently close to equilibrium in order to have a reasonable quadratic expansion of the entropy functional around the equilibrium state, this is

$$S[\phi] = -\frac{1}{2} \int d\mathbf{r} \int d\mathbf{r}' \delta\phi(\mathbf{r}) A(\mathbf{r}, \mathbf{r}') \delta\phi(\mathbf{r}')$$

where we have neglected a constant irrelevant term. Recall that the Legendre transform of the entropy is the thermodynamic potential, that depends on the conjugate variables $\lambda(\mathbf{r})$. The Legendre transform of a quadratic function is itself quadratic and the thermodynamic potential is now given by

$$\Phi[\lambda] = -\frac{1}{2} \int d\mathbf{r} \int d\mathbf{r}' \lambda(\mathbf{r}) C(\mathbf{r}, \mathbf{r}') \lambda(\mathbf{r}')$$

where the kernel $C(\mathbf{r}, \mathbf{r}')$ is the inverse of the kernel $A(\mathbf{r}, \mathbf{r}')$ in (18.2) in the functional sense

$$\int d\mathbf{r}' C(\mathbf{r}, \mathbf{r}') A(\mathbf{r}', \mathbf{r}'') = \delta(\mathbf{r} - \mathbf{r}'')$$

This equation can be understood as a generalized Ornstein-Zernicke equation. As we know that the second derivatives of the thermodynamic potential give directly the equilibrium correlation of the fluctuations of the field, i.e.

$$C(\mathbf{r}, \mathbf{r}') = \langle \delta\phi(\mathbf{r}) \delta\phi(\mathbf{r}') \rangle$$

we conclude that $A(\mathbf{r}, \mathbf{r}')$ is the inverse of the correlations of the long ranged field. But this implies that $A(\mathbf{r}, \mathbf{r}') \sim \nabla^2$ in a generalized sense. Therefore, the quadratic entropy corresponding to a long ranged field has the form

$$S[\phi] \propto \int d\mathbf{r} (\nabla\phi(\mathbf{r}))^2$$

that shows that it depends *in a local form on the derivatives of the field*. This functional form of the entropy (up to constants) is a direct consequence of the assumed long range nature of the correlations. Conversely, an entropy functional of the form (18.2) predicts long range correlations for the field $\phi(\mathbf{r})$.

Now we go to the dynamic part of the Goldstone theorem. As we will see later in the book, the gradient of the entropy is the driving force of the CG variables. Schematically,

we have that the equation of motion of a field is of the form

$$\partial_t \phi(\mathbf{r}) = \int d\mathbf{r} M(\mathbf{r}, \mathbf{r}') \frac{\delta S}{\delta \phi(\mathbf{r}')}[\phi]$$

where $M(\mathbf{r}, \mathbf{r})$ is a kernel that, in general captures the reversible and irreversible parts of the dynamics. In many cases, we have translation invariance, $M(\mathbf{r}, \mathbf{r}') = M(\mathbf{r} - \mathbf{r}')$. The functional derivative of the entropy is

$$\frac{\delta S}{\delta \phi(\mathbf{r}')}[\phi] = \nabla'^2 \phi(\mathbf{r}')$$

and, therefore, the equation of motion for the field is of the form

$$\partial_t \phi(\mathbf{r}) = \nabla^2 \int d\mathbf{r} M(\mathbf{r} - \mathbf{r}')\phi(\mathbf{r}')$$

We see therefore, that a long ranged field evolves diffusively. This means that the realizations of the fields that are smooth in space (and for which the right hand side is very small) evolve very slowly. In other words, the small wavelength components of the field are always very slow. Therefore, a field that displays long ranged correlations evolves slowly. The physical intuition here is clear, a field that is correlated over long distances cannot change without affecting large portions of the system, and this requires some time.

18.3   The CG variables

In order to describe the solid at the present level of description, we will use the following CG variables.

$$\hat{\rho}_\mathbf{r}(z) = \sum_i^N m_i \delta(\mathbf{r} - \mathbf{q}_i)$$

$$\hat{\mathbf{d}}_\mathbf{r}(z) = \sum_i^N m_i \mathbf{u}_i \delta(\mathbf{r} - \mathbf{q}_i)$$

$$\hat{\mathbf{g}}_\mathbf{r}(z) = \sum_i^N \mathbf{p}_i \delta(\mathbf{r} - \mathbf{q}_i)$$

where $\mathbf{u}_i = (\mathbf{q}_i - \mathbf{q}_i^\alpha)$ is the displacement of particle i with respect to a reference location $\mathbf{q}_i^\alpha$. This reference location are a local minimum of the energy landscape and, therefore, a particular inherent structure. Here $\hat{\rho}_\mathbf{r}$ is the mass density field, $\hat{\mathbf{d}}_\mathbf{r}$ is the *mass displacement density*. Note that the displacement density field $\hat{\mathbf{d}}_\mathbf{r}$ contains in its definition the mass of the particles. This field gives the displacement from their equilibrium positions of all the atoms that are near $\mathbf{r}$. $\hat{\mathbf{g}}_\mathbf{r}$ is the momentum density field.

In addition to the above variables, we will also describe the system at the CG level with the total energy $\hat{H}(z)$, and the characteristic function $\chi(q, q^\alpha)$ of the inherent struc-

ture

$$\hat{H}(z) = \sum_i \frac{\mathbf{p}_i^2}{2m_i} + \hat{\phi}(q)$$

In general, the potential energy $\hat{\phi}(z)$ contains a translation invariant interparticle potential plus a non-invariant contribution due to external fields. For example, for the case of pair-wise interparticle potentials, we have

$$\hat{\phi}(z) = \frac{1}{2} \sum_{ij} \phi_{ij} + \hat{\phi}^{\text{ext}}(q)$$

where ϕ_{ij} is the interparticle potential between particles i, j and $\hat{\phi}^{\text{ext}}(q) = \sum_i \phi^{\text{ext}}(\mathbf{q}_i)$ is the external potential energy. Note that the physical origin of this external potential is left unspecified in what follows and, therefore, could be interpreted as the non-ergodic potential $\hat{\phi}^h(z)$ inducing crystallization introduced in (18.1), (18.1).

The mass and momentum density fields are identical to those used for a hydrodynamic description. It is expected that these variables are slow because they are locally conserved. In addition to this hydrodynamic variables, the solid is described with the mass displacement field, that will be assumed to be also a slow variable. **[Why? Goldstone theorem for justifying the introduction of the displacement field.]**

Note that we could also consider other kinds of displacement variables. For example, we could use as elastic variable a scalar quantity given

$$d(\mathbf{r}) = \sum_i m_i (\mathbf{q}_i - \mathbf{q}_i^0)^2 \delta(\mathbf{r} - \mathbf{q}_i)$$

where $\mathbf{q}_i^0$ is the initial condition of the particle. This gives what we could call the mean root square displacement density field. Such a field could be a candidate for studying the Lindeman criteria for melting. Of course, a more informative variable would be the tensorial counterpart

$$\mathbf{I}(\mathbf{r}) = \sum_i m_i \mathbf{u}_i \mathbf{u}_i \delta(\mathbf{r} - \mathbf{q}_i)$$

that gives a sort of inertia tensor density field, whose trace gives precisely the mean root square displacement density field (18.3).

We will denote the non-equilibrium averages of the CG variables (22.4) as

$$\rho(\mathbf{r}, t) = \text{Tr}[\overline{\rho}_t \hat{\rho}_{\mathbf{r}}]$$
$$\mathbf{d}(\mathbf{r}, t) = \text{Tr}[\overline{\rho}_t \hat{\mathbf{d}}_{\mathbf{r}}]$$
$$\mathbf{g}(\mathbf{r}, t) = \text{Tr}[\overline{\rho}_t \hat{\mathbf{g}}_{\mathbf{r}}]$$
$$E = \text{Tr}[\overline{\rho}_t \hat{H}]$$
$$P(\alpha) = \text{Tr}[\overline{\rho}_t \hat{\chi}^\alpha]$$

Recall that the averages computed with the relevant ensemble are identical to the averages

computed with the real non-equilibrium ensemble, solution of the Liouville equation. The above variables are assumed to be the only slow variables in the system. In particular total energy is constant in time and the probability $P(\alpha)$ is, by assumption, also constant in time as we are considering systems that are trapped in a particular basin of attraction of an inherent structure q^{α}. In what follows, we will assume, that $P(\alpha) = \delta_{\alpha,\alpha_0}$, this is, the system is trapped in a known inherent structure q^{α_0} (as for example a perfect crystal).

18.4   The relevant ensemble and the entropy

The relevant ensemble (12.2) that extremizes the entropy functional (**??**) subject to give the correct averages (22.4) has the form

$$\overline{\rho}_t(z) = \frac{1}{Z[\nu, \boldsymbol{\lambda}, \mathbf{v}, \beta]} \exp\left\{-\beta \hat{H}^{\alpha}(z) - \beta \int d\mathbf{r} \left(\nu(\mathbf{r}, t)\hat{\rho}_{\mathbf{r}}(z) + \boldsymbol{\lambda}(\mathbf{r}, t){\cdot}\hat{\mathbf{d}}_{\mathbf{r}} - \mathbf{v}(\mathbf{r}, t){\cdot}\hat{\mathbf{g}}_{\mathbf{r}}(z)\right)\right\}$$

Here, $\beta\nu(\mathbf{r})$, $\beta\boldsymbol{\lambda}(\mathbf{r})$, $-\beta\mathbf{v}(\mathbf{r})$ and β are the Lagrange multipliers associated to each constrain in (18.3). The particular way of writing these multipliers instead of, for example $\alpha(\mathbf{r}), \beta, \gamma(\mathbf{r})$ is dictated by the physical meaning that $\mathbf{v}(\mathbf{r})$ and β will acquire in the subsequent development. The Hamiltonian that appears in the relevant ensemble is the restricted Hamiltonian defined in (18.1).

The normalization factor is the partition function of the present level of description

$$Z[\nu, \boldsymbol{\lambda}, \mathbf{v}, \beta] \equiv \sum_{N=0}^{\infty} \frac{1}{N!} \int \frac{dz_N}{h^{3N}} \exp\left\{-\beta\hat{H}^{\alpha}(z) - \beta \sum_{i=1}^{N} \left(m\nu(\mathbf{q}_i, t) + m_i\mathbf{u}_i{\cdot}\boldsymbol{\lambda}(\mathbf{q}_i, t) - \mathbf{p}_i{\cdot}\mathbf{v}(\mathbf{q}_i, t)\right)\right\}$$

Here, $\nu, \boldsymbol{\lambda}, \mathbf{v}, \beta$ are the conjugate variables of $\rho, \mathbf{d}, \mathbf{g}, E$, respectively, which are fixed by the condition that the averages of the CG variables (22.4) with the relevant ensemble coincide with the averages $\rho(\mathbf{r}, t), \mathbf{d}(\mathbf{r}, t), \mathbf{g}(\mathbf{r}, t), E$ computed with the actual ensemble, solution of the Liouville equation. This condition can be expressed as

$$\frac{\delta\Phi[\nu, \boldsymbol{\lambda}, \mathbf{v}, \beta]}{\delta\nu(\mathbf{r}, t)} = \beta\rho(\mathbf{r}, t)$$

$$\frac{\delta\Phi[\nu, \mathbf{v}, \boldsymbol{\lambda}, \beta]}{\delta\boldsymbol{\lambda}(\mathbf{r}, t)} = \beta\mathbf{d}(\mathbf{r}, t)$$

$$\frac{\delta\Phi[\nu, \mathbf{v}, \boldsymbol{\lambda}, \beta]}{\delta\mathbf{v}(\mathbf{r}, t)} = -\beta\mathbf{g}(\mathbf{r}, t)$$

$$\frac{\partial\Phi[\nu, \mathbf{v}, \boldsymbol{\lambda}, \beta]}{\partial\beta} = \int d\mathbf{r}\left[\nu(\mathbf{r}, t)\rho(\mathbf{r}, t) + \mathbf{d}(\mathbf{r}, t)\boldsymbol{\lambda}(\mathbf{r}, t) - \mathbf{v}(\mathbf{r}, t)\mathbf{g}(\mathbf{r}, t)\right] + E$$

where the grand potential corresponding to this level of description is given by

$$\Phi[\nu, \boldsymbol{\lambda}, \mathbf{v}, \beta] \equiv -\ln Z[\nu, \boldsymbol{\lambda}, \mathbf{v}, \beta]$$

The Lagrange multipliers $\nu, \boldsymbol{\lambda}, \mathbf{v}, \beta$ are the conjugate variables of $\rho, \mathbf{d}, \mathbf{g}, E$ and, as we know, there is a one to one connection between these fields. Therefore, the functionals $\nu[\rho, \mathbf{d}, \mathbf{g}, e]$, $\boldsymbol{\lambda}[\rho, \mathbf{d}, \mathbf{g}, E]$, $\mathbf{v}[\rho, \mathbf{d}, \mathbf{g}, E]$ and $\beta[\rho, \mathbf{d}, \mathbf{g}, E]$ exist and are unique.

The entropy at the hydrodynamic level is defined as the result of evaluating the entropy functional (**??**) at the relevant ensemble. Because the relevant ensemble itself depends functionally on the hydrodynamic variables the result is the entropy functional of the hydrodynamic variables. By inserting the relevant ensemble Eq.(12.4) in (**??**) and

use of Eq. (22.5), we obtain the entropy functional of this level of description

$$S[\rho, \mathbf{d}, \mathbf{g}, E] = -\Phi[\nu, \boldsymbol{\lambda}, \mathbf{v}, \beta] + \beta \int d\mathbf{r} \left[\nu(\mathbf{r})\rho(\mathbf{r}, t) + \boldsymbol{\lambda}(\mathbf{r}) \cdot \mathbf{d}(\mathbf{r}) - \mathbf{v}(\mathbf{r}) \cdot \mathbf{g}(\mathbf{r}, t) \right] + \beta E$$

The functional derivatives of the hydrodynamic entropy functional satisfies the following relationships,

$$\frac{\delta S[\rho, \mathbf{d}, \mathbf{g}, E]}{\delta \rho(\mathbf{r})} = \beta \nu(\mathbf{r})$$

$$\frac{\delta S[\rho, \mathbf{d}, \mathbf{g}, E]}{\delta \mathbf{d}(\mathbf{r})} = \beta \boldsymbol{\lambda}(\mathbf{r})$$

$$\frac{\delta S[\rho, \mathbf{d}, \mathbf{g}, E]}{\delta \mathbf{g}(\mathbf{r})} = -\beta \mathbf{v}(\mathbf{r})$$

$$\frac{\partial S[\rho, \mathbf{d}, \mathbf{g}, E]}{\partial E} = \beta$$

The entropy and grand potential functionals of this level of description depend, in principle, on three fields. We show now that, in fact, they do actually depend on only two fields, and we may eliminate the velocity field, and present the hydrodynamic functionals in the rest frame. In order to see this, perform the momentum integrals in Eq. (18.4) and obtain

$$Z[\nu, \boldsymbol{\lambda}, \mathbf{v}, \beta] \equiv \sum_{N=0}^{\infty} \frac{1}{N!} \int \prod_{i=1}^{N} \frac{d\mathbf{q}_i}{\Lambda^3} \exp\left\{ -\sum_i^N \beta \left(m_i \nu(\mathbf{q}_i) - \frac{m\mathbf{v}^2(\mathbf{q}_i)}{2} + m_i \mathbf{u}_i \cdot \boldsymbol{\lambda}(\mathbf{q}_i) + \hat{\phi}(q) + \Upsilon^\alpha(q) \right) \right\}$$

where we have introduced the thermal wavelength. This shows that the function $Z[\boldsymbol{\lambda}, \nu, \mathbf{v}, \beta]$ depends on its arguments only through the combination

$$Z[\nu, \boldsymbol{\lambda}, \mathbf{v}, \beta] = Z^{\text{rest}}[\mu, \boldsymbol{\lambda}, \beta]$$

with the chemical potential per unit mass is defined as

$$\mu(\mathbf{r}) = -\nu(\mathbf{r}) + \frac{\mathbf{v}^2(\mathbf{r})}{2}$$

and where the partition function in the rest frame is

$$Z^{\text{rest}}[\mu, \boldsymbol{\lambda}, \beta] \equiv \sum_{N=0}^{\infty} \frac{1}{N!} \int \prod_{i=1}^{N} \frac{d\mathbf{q}_i}{\Lambda^3} \exp\left\{ -\beta \sum_i^N \left(m_i \mathbf{u}_i \cdot \boldsymbol{\lambda}(\mathbf{q}_i) - m_i \mu(\mathbf{q}_i) \right) - \beta \hat{\phi}(q) - \beta \Upsilon^\alpha(q) \right\}$$

This implies that the grand potential $\Phi[\boldsymbol{\lambda}, \nu, \mathbf{v}, \beta]$ is, in fact, a function of only three

variables, of the form

$$\Phi[\nu, \boldsymbol{\lambda}, \mathbf{v}, \beta] = \Phi^{\mathrm{rest}}[\mu, \boldsymbol{\lambda}, \beta]$$

In fact, it can be understood as a function of only two variables, because

$$\sum_i^N \left(m_i(\mathbf{q}_i - \mathbf{q}_i^\alpha)\cdot\boldsymbol{\lambda}(\mathbf{q}_i) - m_i\mu(\mathbf{q}_i)\right) = \sum_i^N \left(m_i\varphi_i(\mathbf{q}_i) - m_i\mu(\mathbf{q}_i)\right)$$

The term $\mu(\mathbf{r})$ is like an ordinary external field acting in the same way for all particles. The first term $\varphi_i(\mathbf{r}) = (\mathbf{r} - \mathbf{q}_i^\alpha)\cdot\boldsymbol{\lambda}(\mathbf{r})$ is like an external potential specific for every particle i. Our aim is to express the thermodynamic potential (??) in terms of the thermodynamic potential of DFT. It is weird because the role of the mass m_i and $\mathbf{q}_i^\alpha$ is essentially the same, so we should be able to relate both thermodynamic potentials. The question is that if we know how to compute the thermodynamic potential with only $\mu(\mathbf{r})$ can we compute by including with $\boldsymbol{\lambda}(\mathbf{r})$?

Introduce

$$\varphi(\mathbf{r}) = \frac{1}{M}\sum_j m_j\varphi_j(\mathbf{r})$$

and consider

$$\sum_i^N m_i\varphi(\mathbf{q}_i) = \sum_i^N m_i\varphi_i(\mathbf{q}_i)$$

The functional derivatives are

$$\frac{\delta\Phi^{\mathrm{rest}}[\mu, \boldsymbol{\lambda}, \beta]}{\delta\mu(\mathbf{r})} = -\beta\rho(\mathbf{r})$$

$$\frac{\delta\Phi^{\mathrm{rest}}[\mu, \boldsymbol{\lambda}, \beta]}{\delta\boldsymbol{\lambda}(\mathbf{r})} = \beta\mathbf{d}(\mathbf{r})$$

$$\frac{\partial\Phi^{\mathrm{rest}}[\mu, \boldsymbol{\lambda}, \beta]}{\partial\beta} = \int d\mathbf{r}\,[\boldsymbol{\lambda}(\mathbf{r})\cdot\mathbf{d}(\mathbf{r}) - \mu(\mathbf{r})\rho(\mathbf{r})] + \phi[\mu, \boldsymbol{\lambda}, \beta]$$

where ϕ is the relevant ensemble average of the potential energy

$$\phi[\mu, \boldsymbol{\lambda}, \beta] = \frac{1}{Z^{\mathrm{rest}}[\mu, \boldsymbol{\lambda}, \beta]}\sum_{N=0}^\infty \frac{1}{N!}\int\prod_{i=1}^N \frac{d\mathbf{q}_i}{\Lambda^3}\exp\left\{-\sum_i^N\beta\left(m_i\mathbf{u}_i\cdot\boldsymbol{\lambda}(\mathbf{q}_i) - m_i\mu(\mathbf{q}_i) + \hat{\phi}(q) + \Upsilon^\alpha(q)\right)\right\}$$
$$\times\left[\hat{\phi}(q) + \Upsilon^\alpha(q)\right]$$

The action of the Galilean operator

We introduce the Galilean operator $\mathscr{G}_t$ whose action on an arbitrary phase function $\hat{X}(\mathbf{r}_i, \mathbf{p}_i)$ is

$$\mathscr{G}_t \hat{X}(\mathbf{q}_i, \mathbf{p}_i) = \hat{X}(\mathbf{q}_i, \mathbf{p}_i - m\mathbf{v}(\mathbf{q}_i))$$

This operator satisfies

$$\mathrm{Tr}[\mathscr{G}_t F] = \mathrm{Tr}[F]$$
$$\mathrm{Tr}[\mathscr{G}_t F \mathscr{G}_t G] = \mathrm{Tr}[FG]$$
$$\mathrm{Tr}[F \mathscr{G}_t G] = \mathrm{Tr}[G \mathscr{G}_t^{-1} F]$$

where the inverse Galilean operator $\mathscr{G}_t^{-1}$ is obtained by just changing the sign of the velocity in the definition (18.4).

The action of the Galilean operator on the CG variables is

$$\mathscr{G}_t \hat{\rho}_{\mathbf{r}}(z) = \hat{\rho}_{\mathbf{r}}(z)$$
$$\mathscr{G}_t \hat{\mathbf{d}}_{\mathbf{r}}(z) = \hat{\mathbf{d}}_{\mathbf{r}}(z)$$
$$\mathscr{G}_t \hat{\mathbf{g}}_{\mathbf{r}}(z) = \hat{\mathbf{g}}_{\mathbf{r}}(z) - \hat{\rho}_{\mathbf{r}}(z)\mathbf{v}(\mathbf{r})$$
$$\mathscr{G}_t \hat{H}^\alpha(z) = \hat{H}^\alpha(z) - \int d\mathbf{r} \hat{\mathbf{g}}_{\mathbf{r}}(z)\mathbf{v}(\mathbf{r}) + \int d\mathbf{r} \frac{\hat{\rho}_{\mathbf{r}}(z)}{2}\mathbf{v}^2(\mathbf{r})$$

The relevant ensemble may be written $\overline{\rho}_t(z) = \mathscr{G}_t \overline{\rho}_t^{\,\mathrm{rest}}(z)$ where the comoving ensemble is defined as

$$\overline{\rho}_t^{\,\mathrm{rest}}(z) \equiv \frac{1}{Z^{\mathrm{rest}}[\mu, \boldsymbol{\lambda}, \beta]} \exp\left\{ -\beta \hat{H}^\alpha(z) - \beta \int d\mathbf{r} \left(\boldsymbol{\lambda}(\mathbf{r}) \hat{\mathbf{d}}_{\mathbf{r}}(z) - \mu(\mathbf{r}) \hat{\rho}_{\mathbf{r}}(z) \right) \right\}$$

Now we calculate the average of CG variables with the comoving ensemble

$$\mathrm{Tr}[\overline{\rho}_t^{\,\mathrm{rest}}(z) \hat{\rho}_{\mathbf{r}}(z)] = \rho(\mathbf{r})$$
$$\mathrm{Tr}[\overline{\rho}_t^{\,\mathrm{rest}}(z) \hat{\mathbf{d}}_{\mathbf{r}}(z)] = \mathbf{d}(\mathbf{r})$$
$$\mathrm{Tr}[\overline{\rho}_t^{\,\mathrm{rest}}(z) \hat{\mathbf{g}}_{\mathbf{r}}(z)] = \mathbf{g}(\mathbf{r}) - \rho(\mathbf{r})\mathbf{v}(\mathbf{r}) = 0$$
$$\mathrm{Tr}[\overline{\rho}_t^{\,\mathrm{rest}}(z) \hat{H}^\alpha(z)] = E - \int d\mathbf{r} \rho(\mathbf{r}) \frac{\mathbf{v}^2(\mathbf{r})}{2}$$

The third equation leads directly to the explicit form or the conjugate field $\mathbf{v}(\mathbf{r})$

$$\mathbf{g}(\mathbf{r}) = \rho(\mathbf{r})\mathbf{v}(\mathbf{r})$$

This equation allows to interpret the conjugate field $\mathbf{v}(\mathbf{r})$ as the velocity field. The rest of equation show that the multipliers $\beta, \boldsymbol{\lambda}, \mu$ depend only on the density, the internal

energy

$$U = E - \int d\mathbf{r}\rho(\mathbf{r})\frac{\mathbf{v}^2(\mathbf{r})}{2}$$

and the displacement density.

Let us explore the consequences of a Galilean transformation on the hydrodynamic entropy. It is obvious that we have the identity

$$\mathrm{Tr}[\mathscr{G}_t\hat{F}] = \mathrm{Tr}[\hat{F}]$$

which is just a change of variables with unit Jacobian. Therefore,

$$S[\rho] = -\mathrm{Tr}[\overline{\rho}\ln\overline{\rho}] = -\mathrm{Tr}[\mathscr{G}_t\hat{\rho}\ln\{\mathscr{G}_t\hat{\rho}\}] = -\mathrm{Tr}[\overline{\rho}^{\mathrm{rest}}\ln\overline{\rho}^{\mathrm{rest}}]$$

Because $\overline{\rho}^{\mathrm{rest}}(z)$ depends only on $\rho, \mathbf{d}, U$, we obtain that the hydrodynamic entropy itself is a function of $\rho, \mathbf{d}, U$ alone, this is

$$S[\rho, \mathbf{d}, \mathbf{g}, E] = S^{\mathrm{rest}}[\rho, \mathbf{d}, U]$$

The functional derivatives of entropy with respect to the relevant variables are

$$\frac{\delta S^{\mathrm{rest}}[\rho, \mathbf{d}, U]}{\delta\rho(\mathbf{r})} = -\beta\mu(\mathbf{r})$$

$$\frac{\delta S^{\mathrm{rest}}[\rho, \mathbf{d}, U]}{\delta\boldsymbol{\lambda}(\mathbf{r})} = \beta\boldsymbol{\lambda}(\mathbf{r})$$

$$\frac{\partial S^{\mathrm{rest}}[\mathbf{d}, \rho, U]}{\partial U} = \beta$$

We can write Eq. (**??**) in the form

$$\Phi^{\mathrm{rest}}[\mu, \boldsymbol{\lambda}, \beta] = \beta U - \beta\int d\mathbf{r}\left\{\mathbf{d}(\mathbf{r})\cdot\boldsymbol{\lambda}(\mathbf{r}) - \rho(\mathbf{r})\mu(\mathbf{r})\right\} - S^{\mathrm{rest}}[\rho, \mathbf{d}, U]$$

That is, the rest frame S^{rest} and Φ^{rest} are Legendre transform of each other.

It is useful to introduce the free energy functional, which is a functional of $\rho, \mathbf{d}$ (and a function of β) in the form

$$F[\rho, \mathbf{d}, \beta] = k_BT\Phi^{\mathrm{rest}}[\mu, \boldsymbol{\lambda}, \beta] + \int d\mathbf{r}\left\{\mathbf{d}(\mathbf{r})\cdot\boldsymbol{\lambda}(\mathbf{r}) - \rho(\mathbf{r})\mu(\mathbf{r})\right\} = U - k_BTS^{\mathrm{rest}}[\rho, \mathbf{d}, U]$$

This is the natural definition of the free energy (internal energy minus temperature times entropy).It generalizes the free energy functional of a fluid to the case of a solid system. The functional derivatives of the free energy are **[There is a wrong sign in previous**

equations]

$$\frac{\delta F}{\delta \rho(\mathbf{r})} = \mu(\mathbf{r})$$

$$-\frac{\delta F}{\delta \mathbf{d}(\mathbf{r})} = \boldsymbol{\lambda}(\mathbf{r})$$

The Lagrange multiplier $\boldsymbol{\lambda}$ has dimensions of force, for which the free energy functional plays the role of a sort of potential.

The action of the translation operator

The effect of the translation operator (**??**) on the relevant variables is the following

$$\mathscr{T}_{\mathbf{c}}\hat{\rho}_{\mathbf{r}}(z) = \sum_{i}^{N} m_i \delta(\mathbf{q}_i + \mathbf{c} - \mathbf{r}) = \hat{\rho}_{\mathbf{r}-\mathbf{c}}(z)$$

$$\mathscr{T}_{\mathbf{c}}\hat{\mathbf{d}}_{\mathbf{r}}(z) = \sum_{i}^{N} m_i(\mathbf{q}_i + \mathbf{c} - \mathbf{q}_i^0)\delta(\mathbf{q}_i + \mathbf{c} - \mathbf{r}) = \hat{\mathbf{d}}_{\mathbf{r}-\mathbf{c}}(z) + \mathbf{c}\hat{\rho}_{\mathbf{r}-\mathbf{c}}(z)$$

$$\mathscr{T}_{\mathbf{c}}\hat{\mathbf{g}}_{\mathbf{r}}(z) = \hat{\mathbf{g}}_{\mathbf{r}-\mathbf{c}}(z)$$

$$\mathscr{T}_{\mathbf{c}}\hat{H}(z) = \mathscr{T}_{\mathbf{c}} \sum_{i}^{N} \left[\frac{\mathbf{p}_i^2}{2m} + \frac{1}{2}\sum_{j} \phi_{ij} + \sum_{i} \phi^{\text{ext}}(\mathbf{q}_i) \right] = \hat{H}(z) + \left[\mathscr{T}_{\mathbf{c}}\phi^{\text{ext}}(q) - \phi^{\text{ext}}(q) \right]$$

Note that the translation operator (**??**) when applied to an arbitrary phase function $\hat{X}(z)$ and being integrated over all phase space satisfies

$$\text{Tr}\left[\mathscr{T}_{\mathbf{c}}\hat{X} \right] = \text{Tr}\left[\hat{X} \right]$$

because the translation is just a change of variables with a unit Jacobian. By using (18.4), the partition function in the rest frame (18.4) is

$$Z^{\text{rest}}[\mu, \boldsymbol{\lambda}, \beta] \equiv \sum_{N=0}^{\infty} \frac{1}{N!} \int \prod_{i=1}^{N} \frac{d\mathbf{q}_i}{\Lambda^3} \mathscr{T}_{\mathbf{c}} \exp\left\{ -\sum_{i}^{N} \beta\left(m_i \mathbf{u}_i \cdot \boldsymbol{\lambda}(\mathbf{q}_i) - m_i \mu(\mathbf{q}_i) + \hat{\phi}(q) \right) \right\}$$

$$= \sum_{N=0}^{\infty} \frac{1}{N!} \int \prod_{i=1}^{N} \frac{d\mathbf{q}_i}{\Lambda^3} \exp\left\{ -\sum_{i}^{N} \beta\left(m_i(\mathbf{u}_i + \mathbf{c}) \cdot \boldsymbol{\lambda}(\mathbf{c} + \mathbf{q}_i) - m_i \mu(\mathbf{c} + \mathbf{q}_i) + \hat{\phi}(q) + \mathscr{T}_{\mathbf{c}}\hat{\phi}^{\text{ext}}(q) \right) \right\}$$

With the translation operator (**??**) that acts on functions of real space, we may write (18.4) in the form

$$Z^{\text{rest}}[\mu, \boldsymbol{\lambda}, \beta] = Z^{\text{rest}}\left[\left(T_{\mathbf{c}}\mu + T_{\mathbf{c}}\boldsymbol{\lambda} \cdot \mathbf{c} + T_{\mathbf{c}}\phi^{\text{ext}} - \phi^{\text{ext}} \right), T_{\mathbf{c}}\boldsymbol{\lambda}, \beta \right]$$

This mathematical identity reflects how the partition function at rest transforms under a change of reference frame by a translation with arbitrary vector $\mathbf{c}$.

By noting that the left hand side of (18.4) is independent on $\mathbf{c}$, we may take the derivative with respect to $\mathbf{c}$ and obtain

$$0 = \frac{\partial}{\partial \mathbf{c}} \Phi^{\text{rest}}[\mu, \boldsymbol{\lambda}, \beta] = \frac{\partial}{\partial \mathbf{c}} \Phi^{\text{rest}} \left[\left(T_{\mathbf{c}} \mu + T_{\mathbf{c}} \boldsymbol{\lambda} \cdot \mathbf{c} + T_{\mathbf{c}} \phi^{\text{ext}} - \phi^{\text{ext}} \right), T_{\mathbf{c}} \boldsymbol{\lambda}, T_{\mathbf{c}} \beta \right]$$

By using the chain rule, and setting the final result to $\mathbf{c} = 0$ we have

$$0 = \frac{\partial}{\partial \mathbf{c}} \Phi^{\text{rest}} \left[\left(T_{\mathbf{c}} \mu + T_{\mathbf{c}} \boldsymbol{\lambda} \cdot \mathbf{c} + \frac{T_{\mathbf{c}} \phi^{\text{ext}} - \phi^{\text{ext}}}{m} \right), T_{\mathbf{c}} \boldsymbol{\lambda}, \beta \right]$$
$$= \int d\mathbf{r} \left(\frac{\delta \Phi^{\text{rest}}}{\delta \mu(\mathbf{r})} \left(\boldsymbol{\nabla} \mu(\mathbf{r}) + \boldsymbol{\lambda}(\mathbf{r}) + \frac{\boldsymbol{\nabla} \phi^{\text{ext}}}{m} \right) + \frac{\delta \Phi^{\text{rest}}}{\delta \boldsymbol{\lambda}(\mathbf{r})} \boldsymbol{\nabla} \boldsymbol{\lambda}(\mathbf{r}) \right)$$

By using the functional derivatives in (18.4) the effect of translations in the system reflects in the following mathematical identity

$$0 = \int d\mathbf{r} \left(-\rho(\mathbf{r}) \boldsymbol{\nabla} \mu(\mathbf{r}) + n(\mathbf{r}) \mathbf{F}^{\text{ext}}(\mathbf{r}) - \rho(\mathbf{r}) \boldsymbol{\lambda}(\mathbf{r}) + \mathbf{d}(\mathbf{r}) \boldsymbol{\nabla} \boldsymbol{\lambda}(\mathbf{r}) \right)$$

This is a mathematical identity to be satisfied by the pair of conjugate variables $\mu(\mathbf{r}), \boldsymbol{\lambda}(\mathbf{r})$, which are in a one to one connection with $\rho(\mathbf{r}), \mathbf{d}(\mathbf{r})$ no matter what values of the latter may take (either the equilibrium values or not). This identity will be crucial to show that total momentum is conserved by the dynamics, when the latter is expressed in terms of the conjugate variables (see below).

18.5   The reversible drift

The time derivatives of the CG variables are given by

$$i\mathcal{L} \hat{\rho}_{\mathbf{r}}(z) = -\nabla \hat{\mathbf{g}}_{\mathbf{r}}(z)$$
$$i\mathcal{L} \hat{\mathbf{d}}_{\mathbf{r}}(z) = \hat{\mathbf{g}}_{\mathbf{r}} - \nabla \cdot \sum_i \mathbf{p}_i \mathbf{u}_i \delta(\mathbf{r} - \mathbf{q}_i)$$
$$i\mathcal{L} \hat{\mathbf{g}}_{\mathbf{r}}(z) = -\sum_i \mathbf{v}_i \mathbf{p}_i \nabla \delta(\mathbf{r} - \mathbf{q}_i) + \sum_i \mathbf{F}_i \delta(\mathbf{r} - \mathbf{q}_i)$$
$$i\mathcal{L} \hat{H}(z) = 0$$

Note that the force term can be expressed in the form

$$\sum_i \mathbf{F}_i \delta(\mathbf{r} - \mathbf{q}_i) = \frac{1}{2} \sum_{kl} \mathbf{F}_{kl} \left[\delta(\mathbf{r} - \mathbf{r}_k) - \delta(\mathbf{r} - \mathbf{r}_l) \right] + \sum_i \mathbf{F}_i^{\text{ext}} \delta(\mathbf{r} - \mathbf{q}_i)$$

where $\mathbf{F}_{ij}$ is the pair-wise force that the particle j exerts on particle i and $\mathbf{F}_i^{\text{ext}}$ is the force on particle i due to the external potential.

Now we take the usual Taylor expansion of the delta function

$$\delta(\mathbf{r} - \mathbf{q}_i) - \delta(\mathbf{r} - \mathbf{q}_j) = -\nabla\mathbf{q}_{ij}\int_0^1 d\epsilon\delta(\mathbf{r} - \mathbf{q}_j - \epsilon\mathbf{q}_{ij})$$

therefore

$$i\mathcal{L}\hat{\rho}_{\mathbf{r}}(z) = -\nabla\hat{\mathbf{g}}_{\mathbf{r}}(z)$$
$$i\mathcal{L}\hat{\mathbf{d}}_{\mathbf{r}}(z) = \hat{\mathbf{g}}_{\mathbf{r}}(z) - \nabla\hat{\mathbf{D}}_{\mathbf{r}}(z)$$
$$i\mathcal{L}\hat{\mathbf{g}}_{\mathbf{r}}(z) = -\nabla\hat{\mathbf{\Sigma}}_{\mathbf{r}}(z) + \hat{n}_{\mathbf{r}}(z)\mathbf{F}^{\text{ext}}(\mathbf{r})$$

We have defined the microscopic displacement flux tensor $\hat{\mathbf{D}}_{\mathbf{r}}(z)$ and momentum flux tensor as $\hat{\mathbf{\Sigma}}_{\mathbf{r}}(z)$ as

$$\hat{\mathbf{D}}_{\mathbf{r}}(z) \equiv \sum_i \mathbf{p}_i\mathbf{u}_i\delta(\mathbf{r} - \mathbf{q}_i)$$

$$\hat{\mathbf{\Sigma}}_{\mathbf{r}}(z) \equiv \sum_i \mathbf{v}_i\mathbf{p}_i\nabla\delta(\mathbf{r} - \mathbf{q}_i) + \frac{1}{2}\sum_{ij}\mathbf{F}_{ij}\mathbf{q}_{ij}\int_0^1 d\epsilon\delta(\mathbf{r} - \mathbf{q}_j - \epsilon\mathbf{q}_{ij})$$

We will need the effect of the Galilean operator (18.4) on these fluxes

$$\mathcal{G}_t^{-1}\hat{\mathbf{D}}_{\mathbf{r}}(z) = \sum_i\mathbf{p}_i\mathbf{u}_i\delta(\mathbf{r} - \mathbf{q}_i) + \mathbf{v}(\mathbf{r})\sum_i m_i\mathbf{u}_i\delta(\mathbf{r} - \mathbf{q}_i) = \hat{\mathbf{D}}_{\mathbf{r}}(z) - \mathbf{v}(\mathbf{r})\hat{\mathbf{d}}_{\mathbf{r}}(z)$$

$$\mathcal{G}_t^{-1}\hat{\mathbf{\Sigma}}_{\mathbf{r}}(z) = \hat{\mathbf{\Sigma}}_{\mathbf{r}}(z) + \mathbf{v}(\mathbf{r})\hat{\mathbf{g}}_{\mathbf{r}} + \hat{\mathbf{g}}_{\mathbf{r}}\mathbf{v}(\mathbf{r}) + \mathbf{v}(\mathbf{r})\mathbf{v}(\mathbf{r})\hat{\rho}_{\mathbf{r}}$$

Now we consider the reversible part $v_i(t)$ in Eq. (12.2). For the mass density we have

$$\partial_t\rho(\mathbf{r}, t)|_{\text{rev}} = \text{Tr}[\overline{\rho}_t i\mathcal{L}\hat{\rho}_{\mathbf{r}}] = -\nabla\mathbf{g}(\mathbf{r}, t)$$

where we have used Eq. (18.5) and the fact that the relevant ensemble average of $\hat{\mathbf{g}}_{\mathbf{r}}$ is precisely the momentum density field $\mathbf{g}(\mathbf{r}, t)$. For the displacement density we have

$$\partial_t\mathbf{d}(\mathbf{r}, t)|_{\text{rev}} = \text{Tr}[\overline{\rho}_t i\mathcal{L}\hat{\mathbf{d}}_{\mathbf{r}}] = \mathbf{g}(\mathbf{r}, t) - \nabla\cdot\text{Tr}[\overline{\rho}_t\hat{\mathbf{D}}_{\mathbf{r}}] = \mathbf{g}(\mathbf{r}, t) - \nabla\cdot\mathbf{v}(\mathbf{r}, t)\mathbf{d}(\mathbf{r}, t)$$

where we have used the Galilean transformation in the last equation.

On the other hand, the reversible part of the momentum density is

$$\partial_t\mathbf{g}(\mathbf{r}, t)|_{\text{rev}} = \text{Tr}[\overline{\rho}_t i\mathcal{L}\hat{\mathbf{g}}_{\mathbf{r}}] = -\nabla\mathbf{\Sigma}(\mathbf{r}, t) + n(\mathbf{r})\mathbf{F}^{\text{ext}}(\mathbf{r})$$

where we have introduced

$$\mathbf{\Sigma}(\mathbf{r}, t) \equiv \text{Tr}[\overline{\rho}_t\hat{\mathbf{\Sigma}}_{\mathbf{r}}]$$

We compute this term by using the Galilean transformation

$$\mathbf{\Sigma}(\mathbf{r},t) = \mathrm{Tr}[\mathscr{G}_t\overline{\rho}_t^{\mathrm{rest}}\hat{\mathbf{\Sigma}}_{\mathbf{r}}] = \mathrm{Tr}[\overline{\rho}_t^{\mathrm{rest}}\mathscr{G}_t^{-1}\hat{\mathbf{\Sigma}}_{\mathbf{r}}] = \mathrm{Tr}\left[\overline{\rho}_t^{\mathrm{rest}}\left(\hat{\mathbf{\Sigma}}_{\mathbf{r}} + \mathbf{v}(\mathbf{r},t)\hat{\mathbf{g}}_{\mathbf{r}} + \hat{\mathbf{g}}_{\mathbf{r}}\mathbf{v}(\mathbf{r},t) + \mathbf{v}(\mathbf{r},t)\mathbf{v}(\mathbf{r},t)\hat{\rho}_{\mathbf{r}}\right)\right]$$

$$= \mathbf{\Pi}(\mathbf{r},t) + \mathbf{v}(\mathbf{r},t)\mathbf{v}(\mathbf{r},t)\rho(\mathbf{r},t)$$

where we have introduced the average of the stress tensor with respect to the comoving ensemble

$$\mathbf{\Pi}(\mathbf{r},t) = \mathrm{Tr}[\overline{\rho}_t^{\mathrm{rest}}\hat{\mathbf{\Sigma}}_{\mathbf{r}}]$$

Therefore, the momentum equation (18.5) can be expressed in the form

$$\partial_t\mathbf{g}(\mathbf{r},t)|_{\mathrm{rev}} = -\boldsymbol{\nabla}\rho(\mathbf{r},t)\mathbf{v}(\mathbf{r},t)\mathbf{v}(\mathbf{r},t) - \boldsymbol{\nabla}\cdot\mathbf{\Pi}(\mathbf{r},t) + n(\mathbf{r})\mathbf{F}^{\mathrm{ext}}(\mathbf{r})$$

where we identify an advective part, a contribution given by the divergence of the stress tensor and, finally, the effect of the external forces. In the absence of external forces, this equation has a divergence form that ensures that total momentum is conserved.

We may obtain an entirely equivalent form for the momentum equation which has a closer connection with the free energy functional. We start from (18.5)

$$\partial_t\mathbf{g}(\mathbf{r},t)|_{\mathrm{rev}} = -\mathrm{Tr}\left[\overline{\rho}_t\sum_i\mathbf{v}_i\mathbf{p}_i\nabla\delta(\mathbf{r}-\mathbf{q}_i)\right] + \mathrm{Tr}\left[\overline{\rho}_t\sum_i\mathbf{F}_i\delta(\mathbf{r}-\mathbf{q}_i)\right]$$

$$= -\mathrm{Tr}\left[\mathscr{G}^{-1}\overline{\rho}_t\sum_i\mathscr{G}^{-1}\mathbf{v}_i\mathbf{p}_i\nabla\delta(\mathbf{r}-\mathbf{q}_i)\right] + \mathrm{Tr}\left[\mathscr{G}^{-1}\overline{\rho}_t\sum_i\mathbf{F}_i\delta(\mathbf{r}-\mathbf{q}_i)\right]$$

$$= -\boldsymbol{\nabla}\mathbf{v}(\mathbf{r})\mathbf{v}(\mathbf{r})\rho(\mathbf{r}) - \boldsymbol{\nabla}k_BTn(\mathbf{r},t) + \mathrm{Tr}\left[\overline{\rho}_t^{\mathrm{rest}}\sum_i\mathbf{F}_i\delta(\mathbf{r}-\mathbf{q}_i)\right]$$

The comoving ensemble (18.4) has the form

$$\overline{\rho}_t^{\mathrm{rest}}(z) = \frac{1}{Z^{\mathrm{rest}}[\mu,\boldsymbol{\lambda},\beta]}\exp\left\{-\beta\sum_i\frac{\mathbf{p}_i^2}{2m_i} - \beta\hat{\phi}(q) - \beta\sum_i^N\left(m_i\mathbf{u}_i\cdot\boldsymbol{\lambda}(\mathbf{q}_i) - m_i\mu(\mathbf{q}_i)\right)\right\}$$

We now compute the average of the force term in the momentum equation in (18.5) with the comoving ensemble (18.5). The momentum integrals give the usual thermal

wavelength factor

$$
\begin{aligned}
\mathrm{Tr}[\overline{\rho}_t^{\mathrm{rest}}\hat{\mathbf{F}}_{\mathbf{r}}] &= \frac{1}{Z^{\mathrm{res}}[\mu,\boldsymbol{\lambda},\beta]} \sum_{N=0}^{\infty} \frac{1}{N!} \int \frac{dq}{\Lambda^{3N}} \left[\sum_{j}^{N} -\frac{\partial \hat{\phi}}{\partial \mathbf{q}_j} \delta(\mathbf{r}-\mathbf{q}_j) \right] e^{-\beta\hat{\phi}} \exp\left\{ -\beta \sum_{i}^{N} (m_i \mathbf{u}_i \cdot \boldsymbol{\lambda}(\mathbf{q}_i) - m_i \mu(\mathbf{q}_i)) \right\} \\
&= \frac{1}{Z^{\mathrm{res}}[\mu,\boldsymbol{\lambda},\beta]} \sum_{N=0}^{\infty} \frac{1}{N!} \int \frac{dq}{\Lambda^{3N}} \exp\left\{ -\beta \sum_{i}^{N} (m_i \mathbf{u}_i \cdot \boldsymbol{\lambda}(\mathbf{q}_i) - m_i \mu(\mathbf{q}_i)) \right\} k_B T \sum_{j}^{N} \delta(\mathbf{r}-\mathbf{q}_j) \frac{\partial}{\partial \mathbf{q}_j} e^{-\beta\hat{\phi}} \\
&= \frac{1}{Z^{\mathrm{res}}[\mu,\boldsymbol{\lambda},\beta]} \sum_{N=0}^{\infty} \frac{1}{N!} \int \frac{dq}{\Lambda^{3N}} e^{-\beta\hat{\phi}} k_B T \sum_{j}^{N} -\frac{\partial}{\partial \mathbf{q}_j} \left[\delta(\mathbf{r}-\mathbf{q}_j) \exp\left\{ -\beta \sum_{i}^{N} (m_i \mathbf{u}_i \cdot \boldsymbol{\lambda}(\mathbf{q}_i) - m_i \mu(\mathbf{q}_i)) \right\} \right] \\
&= \frac{1}{Z^{\mathrm{res}}[\mu,\boldsymbol{\lambda},\beta]} \sum_{N=0}^{\infty} \frac{1}{N!} \int \frac{dq}{\Lambda^{3N}} e^{-\beta\hat{\phi}} \sum_{j}^{N} \exp\left\{ -\beta \sum_{i\neq j}^{N} (m_i \mathbf{u}_i \cdot \boldsymbol{\lambda}(\mathbf{q}_i) - m_i \mu(\mathbf{q}_i)) \right\} \\
&\quad \times k_B T \left[-\frac{\partial}{\partial \mathbf{q}_j} \delta(\mathbf{r}-\mathbf{q}_j) \exp\left\{ -\beta (m_j \mathbf{u}_j \cdot \boldsymbol{\lambda}(\mathbf{q}_j) - m_j \mu(\mathbf{q}_j)) \right\} \right] \\
&= k_B T \boldsymbol{\nabla} n(\mathbf{r}) - \rho(\mathbf{r}) \boldsymbol{\nabla}\mu(\mathbf{r}) + \rho(\mathbf{r})\boldsymbol{\lambda}(\mathbf{r}) + \mathbf{d}(\mathbf{r}) \cdot \boldsymbol{\nabla}\boldsymbol{\lambda}(\mathbf{r})
\end{aligned}
$$

Therefore, the momentum equation (18.5) becomes

$$
\partial_t \mathbf{g}(\mathbf{r},t)\big|_{\mathrm{rev}} = -\boldsymbol{\nabla}\mathbf{v}(\mathbf{r})\mathbf{v}(\mathbf{r})\rho(\mathbf{r}) - \rho(\mathbf{r})\boldsymbol{\nabla}\mu(\mathbf{r}) + \rho(\mathbf{r})\boldsymbol{\lambda}(\mathbf{r}) + \mathbf{d}(\mathbf{r}) \cdot \boldsymbol{\nabla}\boldsymbol{\lambda}(\mathbf{r})
$$

Note that the momentum density written in this way is explicitly given in terms of conjugate variables, this is, the derivatives of the entropy (or free energy) functional. In this form, it is not obvious that total momentum is conserved in the absence of external forces, because this equation (18.5) is not in divergence form. However, the mathematical identity (18.4) ensures that, indeed, total momentum is conserved when there are no external forces.

In summary, the reversible part of the dynamics is given by

$$
\begin{aligned}
\partial_t \rho\big|_{\mathrm{rev}} &= -\nabla\mathbf{g} \\
\partial_t \mathbf{d}\big|_{\mathrm{rev}} &= \mathbf{g} - \nabla\cdot\mathbf{v}\mathbf{d} \\
\partial_t \mathbf{g}\big|_{\mathrm{rev}} &= -\boldsymbol{\nabla}\cdot\mathbf{v}\mathbf{v}\rho - \boldsymbol{\nabla}\cdot\boldsymbol{\Pi} + n\mathbf{F}^{\mathrm{ext}} \\
&= -\boldsymbol{\nabla}\cdot\mathbf{v}\mathbf{v}\rho - \rho\boldsymbol{\nabla}\mu + \rho\boldsymbol{\lambda} + \mathbf{d}\cdot\boldsymbol{\nabla}\boldsymbol{\lambda}
\end{aligned}
$$

The displacement field is defined as

$$
\mathbf{u}(\mathbf{r},t) = \frac{\mathbf{d}(\mathbf{r},t)}{\rho(\mathbf{r},t)}
$$

and is, therefore, different from the displacement *density* field $\mathbf{d}(\mathbf{r},t)$. If we take the time derivative of the displacement field and use the first two equations in (18.5) we obtain that the displacement field satisfies the following equation

$$
\partial_t \mathbf{u}\big|_{\mathrm{rev}} = \mathbf{v} - \mathbf{v}\cdot\boldsymbol{\nabla}\mathbf{u}
$$

If we consider just the reversible variation of the displacement field we observe that in a Lagrangian frame, the substantial derivative of the displacement field is the velocity field. This argument shows that the initial displacement density variable is the natural one to choose.

The form (18.5) is particularly suited to show that the entropy remains invariant under the reversible evolution, as we may easily check

$$\partial_t S[\rho, \mathbf{d}, \mathbf{g}] = \int d\mathbf{r} \left[\frac{\delta S}{\delta \rho(\mathbf{r})} \partial_t \rho(\mathbf{r}) + \frac{\delta S}{\delta \mathbf{d}(\mathbf{r})} \cdot \partial_t \mathbf{d}(\mathbf{r}) + \frac{\delta S}{\delta \mathbf{g}(\mathbf{r})} \cdot \partial_t \mathbf{g}(\mathbf{r}) \right]$$

$$= \beta \int d\mathbf{r} \left[-\nu \boldsymbol{\nabla} \cdot \mathbf{g} + \boldsymbol{\lambda} \cdot [\mathbf{g} - \nabla \cdot \mathbf{v} \mathbf{d}] - \mathbf{v} \cdot [-\boldsymbol{\nabla} \mathbf{v} \mathbf{v} \rho - \rho \boldsymbol{\nabla} \mu + \rho \boldsymbol{\lambda} + \mathbf{d} \cdot \boldsymbol{\nabla} \boldsymbol{\lambda}] \right] = 0$$

where we see that, after integration by parts and the definition (18.4), every term cancels with another one.

18.6 The connection between the thermodynamic free energy and the functional free energy

18.7 The irreversible part of the dynamics

And finally we calculate the irreversible part of Eq. (12.2). The effect of the projection operator on the time derivatives of the CG variables is

$$\mathcal{Q}_t i \mathcal{L} \hat{\rho}_{\mathbf{r}}(z) = 0$$
$$\mathcal{Q}_t i \mathcal{L} \hat{\mathbf{d}}_{\mathbf{r}}(z) = -\nabla \mathcal{Q}_t \hat{\mathbf{D}}_{\mathbf{r}}(z)$$
$$\mathcal{Q}_t i \mathcal{L} \hat{\mathbf{g}}_{\mathbf{r}}(z) = -\nabla \mathcal{Q}_t \hat{\boldsymbol{\Sigma}}_{\mathbf{r}}(z)$$
$$\mathcal{Q}_t i \mathcal{L} \hat{H}(z) = 0$$

where we have used that the projector $\mathcal{Q}_t$ acting on any CG variables vanishes.

The irreversible part $\sum_j D_{ij} \lambda_j(t)$ of the general Eq. (12.2) becomes, for the hydroelastic fields

$$\left. \begin{pmatrix} \partial_t \rho(\mathbf{r}) \\ \partial_t \mathbf{d}(\mathbf{r}) \\ \partial_t \mathbf{g}(\mathbf{r}) \\ \partial_t E \end{pmatrix} \right|_{\text{irr}} = k_B T \int d\mathbf{r}' \begin{pmatrix} M_{\mathbf{rr}'}^{\rho\rho} & M_{\mathbf{rr}'}^{\rho\mathbf{d}} & M_{\mathbf{rr}'}^{\rho\mathbf{g}} & M_{\mathbf{rr}'}^{\rho E} \\ M_{\mathbf{rr}'}^{\mathbf{d}\rho} & M_{\mathbf{rr}'}^{\mathbf{dd}} & M_{\mathbf{rr}'}^{\mathbf{dg}} & M_{\mathbf{rr}'}^{\mathbf{d}E} \\ M_{\mathbf{rr}'}^{\mathbf{g}\rho} & M_{\mathbf{rr}'}^{\mathbf{gd}} & M_{\mathbf{rr}'}^{\mathbf{gg}} & M_{\mathbf{rr}'}^{\mathbf{g}E} \\ M_{\mathbf{rr}'}^{E\rho} & M_{\mathbf{rr}'}^{E\mathbf{d}} & M_{\mathbf{rr}'}^{E\mathbf{g}} & M_{\mathbf{rr}'}^{EE} \end{pmatrix} \begin{pmatrix} \beta\nu(\mathbf{r}') \\ \beta\boldsymbol{\lambda}(\mathbf{r}') \\ -\beta\mathbf{v}(\mathbf{r}') \\ \beta \end{pmatrix}$$

Because of the first Eq. (18.7), all matrix elements with a ρ, E superindex vanish. The rest of matrix elements are all of the form $M_{\mathbf{rr}'}^{\alpha\beta} = \boldsymbol{\nabla}_{\mathbf{r}} \boldsymbol{\nabla}_{\mathbf{r}'} \boldsymbol{\Xi}_{\mathbf{rr}'}^{ab}$ where $\boldsymbol{\Xi}_{\mathbf{rr}'}^{ab}$ is a kernel of

transport coefficients

$$\boldsymbol{\Xi}_{\mathbf{rr'}}^{ab} \equiv \frac{1}{k_B T} \int_0^\infty dt' \mathrm{Tr}[\overline{\rho}_t(\mathcal{Q}_t \hat{\mathbf{A}}_{\mathbf{r}}) G_{tt'}(\mathcal{Q}_{t'} \hat{\mathbf{B}}_{\mathbf{r'}})]$$

where $\hat{\mathbf{A}}_{\mathbf{r}}, \hat{\mathbf{B}}_{\mathbf{r}}$ are the corresponding the tensors $\hat{\mathbf{D}}_{\mathbf{r}}, \hat{\boldsymbol{\Pi}}_{\mathbf{r}}$.

The resulting irreversible parts of the hydroelasticity equations are

$$\partial_t \rho(\mathbf{r}, t)|_{\mathrm{irr}} = 0$$

$$\partial_t \mathbf{d}(\mathbf{r}, t)|_{\mathrm{irr}} = -\boldsymbol{\nabla}_{\mathbf{r}} \int d\mathbf{r'} \boldsymbol{\Xi}_{\mathbf{rr'}}^{\mathbf{dd}} \boldsymbol{\nabla}_{\mathbf{r'}} \boldsymbol{\lambda}_{\mathbf{r'}} + \boldsymbol{\nabla}_{\mathbf{r}} \int d\mathbf{r'} \boldsymbol{\Xi}_{\mathbf{rr'}}^{\mathbf{dg}} \boldsymbol{\nabla}_{\mathbf{r'}} \mathbf{v}_{\mathbf{r'}}$$

$$\partial_t \mathbf{g}(\mathbf{r}, t)|_{\mathrm{irr}} = -\boldsymbol{\nabla}_{\mathbf{r}} \int d\mathbf{r'} \boldsymbol{\Xi}_{\mathbf{rr'}}^{\mathbf{gd}} \boldsymbol{\nabla}_{\mathbf{r'}} \boldsymbol{\lambda}_{\mathbf{r'}} + \boldsymbol{\nabla}_{\mathbf{r}} \int d\mathbf{r'} \boldsymbol{\Xi}_{\mathbf{rr'}}^{\mathbf{gg}} \boldsymbol{\nabla}_{\mathbf{r'}} \mathbf{v}_{\mathbf{r'}}$$

$$\partial_t E(t)|_{\mathrm{irr}} = 0$$

The non-local transport kernels $\boldsymbol{\Xi}_{\mathbf{rr'}}^{ab}$ depend on the time-dependent macroscopic state $\rho(\mathbf{r}, t), \mathbf{d}(\mathbf{r}, t), \mathbf{g}(\mathbf{r}, t), E$ through the relevant ensemble $\overline{\rho}_t$. As such it is a formal object and until approximations to make this object explicit are made, the theory has null predictive power. The first approximation restricts to slowly varying in space fields. In this case, we he near equilibrium assumption. At equilibrium the conjugate fields vanish and it is possible to approximate the relevant ensemble with the equilibrium ensemble. For near equilibrium situations, we have

$$\boldsymbol{\Xi}_{\mathbf{rr'}}^{ab} \approx \int_0^\infty dt' \mathrm{Tr}[\rho^{\mathrm{eq}}(\delta \hat{\mathbf{A}}_{\mathbf{r}}) G_{tt'}(\delta \hat{\mathbf{B}}_{\mathbf{r'}})]$$

where the effect of the projector $\mathcal{Q}$ turns out to be to simply subtract the equilibrium average, this is $\delta \hat{\mathbf{A}}_{\mathbf{r}} = \hat{\mathbf{A}}_{\mathbf{r}} - \langle \hat{\mathbf{A}}_{\mathbf{r}} \rangle^{\mathrm{eq}}$. The result of this approximation is that the transport kernels do not depend on the CG variables anymore and they become state independent.

Note that the explicit form of the correlation function cannot be known because it involves the formal time propagator $G_{tt'}$ referred to as the projected dynamics. A usual approximation is to take the real dynamics instead of the projected dynamics, leading to the usual Green-Kubo expressions for transport coefficients. An evaluation through molecular simulations of the non-local transport kernel is then possible. However, note that such an evaluation requires to perform one MD simulation for every $\mathbf{r}, \mathbf{r'}$ combination. Even by assuming isotropy and homogeneity, this is, that the kernels depend on the distance between these two points, it is necessary to perform an MD simulation for every relative distance. An alternative to this procedure is to assume that the correlations may be approximated with an exponential decay,

$$\mathrm{Tr}[\rho^{\mathrm{eq}}(\delta \hat{\mathbf{A}}_{\mathbf{r}}) G_{tt'}(\delta \hat{\mathbf{B}}_{\mathbf{r'}}(t'))] \approx \exp\{-t/\tau_{ab}\} \mathrm{Tr}[\rho^{\mathrm{eq}} \delta \hat{\mathbf{A}}_{\mathbf{r}} \delta \hat{\mathbf{B}}_{\mathbf{r'}}]$$

where τ_{ab} are characteristic times that play the role of adjustable parameters in the theory. Note that at $t = 0$ the approximation (18.7) is exact. The static averages $\mathrm{Tr}[\rho^{\mathrm{eq}} \delta \hat{\mathbf{A}}_{\mathbf{r}} \delta \hat{\mathbf{B}}_{\mathbf{r'}}]$ are more accessible than the correlations, and one can express in general these static averages in terms of correlation functions for which density functional approaches may provide explicit expressions.

However, in the present work we restrict to situations in which the relevant fields vary slowly in space. By this we mean that they vary in length scales much larger than the correlation length of the transport kernel correlations. In those situations, the space dependence of transport kernels may be approximated with a Dirac delta function, this is

$$\boldsymbol{\Xi}_{\mathbf{rr'}}^{ab} \approx \boldsymbol{\Xi}^{ab}\delta(\mathbf{r} - \mathbf{r'})$$

$$\boldsymbol{\Xi}^{ab} \equiv \frac{1}{V_T} \int d\mathbf{r} \int d\mathbf{r'} \int_0^\infty dt' \mathrm{Tr}[\rho^{\mathrm{eq}}(\delta\hat{\mathbf{A}}_{\mathbf{r}}) \exp\{i\mathcal{L}t\}(\delta\hat{\mathbf{B}}_{\mathbf{r'}})]$$

$$= \frac{1}{V_T} \int_0^\infty dt' \mathrm{Tr}[\rho^{\mathrm{eq}}(\delta\hat{\mathbf{A}}) \exp\{i\mathcal{L}t\}(\delta\hat{\mathbf{B}})]$$

where $\hat{\mathbf{A}} = \int d\mathbf{r}\hat{\mathbf{A}}_{\mathbf{r}}$, $\hat{\mathbf{B}} = \int d\mathbf{r}\hat{\mathbf{B}}_{\mathbf{r}}$ are the corresponding space integrals of the local fluxes (18.5), this is

$$\hat{\mathbf{D}}(z) \equiv \sum_i \mathbf{p}_i\mathbf{u}_i$$

$$\hat{\boldsymbol{\Sigma}}(z) \equiv \frac{1}{2} \sum_{ij} \mathbf{F}_{ij}\mathbf{q}_{ij} + \sum_i \mathbf{v}_i\mathbf{p}_i$$

18.8   The transport equation

The final hydrodynamic equations are obtained by collecting Eqs. (18.5), (18.5), (5.4)and
(**??**),(**??**)and (**??**) this is

$$\partial_t \rho(\mathbf{r}, t) = -\nabla \cdot \mathbf{g}(\mathbf{r}, t)$$

$$\partial_t \mathbf{d}(\mathbf{r}, t) = \mathbf{g}(\mathbf{r}, t) - \nabla \cdot \mathbf{v}(\mathbf{r}, t) \mathbf{d}(\mathbf{r}, t) - \nabla \Xi^{\mathbf{dd}} \nabla \boldsymbol{\lambda}(\mathbf{r}, t) + \nabla \Xi^{\mathbf{dg}} \nabla \mathbf{v}(\mathbf{r}, t)$$

$$\partial_t \mathbf{g}(\mathbf{r}, t) = -\nabla \mathbf{v}(\mathbf{r}, t) \mathbf{v}(\mathbf{r}, t) \rho(\mathbf{r}, t) - \nabla \Pi(\mathbf{r}, t) - \nabla \Xi^{\mathbf{gd}} \nabla \boldsymbol{\lambda}(\mathbf{r}, t) + \nabla \Xi^{\mathbf{gg}} \nabla \mathbf{v}(\mathbf{r}, t)$$

$$\partial_t E = 0$$

There are no irreversible terms in the evolution of the density field, which obeys the well-
known continuity equation. The above equations show that mass, momentum and energy
are exactly conserved in the absence of external forces, because then, the equations are in
divergence form. As a consequence, we may consider the total displacement field, defined
as

$$\mathbf{D} \equiv \int d\mathbf{r} \mathbf{d}(\mathbf{r}, t)$$

This vector is just the displacement of the center of mass of the system with respect
to the center of mass of the reference system. The total displacement field satisfies the
following dynamic equation

$$\frac{d\mathbf{D}}{dt}(t) = \int d\mathbf{r} \mathbf{g}(\mathbf{r}, t) = \mathbf{P}$$

In the absence of external forces, total momentum is conserved and, by choosing the
reference frame where the center of mass of the system is at rest, we observe that $\mathbf{D}$ is
also a conserved quantity.

The above equations also show that the entropy is a non-decaying function of time.
This implies that the equilibrium state will be one in which the entropy (22.4) takes its
maximum value, subject to the conditions that the total mass, displacement, momen-
tum, and energy are conserved. Therefore, the equilibrium state is obtained from the
maximization of

$$S[\rho, \mathbf{d}, \mathbf{g}, E] + \beta_0 \nu_0 \int d\mathbf{r} \rho(\mathbf{r}) + \beta_0 \boldsymbol{\lambda}_0 \int d\mathbf{r} \mathbf{d}(\mathbf{r}) + \beta_0 \boldsymbol{v}_0 \int d\mathbf{r} \mathbf{g}(\mathbf{r}) + \beta_0 E$$

where $\mu_0, \boldsymbol{\lambda}_0, \boldsymbol{v}_0, \beta_0$ are the Lagrange multipliers enforcing the conservation constraints.
By taking the derivatives of the above functional, and setting them to zero we obtain the
equations to be satisfied by the equilibrium fields, which on account of (22.4) are simply

$$\nu(\mathbf{r}) = \nu_0$$

$$\boldsymbol{\lambda}(\mathbf{r}) = \boldsymbol{\lambda}_0$$

$$\mathbf{v}(\mathbf{r}) = \mathbf{v}_0$$

$$\beta = \beta_0$$

Therefore, at equilibrium all the conjugate variable fields become constant.

At equilibrium, the relevant ensemble (18.4) becomes

$$\overline{\rho}_t(z) = \frac{1}{Z[\nu_0, \boldsymbol{\lambda}_0, \mathbf{v}_0, \beta_0]} \exp\left\{-\beta_0 \hat{H}(z) - \beta_0 \nu_0 \mathcal{N}(z) + \beta_0 \boldsymbol{\lambda}_0 \cdot \hat{\mathbf{D}}(z) - \beta_0 \mathbf{v}_0 \cdot \hat{\mathbf{P}}(z)\right\}$$

By choosing the reference frame of the center of mass, for which $\hat{\mathbf{D}}(z) = 0, \hat{\mathbf{P}}(z) = 0$, we obtain the usual form of the equilibrium ensemble.

18.9   Models and Approximations

[I want to propose a model of free energy that captures the solid-liquid transition and, therefore, makes the dependence on d(r) such that the dependence in the liquid phase disappears. Maybe it can be dealt with in a Gaussian fashion, such that some correlations become highly divergent in the liquid phase and, therefore, the inverse vanish. The inverse are the coefficients in front of d(r). Also, I have to pay attention to translation invariance, because it is said that "if the crystal is displaced as a whole, the free energy is constant, implies that the dependence on d(r) is through the gradients only." Perhaps the Gaussian approximation can be reached from the harmonic approximation, but may be not. Another intuition is that the free energy needs to include the crystallization potential, that vanishes in the liquid state (and then the ensemble is translation invariant). Therefore, it looks like the quadratic coefficients in front of d(r) should depend on the crystallization potential, and somehow vanish when the potential is zero and the system is translation invariant. Maybe there is a zero eigenvalue in the correlations, due to translation invariance?]

18.9.1   The harmonic approximation

For sufficiently low temperatures, we expect that the particles of the system will be exploring a tiny neighborhood of the minimum of the potential energy. In order to obtain the effective ensemble, we could expand the potential energy around its minima, denote with q^α. This particular microstate may correspond either to a lattice structure or, with more generality, to any inherent structure that *we assume* the system is trapped. Because the potential energy may depend on an externally imposed field, the location of the minima q^α depends on the actual value of the external field and changes if, for example, we compress or twist the system with external forces.

According to this picture, we may expand the potential energy around a local minimum q^α

$$\phi(q) = \phi(q^\alpha) + \sum_i (\mathbf{q}_i - \mathbf{q}_i^\alpha) \frac{\partial \phi}{\partial \mathbf{q}_i}(q^\alpha) + \frac{1}{2} \sum_{ij} (\mathbf{q}_i - \mathbf{q}_i^\alpha)(\mathbf{q}_j - \mathbf{q}_j^\alpha) \frac{\partial^2 \phi}{\partial \mathbf{q}_i \partial \mathbf{q}_j}(q^\alpha)$$

The linear term vanishes because q^α is precisely the assumed minimum of the potential, where the first derivative vanish. Therefore, the potential is given by

$$\phi_0(q) = \frac{1}{2} \sum_{ij} (\mathbf{q}_i - \mathbf{q}_i^\alpha) \mathbf{K}_{ij} (\mathbf{q}_j - \mathbf{q}_j^\alpha)$$

where $\mathbf{K}_{ij}$ is the Hessian matrix of the potential function and the constant term is irrelevant and is neglected. This potential energy takes a pair-wise form and depends parametrically on inherent structure microstate q^α. Note that, while in the absence of external fields the original potential of interaction is translation invariant, the harmonic potential is not translation invariant with respect to q (although it is obviously invariant under a simultaneous translation of q and q^α). Note that for a perfect lattice inherent structure, the Hessian matrix needs to satisfy the following degeneracy condition

$$\mathbf{L} \cdot \left[\sum_{ij} \mathbf{K}_{ij} \right] \cdot \mathbf{L} = 0$$

for any lattice vector $\mathbf{L}$.

Instead, we may simply assume that the effective ensemble is a Gaussian of the form

$$\rho_0(z) = \frac{1}{Z} \exp \left\{ -\beta \hat{H}_\alpha(z) \right\}$$

where the effective Hamiltonian is given by

$$\hat{H}_\alpha(z) = \sum_i^N \frac{\mathbf{p}_i^2}{2m_i} + \frac{1}{2} \sum_{ij} (\mathbf{q}_i - \mathbf{q}_i^\alpha) \mathbf{K}_{ij} (\mathbf{q}_j - \mathbf{q}_j^\alpha)$$

This ensemble predicts that the density field will be bumpy

$$\rho_0^{\text{eq}}(\mathbf{r}) = \frac{1}{Q} \int du \sum_i^N \delta(\mathbf{r} - \mathbf{q}_i^\alpha - \mathbf{u}_i) \exp \left\{ -\beta \frac{1}{2} \sum_{ij} \mathbf{u}_i \mathbf{K}_{ij} \mathbf{u}_j \right\}$$

where momentum integrals have been trivially performed and the change of variables $\mathbf{u}_i = \mathbf{q}_i - \mathbf{q}_i^\alpha$ is taken. The integral is of the form (24.1.3) which is evaluated in (**??**) in the form

$$\Omega(y, J) = \frac{1}{\Omega_0(J)} \int dx \exp \left\{ -\frac{1}{2} x^T A x + J^T x \right\} \delta(\Pi x - y) = \frac{\det \overline{A}^{1/2}}{(2\pi)^{M/2}} \exp \left\{ -\frac{1}{2} (y + \Pi A^{-1} J)^T \overline{A} (y + \Pi A^{-1} J) \right\}$$

In the present case, $x \to \mathbf{u}$, $y \to \mathbf{r} - \mathbf{q}_i^\alpha$, $A \in \mathbb{R}^{N \times N} \to \mathbf{K}$ is invertible, $\Pi \in \mathbb{R}^{M \times N}$ is rectangular matrix that when applied to q picks $\mathbf{q}_i$, and $J \in \mathbb{R}^N = 0$.

$$\overline{A} \equiv \left[\Pi A^{-1} \Pi^T \right]^{-1} \to \mathbf{K}_{ii}^{-1}$$

and, therefore,

$$\rho_0^{\text{eq}}(\mathbf{r}) = \sum_i^N \frac{\sqrt{\det \overline{\mathbf{K}}_{ii}^{-1}}}{(2\pi)^{M/2}} \exp\left\{-\frac{1}{2}(\mathbf{r} - \mathbf{q}_i^\alpha)\mathbf{K}_{ii}(\mathbf{r} - \mathbf{q}_i^\alpha)\right\}$$

which is a collection of Gaussians centered around the lattice locations

We will compute explicitly the partition function (18.4) when the potential energy per particle is given by the above expression. We have

$$\overline{Z}[\mu, \boldsymbol{\lambda}, \beta] \equiv \sum_{N=0}^{\infty} \frac{1}{N!} \int \prod_{i=1}^N \frac{d\mathbf{q}_i}{\Lambda^3} \exp\left\{-\sum_i^N \beta\left(m_i \mathbf{u}_i \cdot \boldsymbol{\lambda}(\mathbf{q}_i) - m_i \mu(\mathbf{q}_i) + \frac{1}{2}\mathbf{u}_i \sum_j \mathbf{K}_{ij} \mathbf{u}_j\right)\right\}$$

Perform the change of variables $\mathbf{q}_i \to \mathbf{u}_i = \mathbf{q}_i - \mathbf{q}_i^\alpha$.

$$\overline{Z}[\mu, \boldsymbol{\lambda}, \beta] \equiv \sum_{N=0}^{\infty} \frac{1}{N!} \int \prod_{i=1}^N \frac{d\mathbf{u}_i}{\Lambda^3} \exp\left\{-\sum_i^N \beta\left(m_i \mathbf{u}_i \cdot \boldsymbol{\lambda}(\mathbf{q}_i^\alpha + \mathbf{u}_i) - m_i \mu(\mathbf{q}_i^\alpha + \mathbf{u}_i) + \frac{1}{2}\mathbf{u}_i \sum_j \mathbf{K}_{ij} \mathbf{u}_j\right)\right\}$$

It seems consistent to expand the conjugate variables to second order in the displacements, in accordance with the similar expansion in the potential energy. Therefore, we approximate

$$\boldsymbol{\lambda}(\mathbf{q}_i^\alpha + \mathbf{u}_i) \approx \boldsymbol{\lambda}(\mathbf{q}_i^\alpha) + \mathbf{u}_i \cdot \boldsymbol{\nabla}\boldsymbol{\lambda}(\mathbf{q}_i^\alpha)$$

$$\mu(\mathbf{q}_i^\alpha + \mathbf{u}_i) \approx \mu(\mathbf{q}_i^\alpha) + \mathbf{u}_i \cdot \boldsymbol{\nabla}\mu(\mathbf{q}_i^\alpha) + \frac{1}{2}\mathbf{u}_i \mathbf{u}_i : \boldsymbol{\nabla}\boldsymbol{\nabla}\mu(\mathbf{q}_i^\alpha)$$

By substitution into (**??**) and neglect of second order terms in the displacements we arrive at

$$\overline{Z}[\mu, \boldsymbol{\lambda}, \beta] \equiv \sum_{N=0}^{\infty} \frac{1}{N!} \int \prod_{i=1}^N \frac{d\mathbf{u}_i}{\Lambda^3} \exp\left\{-\beta \sum_i^N (m_i \mathbf{u}_i \cdot \boldsymbol{\lambda}(\mathbf{q}_i^\alpha) - m_i \mu(\mathbf{q}_i^\alpha)) + \beta \sum_{ij} \frac{1}{2}\mathbf{u}_i \overline{\mathbf{K}}_{ij} \mathbf{u}_j\right\}$$

where we have introduced the new matrix

$$\overline{\mathbf{K}}_{ij} = \mathbf{K}_{ij}(q^\alpha) + \delta_{ij} m_i \left[\boldsymbol{\nabla}\boldsymbol{\lambda}(\mathbf{q}_i^\alpha) - \boldsymbol{\nabla}\boldsymbol{\nabla}\mu(\mathbf{q}_i^\alpha)\right]$$

In this approximation the integral becomes a Gaussian integral in $\mathbf{u}$ that is simple to

integrate (provided that the matrix $\overline{\mathbf{K}}_{ij}$ is invertible, more on this later). This is

$$\overline{Z}[\mu, \boldsymbol{\lambda}, \beta] = \sum_{N=0}^{\infty} \frac{1}{N!} \frac{1}{\Lambda^{3N}} \exp\left\{ \sum_i^N \beta m_i \mu(\mathbf{q}_i^\alpha) \right\} \int \prod_{i=1}^N d\mathbf{u}_i \exp\left\{ -\sum_i^N \beta m_i \boldsymbol{\lambda}(\mathbf{q}_i^\alpha)\cdot\mathbf{u}_i - \beta\frac{1}{2} \sum_{ij}^N \mathbf{u}_i \overline{\mathbf{K}}_{ij} \mathbf{u}_j \right\}$$

The Gaussian integral is of the form

$$\int dz \exp\left\{ -\frac{1}{2} z^T A z + J^T z \right\} = \frac{(2\pi)^{N/2}}{\det A^{1/2}} \exp\left\{ \frac{1}{2} J^T A^{-1} J \right\}$$

Therefore,

$$\overline{Z}[\mu, \boldsymbol{\lambda}, \beta] = \sum_{N=0}^{\infty} \frac{1}{N!} \frac{1}{\Lambda^{3N}} \exp\left\{ \sum_i^N \beta m_i \mu(\mathbf{q}_i^\alpha) \right\} \int \prod_{i=1}^N d\mathbf{u}_i \exp\left\{ -\sum_i^N \beta m_i \boldsymbol{\lambda}(\mathbf{q}_i^\alpha)\cdot\mathbf{u}_i - \beta\frac{1}{2} \sum_{ij}^N \mathbf{u}_i \overline{\mathbf{K}}_{ij} \mathbf{u}_j \right\}$$

$$= \sum_{N=0}^{\infty} \frac{1}{N!} \frac{(2\pi k_B T)^{3N/2}}{\Lambda^{3N} \det[\mathbf{K}]^{1/2}} \exp\left\{ \sum_i^N \beta m_i \mu(\mathbf{q}_i^\alpha) + \frac{\beta}{2} \sum_{ij}^N \boldsymbol{\lambda}(\mathbf{q}_i^\alpha) m_i \left[\overline{\mathbf{K}}_{ij}\right]^{-1} m_j \boldsymbol{\lambda}(\mathbf{q}_j^\alpha) \right\}$$

Because the thermal wavelength is

$$\Lambda(\beta) \equiv \left(\frac{h^2\beta}{2m\pi} \right)^{\frac{1}{2}}$$

we have

$$\overline{Z}[\mu, \boldsymbol{\lambda}, \beta] = \sum_{N=0}^{\infty} \frac{1}{N!} \exp\left\{ -\frac{1}{2}\ln\frac{\sqrt{M}}{h} \det[\overline{\mathbf{K}}] + \sum_i^N \beta m_i \mu(\mathbf{q}_i^\alpha) + \frac{\beta}{2} \sum_{ij}^N \boldsymbol{\lambda}(\mathbf{q}_i^\alpha) m_i \left[\overline{\mathbf{K}}_{ij}\right]^{-1} m_j \boldsymbol{\lambda}(\mathbf{q}_j^\alpha) \right\}$$

Let us write in a continuum like form

$$\sum_i^N \beta m_i \mu(\mathbf{q}_i^\alpha) = N \int d\mathbf{r}\, \overline{n}_\mathbf{r}(q^\alpha) \mu(\mathbf{r})$$

$$\sum_{ij}^N \boldsymbol{\lambda}(\mathbf{q}_i^\alpha) \left[\mathbf{K}_{ij}\right]^{-1} \boldsymbol{\lambda}(\mathbf{q}_j^\alpha) = N \int d\mathbf{r} \int d\mathbf{r}'\, \boldsymbol{\lambda}(\mathbf{r}) \overline{\mathbf{K}}(\mathbf{r}, \mathbf{r}') \boldsymbol{\lambda}(\mathbf{r}')$$

where

$$\overline{n}_{\mathbf{r}}(q^\alpha) = \frac{1}{N} \sum_i^N m_i \delta(\mathbf{r} - \mathbf{r}_i)$$

$$\mathbf{K}^{-1}(\mathbf{r}, \mathbf{r}') = \frac{1}{N} \sum_{ij}^N \delta(\mathbf{r} - \mathbf{q}_i^\alpha) [\mathbf{K}_{ij}]^{-1} \delta(\mathbf{r}' - \mathbf{q}_j^\alpha)$$

We assume that these two functions are independent of N in the thermodynamic limit. In addition, because the logarithm of the determinant is the trace of the logarithm, we have

$$\ln \det \overline{K} = \sum_i^N \ln \overline{K}_{ii}$$

We also assume that this term scales as N in the thermodynamic limit. In summary, we may write the partition function (18.9.1) as

$$\overline{Z}[\mu, \boldsymbol{\lambda}, \beta] = \sum_{N=0}^\infty \frac{1}{N!} \left[e^{-\beta F} \right]^N = \exp\{e^{-\beta F}\}$$

and the thermodynamic potential is

$$\Phi[\mu, \boldsymbol{\lambda}, \beta] = -\exp\left\{ -\beta \left[\ln \det \overline{\mathbf{K}} + \int d\mathbf{r} \overline{n}_{\mathbf{r}}(q^\alpha)\mu(\mathbf{r}) + \int d\mathbf{r} \int d\mathbf{r}' \boldsymbol{\lambda}(\mathbf{r}) \overline{\mathbf{K}}(\mathbf{r}, \mathbf{r}') \boldsymbol{\lambda}(\mathbf{r}') \right] \right\}$$

This is an explicit expression for the thermodynamic potential in terms of the conjugate variables. Note that the conjugate variables appear also inside the kernel $\overline{\mathbf{K}}(\mathbf{r}, \mathbf{r}')$. In a first approximation, we will neglect the contribution of the space derivatives of the conjugate variables on the stiffness matrix (??), i.e. we will assume that $\overline{K}_{ij} \approx K_{ij}$. In this way, the thermodynamic potential is just a Gaussian in the conjugate variables. The connection between the conjugate variables and the CG variables is given by (18.4)

$$\frac{\delta \Phi^{\text{rest}}[\mu, \boldsymbol{\lambda}, \beta]}{\delta \mu(\mathbf{r})} = -\beta \rho(\mathbf{r})$$

$$\frac{\delta \Phi^{\text{rest}}[\mu, \boldsymbol{\lambda}, \beta]}{\delta \boldsymbol{\lambda}(\mathbf{r})} = \beta \mathbf{d}(\mathbf{r})$$

$$\frac{\partial \Phi^{\text{rest}}[\mu, \boldsymbol{\lambda}, \beta]}{\partial \beta} = \int d\mathbf{r} \left[\boldsymbol{\lambda}(\mathbf{r}) \cdot \mathbf{d}(\mathbf{r}) - \mu(\mathbf{r})\rho(\mathbf{r}) \right] + \phi[\mu, \boldsymbol{\lambda}, \beta]$$

18.10 Local model for the entropy functional, first attempt

Let us assume that the entropy functional is given by the following local function

$$S^{\text{rest}}[\rho, \mathbf{d}, u] = \int d\mathbf{r} s(\rho(\mathbf{r}), \mathbf{d}(\mathbf{r}), u(\mathbf{r}))$$

I would like to show that these proposal is incompatible with translational invariance.

We assume extensivity, this is, that the macroscopic entropy is a first order function of its arguments, this is

$$S(M, \mathbf{D}, U, V) = V s\left(\frac{M}{V}, \frac{\mathbf{D}}{V}, \frac{U}{V}\right)$$

This implies that

$$\pi(\rho, \mathbf{d}, u) \equiv \frac{\partial}{\partial V} S(M, \mathbf{D}, U, V) = s(\rho, \mathbf{d}, u) - \rho s_\rho - \mathbf{d} s_{\mathbf{d}} - u s_u$$

Of course, if we do not know anything about the macroscopic entropy and its extensivity, this equation could be understood simply as a definition of the pressure π.

If we take the gradient of this

$$\nabla \pi(\rho, \mathbf{d}, u) = s_\rho \nabla \rho + s_{\mathbf{d}} \nabla \mathbf{d} + s_u \nabla u - \nabla(\rho s_\rho) - \nabla(\mathbf{d} s_{\mathbf{d}}) - \nabla(u s_u)$$
$$= -\rho \nabla(s_\rho) - \mathbf{d} \nabla(s_{\mathbf{d}}) - u \nabla(s_u)$$

If we integrate over all space and assume that at the infinity the fields vanish, we have

$$0 = \int d\mathbf{r} \nabla \pi(\rho, \mathbf{d}, u) = \int d\mathbf{r} \left[-\rho \nabla(s_\rho) - \mathbf{d} \nabla(s_{\mathbf{d}}) - u \nabla(s_u) \right]$$

But this identity is just an expression of translational invariance that takes the form

$$0 = \int d\mathbf{r} \left[s_\rho \nabla \rho + s_{\mathbf{d}} \nabla \mathbf{d} + s_u \nabla u \right]$$

Therefore, we have derived translational invariance from extensivity.

Now let us consider the full entropy

$$S[\rho, \mathbf{d}, \mathbf{g}, e] = S^{\text{rest}}\left[\rho, \mathbf{d}, e - \frac{\mathbf{g}^2}{2\rho}\right] = \int d\mathbf{r} \left[s\left(\rho(\mathbf{r}), \mathbf{d}(\mathbf{r}), e(\mathbf{r}) - \frac{\mathbf{g}^2(\mathbf{r})}{2\rho}\right) \right]$$

The zero entropy production is

$$\int d\mathbf{r} \left[\partial_t \rho(\mathbf{r}) \frac{\delta S}{\delta \rho(\mathbf{r})} + \partial_t \mathbf{d}(\mathbf{r}) \frac{\delta S}{\delta \mathbf{d}(\mathbf{r})} + \partial_t \mathbf{g}(\mathbf{r}) \frac{\delta S}{\delta \mathbf{g}(\mathbf{r})} + \partial_t e(\mathbf{r}) \frac{\delta S}{\delta e(\mathbf{r})} \right] = 0$$

where the reversible part is

$$\partial_t \rho\big|_{\mathrm{rev}} = -\nabla \mathbf{g}$$
$$\partial_t \mathbf{d}\big|_{\mathrm{rev}} = \mathbf{g} - \nabla{\cdot}\mathbf{vd}$$
$$\partial_t \mathbf{g}\big|_{\mathrm{rev}} = -\nabla\mathbf{\Pi} - \nabla\mathbf{vg}$$
$$\partial_t e\big|_{\mathrm{rev}} = -\nabla e\mathbf{v} - \nabla\mathbf{\Pi}\mathbf{v}$$

Therefore

$$\int d\mathbf{r} \left[-\nabla \mathbf{g} \left(s_\rho + s_u \frac{\mathbf{v}^2}{2} \right) + [\mathbf{g} - \nabla \cdot \mathbf{vd}] \, s_{\mathbf{d}} + [\nabla \mathbf{\Pi} + \nabla \mathbf{vg}] \, (s_u \mathbf{v}) - [\nabla e \mathbf{v} + \nabla \mathbf{\Pi v}] \, s_u \right] = 0$$

The terms involving $\mathbf{\Pi}$ give

$$[\nabla \mathbf{\Pi}] \, s_u \mathbf{v} - [\nabla \mathbf{\Pi v}] \, s_u = -s_u \mathbf{\Pi} : \nabla \mathbf{v}$$

Next we consider the rest of terms

$$\int d\mathbf{r} \left[-\nabla \mathbf{g} \left(s_\rho + s_u \frac{\mathbf{v}^2}{2} \right) + (\nabla \mathbf{vg}) s_u \mathbf{v} - [\nabla e \mathbf{v}] \, s_u \right]$$

$$= \int d\mathbf{r} \left[-\nabla \mathbf{g} \left(s_\rho + s_u \frac{\mathbf{v}^2}{2} \right) + (\nabla \mathbf{vg}) s_u \mathbf{v} - \left[\nabla (u + \frac{1}{2} \mathbf{g} \cdot \mathbf{v}) \mathbf{v} \right] s_u \right]$$

Let us consider only the terms with s_u in this expression (except $(\nabla u \mathbf{v}) s_u$)

$$\int d\mathbf{r} s_u \left[-(\nabla \mathbf{g}) \frac{\mathbf{v}^2}{2} + (\nabla \mathbf{vg}) \mathbf{v} - \nabla \left(\frac{\mathbf{v}^2}{2} \mathbf{g} \right) \right]$$

$$= \int d\mathbf{r} s_u \left[-(\nabla \mathbf{g}) \frac{\mathbf{v}^2}{2} + (\nabla \mathbf{vg}) \mathbf{v} - \nabla \left(\frac{\mathbf{v}^2}{2} \mathbf{g} \right) \right]$$

$$= \int d\mathbf{r} s_u \left[-(\nabla \mathbf{g}) \frac{\mathbf{v}^2}{2} + (\nabla \mathbf{vg}) \mathbf{v} - \nabla \left(\frac{\mathbf{v}^2}{2} \mathbf{g} \right) \right] = 0$$

In this way

$$0 = \int d\mathbf{r} \left[-\nabla \mathbf{g} \, (s_\rho) + [\mathbf{g} - \nabla \cdot \mathbf{vd}] \, s_{\mathbf{d}} - s_u \mathbf{\Pi} : \nabla \mathbf{v} - [\nabla u \mathbf{v}] \, s_u \right]$$

$$= \int d\mathbf{r} \left[-s_\rho \rho \nabla \mathbf{v} - s_\rho \mathbf{v} \nabla \rho + \mathbf{g} s_{\mathbf{d}} - s_{\mathbf{d}} \mathbf{v} \cdot \nabla \mathbf{d} - s_{\mathbf{d}} \mathbf{d} \nabla \cdot \mathbf{v} - s_u \mathbf{\Pi} : \nabla \mathbf{v} - s_u u \nabla \mathbf{v} - s_u \mathbf{v} \nabla u \right]$$

$$= \int d\mathbf{r} \left[-\mathbf{v} s_\rho \nabla \rho - s_{\mathbf{d}} \mathbf{v} \cdot \nabla \mathbf{d} - s_u \mathbf{v} \nabla u - s_\rho \rho \nabla \mathbf{v} - s_{\mathbf{d}} \mathbf{d} \nabla \cdot \mathbf{v} - s_u u \nabla \mathbf{v} + \mathbf{g} s_{\mathbf{d}} - s_u \mathbf{\Pi} : \nabla \mathbf{v} \right]$$

$$= \int d\mathbf{r} \mathbf{v} \cdot [-s_\rho \nabla \rho - s_{\mathbf{d}} \nabla \mathbf{d} - s_u \nabla u + \nabla s_\rho \rho + \nabla s_{\mathbf{d}} \mathbf{d} + \nabla s_u u + \nabla s_u \mathbf{\Pi}] + \int d\mathbf{r} \mathbf{g} s_{\mathbf{d}}$$

$$= \int d\mathbf{r} \mathbf{v} \cdot [\nabla [-s + s_\rho \rho + s_{\mathbf{d}} \mathbf{d} + s_u u + s_u \mathbf{\Pi}] + \rho s_{\mathbf{d}}]$$

$$= \int d\mathbf{r} \mathbf{v} \cdot [\nabla [s_u \pi + s_u \mathbf{\Pi}] + \rho s_{\mathbf{d}}]$$

Because this is true for all velocity fields $\mathbf{v}$ we must have

$$\nabla [s_u \pi + s_u \mathbf{\Pi}] + \rho s_{\mathbf{d}} = 0$$

We write $\mathbf{\Pi} = \pi\mathbf{1} - \mathbf{\Delta}$ and we have

$$\rho s_{\mathbf{d}} = \nabla s_u \mathbf{\Delta}$$
$$\rho s_{\mathbf{d}} = s_u \nabla \mathbf{\Delta} + \mathbf{\Delta}\nabla s_u$$
$$\nabla\mathbf{\Delta} = \frac{1}{s_u}\left[\rho s_{\mathbf{d}} - \mathbf{\Delta}\nabla s_u\right]$$

When we compute in the momentum equation the term $\nabla\mathbf{\Pi}$ we will have

$$\nabla\mathbf{\Pi} = \nabla\pi - \nabla\mathbf{\Delta}$$
$$= \nabla\pi - \frac{1}{s_u}\left[\rho s_{\mathbf{d}} - \mathbf{\Delta}\nabla s_u\right]$$

Unfortunately, the last term is not a divergence and, therefore, momentum will not be conserved unless this last term vanishes. This implies that we should have $s_{\mathbf{d}} = 0$ and $\mathbf{\Delta} = 0$ in order to respect reversibility and momentum conservation.

18.11   Local model for the entropy functional, second attempt

We consider the following particular model for the entropy functional

$$S^{\text{rest}}[\rho, \mathbf{d}, u] = \int d\mathbf{r} \left[s(\rho, u) + \mathbf{c}(\rho, u)\cdot\mathbf{d} + \mathbf{B}(\rho, u) : \nabla\mathbf{d} \right]$$

This form is the simplest one that is linear in the displacement fields. In fact, we may consider the more general case

$$S^{\text{rest}}[\rho, \mathbf{d}, u] = \int d\mathbf{r} \left[s(\rho, \mathbf{d}, u) + \mathbf{B}(\rho, u) : \nabla\mathbf{d} \right]$$

It requires the gradient because if the gradient is not present we fall back to the previous example. The original entropy is given from (18.4) as

$$S[\rho, \mathbf{d}, \mathbf{g}, e] = S^{\text{rest}} \left[\rho, \mathbf{d}, e - \frac{\mathbf{g}^2}{2\rho} \right]$$

$$= \int d\mathbf{r} \left[s \left(\rho, \mathbf{d}, e - \frac{\mathbf{g}^2}{2\rho} \right) + \mathbf{B} \left(\rho, e - \frac{\mathbf{g}^2}{2\rho} \right) : \nabla\mathbf{d} \right]$$

where the position dependence of all functions has been omitted. Let us compute the functional derivatives

$$\frac{\delta S}{\delta \rho} = s_\rho + s_u \frac{\mathbf{v}^2}{2} + A_\rho + A_u \frac{\mathbf{v}^2}{2}$$

$$\frac{\delta S}{\delta \mathbf{d}} = s_{\mathbf{d}} - \nabla\cdot\mathbf{B}$$

$$\frac{\delta S}{\delta \mathbf{g}} = -s_u \mathbf{v} - A_u \mathbf{v}$$

$$\frac{\delta S}{\delta e} = s_u + A_u$$

$$A_\rho \equiv \mathbf{B}_\rho : \mathbf{d}$$

$$A_u \equiv \mathbf{B}_u : \mathbf{d}$$

Translational invariance implies

$$\int d\mathbf{r} \left[\left(s_\rho + s_u \frac{\mathbf{v}^2}{2} + A_\rho + A_u \frac{\mathbf{v}^2}{2} \right) \nabla\rho + (s_{\mathbf{d}} - \nabla\cdot\mathbf{B}) \nabla\mathbf{d} - (s_u \mathbf{v} + A_u \mathbf{v}) \nabla\mathbf{g} + (s_u + A_u)\nabla e \right] = 0$$

$$\int d\mathbf{r} \left[\left(s_\rho + s_u \frac{\mathbf{v}^2}{2} + A_\rho + A_u \frac{\mathbf{v}^2}{2} \right) \nabla\rho + (s_{\mathbf{d}} - \nabla\cdot\mathbf{B}) \nabla\mathbf{d} - (s_u \mathbf{v} + A_u \mathbf{v}) \nabla\mathbf{g} + (s_u + A_u)\nabla(u + \mathbf{g}^2/2\rho) \right] = 0$$

$$\int d\mathbf{r} \left[(s_\rho + A_\rho) \nabla\rho + (s_{\mathbf{d}} - \nabla\cdot\mathbf{B}) \nabla\mathbf{d} + (s_u + A_u)\nabla u \right] = 0$$

We know that the reversible part of the dynamics gives zero entropy production. This is

$$\int d\mathbf{r} \left[\partial_t \rho(\mathbf{r}) \frac{\delta S}{\delta \rho(\mathbf{r})} + \partial_t \mathbf{d}(\mathbf{r}) \frac{\delta S}{\delta \mathbf{d}(\mathbf{r})} + \partial_t \mathbf{g}(\mathbf{r}) \frac{\delta S}{\delta \mathbf{g}(\mathbf{r})} + \partial_t e(\mathbf{r}) \frac{\delta S}{\delta e(\mathbf{r})} \right] = 0$$

where the reversible part is

$$\partial_t \rho|_{\text{rev}} = -\nabla \mathbf{g}$$
$$\partial_t \mathbf{d}|_{\text{rev}} = \mathbf{g} - \nabla \cdot \mathbf{vd}$$
$$\partial_t \mathbf{g}|_{\text{rev}} = -\nabla \mathbf{\Pi} - \nabla \mathbf{vg}$$
$$\partial_t e|_{\text{rev}} = -\nabla e \mathbf{v} - \nabla \mathbf{\Pi} \mathbf{v}$$

Therefore

$$\int d\mathbf{r} \left[-\nabla \mathbf{g} \frac{\delta S}{\delta \rho(\mathbf{r})} + [\mathbf{g} - \nabla \cdot \mathbf{vd}] \frac{\delta S}{\delta \mathbf{d}(\mathbf{r})} - [\nabla \mathbf{\Pi} + \nabla \mathbf{vg}] \frac{\delta S}{\delta \mathbf{g}(\mathbf{r})} - [\nabla e \mathbf{v} + \nabla \mathbf{\Pi} \mathbf{v}] \frac{\delta S}{\delta e(\mathbf{r})} \right] = 0$$

Let us move now to the more general case

$$\int d\mathbf{r} \left[-\nabla \mathbf{g} \frac{\delta S}{\delta \rho(\mathbf{r})} + [\mathbf{g} - \nabla \cdot \mathbf{vd}] \frac{\delta S}{\delta \mathbf{d}(\mathbf{r})} - [\nabla \mathbf{\Pi} + \nabla \mathbf{vg}] \frac{\delta S}{\delta \mathbf{g}(\mathbf{r})} - [\nabla e \mathbf{v} + \nabla \mathbf{\Pi} \mathbf{v}] \frac{\delta S}{\delta e(\mathbf{r})} \right] = 0$$

$$\frac{\delta S}{\delta \rho} = s_\rho + s_u \frac{\mathbf{v}^2}{2} + A_\rho + A_u \frac{\mathbf{v}^2}{2}$$
$$\frac{\delta S}{\delta \mathbf{d}} = s_{\mathbf{d}} - \nabla \cdot \mathbf{B}$$
$$\frac{\delta S}{\delta \mathbf{g}} = -s_u \mathbf{v} - A_u \mathbf{v}$$
$$\frac{\delta S}{\delta e} = s_u + A_u$$

Therefore,

$$
0 = \int d\mathbf{r} \left[-\nabla\mathbf{g} \left(s_\rho + s_u \frac{\mathbf{v}^2}{2} + A_\rho + A_u \frac{\mathbf{v}^2}{2} \right) + [\mathbf{g} - \nabla\cdot\mathbf{vd}] \left(s_\mathbf{d} - \nabla\cdot\mathbf{B} \right) \right.
$$
$$
- [\nabla\mathbf{\Pi} + \nabla\mathbf{vg}] \left(-s_u\mathbf{v} - A_u\mathbf{v} \right) - [\nabla e\mathbf{v} + \nabla\mathbf{\Pi}\mathbf{v}] \left(s_u + A_u \right)] = 0
$$

$$
= \int d\mathbf{r} \left[-\nabla\mathbf{g} \left(s_\rho + s_u \frac{\mathbf{v}^2}{2} \right) - \nabla\mathbf{g} \left(A_\rho + A_u \frac{\mathbf{v}^2}{2} \right) \right.
$$
$$
+ [\mathbf{g} - \nabla\cdot\mathbf{vd}] \left(s_\mathbf{d} - \nabla\cdot\mathbf{B} \right) + [\nabla\mathbf{\Pi} + \nabla\mathbf{vg}] \, s_u\mathbf{v} + [\nabla\mathbf{\Pi} + \nabla\mathbf{vg}] \left(A_u\mathbf{v} \right)
$$
$$
- [\nabla e\mathbf{v} + \nabla\mathbf{\Pi}\mathbf{v}] \, s_u - [\nabla e\mathbf{v} + \nabla\mathbf{\Pi}\mathbf{v}] \, A_u]
$$

The terms that do not involve $\mathbf{B}$ have been already computed and simplify to

$$
\int d\mathbf{r}\mathbf{v}\cdot \left[\nabla \left[s_u\pi + s_u\mathbf{\Pi} \right] + \rho s_\mathbf{d} \right]
$$

$$0 = \int d\mathbf{r} \left[-(\nabla \mathbf{g}) \left(A_\rho + A_u \frac{\mathbf{v}^2}{2} \right) - [\mathbf{g} - \nabla \cdot \mathbf{vd}] \, \nabla \cdot \mathbf{B} + \mathbf{v} \cdot [\nabla [s_u \pi + s_u \mathbf{\Pi}] + \rho s_\mathbf{d}] \right.$$
$$\left. + [\nabla \mathbf{\Pi} + \nabla \mathbf{vg}] (A_u \mathbf{v}) - [\nabla e \mathbf{v} + \nabla \mathbf{\Pi v}] A_u \right]$$

Group

$$0 = \int d\mathbf{r} \left[\underbrace{-(\nabla \mathbf{g}) A_\rho -(\nabla \mathbf{g}) A_u \frac{\mathbf{v}^2}{2} + (\nabla \mathbf{vg}) (A_u \mathbf{v}) - \nabla \left(\mathbf{g} \frac{\mathbf{v}^2}{2} \right) A_u}_{=0} \right.$$

$$\left. - [\mathbf{g} - \nabla \cdot \mathbf{vd}] \, \nabla \cdot \mathbf{B} + \mathbf{v} \cdot [\nabla [s_u \pi + s_u \mathbf{\Pi}] + \rho s_\mathbf{d}] + \underbrace{\nabla \mathbf{\Pi}(A_u \mathbf{v}) - \nabla \mathbf{\Pi v} (A_u)}_{-A_u \mathbf{\Pi}:\nabla \mathbf{v}} -(\nabla u \mathbf{v}) (A_u) \right]$$

$$= \int d\mathbf{r} \left[-(\nabla \mathbf{g}) A_\rho - [\mathbf{g} - \nabla \cdot \mathbf{vd}] \, \nabla \cdot \mathbf{B} + \mathbf{v} \cdot [\nabla [s_u \pi + s_u \mathbf{\Pi}] + \rho s_\mathbf{d}] - A_u \mathbf{\Pi} : \nabla \mathbf{v} - A_u \nabla u \mathbf{v} \right]$$

The two terms

$$-A_\rho (\nabla \mathbf{g}) - A_u \nabla u \mathbf{v} = -A_\rho \rho \nabla \mathbf{v} - \mathbf{v} A_\rho \nabla \rho - A_u u \nabla \mathbf{v} - \mathbf{v} A_u \nabla u$$
$$= -A_\rho \rho \nabla \mathbf{v} - A_u u \nabla \mathbf{v} \underbrace{-\mathbf{v} A_\rho \nabla \rho - \mathbf{v} A_u \nabla u}_{-\mathbf{v} \cdot (\nabla \mathbf{B}):\nabla \mathbf{d}}$$

$$0 = \int d\mathbf{r} \left[\mathbf{v} \nabla A_\rho \rho + \mathbf{v} \nabla A_u u - \mathbf{v} \cdot (\nabla \mathbf{B}) : \nabla \mathbf{d} - [\mathbf{g} - \nabla \cdot \mathbf{vd}] \, \nabla \cdot \mathbf{B} \right.$$
$$\left. + \mathbf{v} \cdot [\nabla [s_u \pi + s_u \mathbf{\Pi}] + \rho s_\mathbf{d}] + \mathbf{v} \nabla (A_u \mathbf{\Pi})] \right]$$

$$= \int d\mathbf{r} \mathbf{v} \nabla [A_\rho \rho + A_u u + \pi s_u + \mathbf{\Pi} s_u + A_u \mathbf{\Pi}]$$
$$+ \int d\mathbf{r} \left[\mathbf{v} \rho s_\mathbf{d} - \mathbf{v} \cdot (\nabla \mathbf{B}) : \nabla \mathbf{d} - [\mathbf{g} - \nabla \cdot \mathbf{vd}] \, \nabla \cdot \mathbf{B} \right]$$

$$= \int d\mathbf{r} \mathbf{v} \nabla [A_\rho \rho + A_u u + \pi s_u + \mathbf{\Pi} s_u + A_u \mathbf{\Pi}]$$
$$+ \int d\mathbf{r} \left[\mathbf{v} \rho s_\mathbf{d} - \mathbf{v} \cdot (\nabla \mathbf{B}) : \nabla \mathbf{d} - \mathbf{v} \rho \nabla \cdot \mathbf{B} + \mathbf{v} \cdot (\nabla \nabla \cdot \mathbf{B}) \mathbf{d} + \mathbf{v} \cdot (\nabla \mathbf{d}) \nabla \cdot \mathbf{B} \right]$$

I don't see how to express the last term. However, if $\mathbf{B}$ is independent of the state, the last term vanish. We obtain in this case

$$\nabla\left[\pi s_u + \mathbf{\Pi} s_u\right] + \rho s_\mathbf{d} = 0$$

18.12   Local model for the entropy functional, third attempt

Now we try only displacements

$$S^{\text{rest}}[\rho, \mathbf{d}, u] = \int d\mathbf{r} \left[s(\rho, u) + \mathbf{C}_{\mu\nu\mu'\nu'} \nabla_\mu \mathbf{u}_\nu \nabla_{\mu'} \mathbf{u}_{\nu'} \right]$$

The derivatives are

$$\frac{\delta S}{\delta \rho} = s_\rho + s_u \frac{\mathbf{v}^2}{2} + \frac{\delta}{\delta \rho} \mathbf{C}_{\mu\nu\mu'\nu'} \nabla_\mu \frac{\mathbf{d}_\nu}{\rho} \nabla_{\mu'} \frac{\mathbf{d}_{\nu'}}{\rho}$$

$$\frac{\delta S}{\delta \mathbf{d}} = \frac{\delta}{\delta \mathbf{d}} \mathbf{C}_{\mu\nu\mu'\nu'} \nabla_\mu \mathbf{u}_\nu \nabla_{\mu'} \mathbf{u}_{\nu'}$$

$$\frac{\delta S}{\delta \mathbf{g}} = -s_u \mathbf{v} - A_u \mathbf{v}$$

$$\frac{\delta S}{\delta e} = s_u + A_u$$

Rehacer, mostrando que, necesariamente $\boldsymbol{\lambda} = 0$ en equilibrio. Let us consider for future reference the case that the conjugate fields are constant in space. In this case, the grand canonical partition function takes the form

$$\overline{\Xi}^H[\mu, \boldsymbol{\lambda}, \beta] \equiv \sum_{N=0}^{\infty} \frac{1}{N! h^{3N}} \int d\mathbf{r}_1 \cdots d\mathbf{r}_N \prod_{i=1}^{N} \left(\frac{2m\pi}{\beta} \right)^{\frac{3}{2}} \exp \left\{ \beta m N \mu - \beta \left(\sum_i^N m_i \mathbf{u}_i \cdot \boldsymbol{\lambda} + \frac{1}{2} \sum_{ij}^N \phi_{ij} \right) \right\}$$

To fix ideas, consider an elastic solid for which the pair potential is of the form $\phi_{ij} = \frac{1}{2} \mathbf{u}_i K_N^{ij} \mathbf{u}_j$, with K_N^{ij} a stiffness matrix. We may complete the square and obtain

$$\overline{\Xi}^H[\mu, \boldsymbol{\lambda}, \beta] \equiv \sum_{N=0}^{\infty} \frac{e^{\beta m \mu N}}{N! h^{3N}} \left(\frac{2m\pi}{\beta} \right)^{\frac{3N}{2}} \int d\mathbf{r}_1 \cdots d\mathbf{r}_N \exp \left\{ -\beta \left(\frac{1}{2} (\mathbf{u} - \mathbf{K}^{-1} \boldsymbol{\lambda}) \mathbf{K}_N (\mathbf{u} - \mathbf{K}_N^{-1} \boldsymbol{\lambda}) \right) \right\} \exp \left\{ -\frac{\beta}{2} \boldsymbol{\lambda} \mathbf{K}_N^{-1} \boldsymbol{\lambda} \right\}$$

$$= \sum_{N=0}^{\infty} \frac{e^{\beta m \mu N}}{N! h^{3N}} \left(\frac{2m\pi}{\beta} \right)^{\frac{3N}{2}} \int d^N \mathbf{u} \exp \left\{ -\beta \frac{1}{2} \mathbf{u} \mathbf{K} \mathbf{u} \right\} \exp \left\{ -\frac{\beta}{2} \boldsymbol{\lambda} \mathbf{K}_N^{-1} \boldsymbol{\lambda} \right\}$$

$$= \sum_{N=0}^{\infty} \frac{e^{\beta m \mu N}}{N!} \left(\frac{2m\pi}{h^2 \beta} \right)^{\frac{3N}{2}} \frac{1}{\det \mathbf{K}_N} \exp \left\{ -\frac{\beta}{2} \boldsymbol{\lambda} \mathbf{K}_N^{-1} \boldsymbol{\lambda} \right\}$$

where a simple change of variables has been performed in the second equality sign, and the Gaussian integral has been performed in the last one.

18.13   Appendix: the stress tensor in term of the pair correlation

We now use the definition (**??**) and (18.4) and obtain

$$
\mathrm{Tr}[\overline{\rho}_t^{\mathrm{rest}}(z)\hat{\boldsymbol{\Sigma}}_{\mathbf{r}}] = \mathrm{Tr}\left[\frac{1}{\Xi}\exp\left\{-\int d\mathbf{r}\beta(\mathbf{r},t)\left(\hat{e}_{\mathbf{r}}(z)+\boldsymbol{\lambda}(\mathbf{r},t)\hat{\mathbf{d}}_{\mathbf{r}}(z)-\mu(\mathbf{r},t)\hat{\rho}_{\mathbf{r}}(z)\right)\right\}\right.
$$
$$
\left.\times\frac{1}{2}\sum_{ij}\mathbf{F}_{ij}\mathbf{q}_{ij}\int_0^1 d\epsilon\delta(\mathbf{r}-\mathbf{q}_j-\epsilon\mathbf{q}_{ij})+\sum_i\mathbf{v}_i\mathbf{p}_i\delta(\mathbf{r}-\mathbf{q}_i)\right]
$$

The momentum integrals may be performed explicitly, with the result

$$
\mathrm{Tr}[\overline{\rho}_t^{\mathrm{rest}}(z)\hat{\boldsymbol{\Sigma}}_{\mathbf{r}}] = \frac{\rho(\mathbf{r},t)}{m\beta(\mathbf{r},t)} + \mathrm{Tr}\left[\frac{1}{\Xi}\exp\left\{-\sum_i^N\beta(\mathbf{q}_i,t)\left(m_i\mathbf{u}_i\cdot\boldsymbol{\lambda}(\mathbf{q}_i,t)-m_i\mu(\mathbf{q}_i,t)+\frac{1}{2}\sum_j\phi_{ij}\right)\right\}\right.
$$
$$
\left.\times\frac{1}{2}\sum_{ij}\mathbf{F}_{ij}\mathbf{q}_{ij}\int_0^1 d\epsilon\delta(\mathbf{r}-\mathbf{q}_j-\epsilon\mathbf{q}_{ij})\right]
$$

The last term may be written as

$$
\frac{1}{2}\sum_{ij}'\int d\mathbf{r}'\delta(\mathbf{r}'-\mathbf{q}_i)\int d\mathbf{r}''\delta(\mathbf{r}''-\mathbf{q}_j)\mathbf{F}_{ij}\mathbf{q}_{ij}\int_0^1 d\epsilon\delta(\mathbf{r}-\mathbf{q}_j-\epsilon\mathbf{q}_{ij})
$$
$$
=\frac{1}{2}\int d\mathbf{r}'\int d\mathbf{r}''\mathbf{F}(\mathbf{r}'-\mathbf{r}'')(\mathbf{r}'-\mathbf{r}'')\int_0^1 d\epsilon\delta(\mathbf{r}-\mathbf{r}'-\epsilon(\mathbf{r}''-\mathbf{r}'))\sum_{ij}'\delta(\mathbf{r}'-\mathbf{q}_j)\delta(\mathbf{r}''-\mathbf{q}_i)
$$

We now introduce the following pair correlation

$$
g^{(2)}(\mathbf{r}',\mathbf{r}'') = \mathrm{Tr}\left[\frac{1}{\Xi}\exp\left\{-\sum_i^N\beta(\mathbf{q}_i,t)\left(m_i\mathbf{u}_i\cdot\boldsymbol{\lambda}(\mathbf{q}_i,t)-m_i\mu(\mathbf{q}_i,t)+\frac{1}{2}\sum_j\phi_{ij}\right)\right\}\sum_{ij}'\delta(\mathbf{r}'-\mathbf{q}_j)\delta(\mathbf{r}''-\mathbf{q}_i)\right]
$$

Note that within the range of the interaction σ, for which $|\mathbf{r}'-\mathbf{r}''| < \sigma$ the conjugate variables $\beta(\mathbf{r},t),\boldsymbol{\lambda}(\mathbf{r},t),\mu(\mathbf{r},t)$ do not change appreciably and we may approximate

$$
g^{(2)}(\mathbf{r}',\mathbf{r}''|\beta,\boldsymbol{\lambda},\mu) = \mathrm{Tr}\left[\frac{1}{\Xi}\exp\left\{-\beta(\mathbf{r}',t)\left(\sum_i^N m_i\mathbf{u}_i\cdot\boldsymbol{\lambda}(\mathbf{r}',t)-mN\mu(\mathbf{r},t)+\frac{1}{2}\sum_{ij}^N\phi_{ij}\right)\right\}\sum_{ij}'\delta(\mathbf{r}'-\mathbf{q}_j)\delta(\mathbf{r}''-\mathbf{q}_i)\right]
$$

In this way, we may write

$$\text{Tr}[\overline{\rho}_t^{\text{rest}}(z)\hat{\mathbf{\Sigma}}_{\mathbf{r}}] = \frac{1}{2} \int d\mathbf{r}' \int d\mathbf{r}'' \mathbf{F}(\mathbf{r}' - \mathbf{r}'')(\mathbf{r}' - \mathbf{r}'') \int_0^1 d\epsilon \delta(\mathbf{r} - \mathbf{r}' - \epsilon(\mathbf{r}'' - \mathbf{r}'))g^{(2)}(\mathbf{r}', \mathbf{r}''|\beta, \boldsymbol{\lambda}, \mu)$$

$$= \frac{1}{2} \int_0^1 d\epsilon\epsilon^2 \int d\mathbf{r}' \int d\mathbf{r}'' \mathbf{F}(\epsilon(\mathbf{r}' - \mathbf{r}''))\epsilon(\mathbf{r}' - \mathbf{r}'')\delta(\mathbf{r} - \frac{1}{\epsilon}\mathbf{r}' + (\mathbf{r}'' - \mathbf{r}'))g^{(2)}(\mathbf{r}', \mathbf{r}''|\beta, \boldsymbol{\lambda}, \mu)$$

18.14 Appendix: Microscopic expression of the stress tensor

We now use the definition (**??**) and (18.4) and obtain

$$\text{Tr}[\overline{\rho}_t^{\text{rest}}(z)\hat{\mathbf{\Sigma}}_{\mathbf{r}}] = \text{Tr}\left[\frac{1}{\Xi}\exp\left\{-\int d\mathbf{r}\beta(\mathbf{r}, t)\left(\hat{e}_{\mathbf{r}}(z) + \boldsymbol{\lambda}(\mathbf{r}, t)\hat{\mathbf{d}}_{\mathbf{r}}(z) - \mu(\mathbf{r}, t)\hat{\rho}_{\mathbf{r}}(z)\right)\right\}\right.$$

$$\left. \times \frac{1}{2}\sum_{ij}\mathbf{F}_{ij}\mathbf{r}_{ij}\int_0^1 d\epsilon\delta(\mathbf{r} - \mathbf{r}_j - \epsilon\mathbf{r}_{ij}) + \sum_i \mathbf{v}_i\mathbf{p}_i\delta(\mathbf{r} - \mathbf{r}_i)\right]$$

The momentum integrals may be performed explicitly, with the result

$$\text{Tr}[\overline{\rho}_t^{\text{rest}}(z)\hat{\mathbf{\Sigma}}_{\mathbf{r}}] = \frac{\rho(\mathbf{r}, t)}{m\beta(\mathbf{r}, t)} + \text{Tr}\left[\frac{1}{\Xi}\exp\left\{-\sum_i^N \beta(\mathbf{r}_i, t)\left(m_i\mathbf{u}_i\cdot\boldsymbol{\lambda}(\mathbf{r}_i, t) - m_i\mu(\mathbf{r}_i, t) + \frac{1}{2}\sum_j \phi_{ij}\right)\right\}\right.$$

$$\left. \times \frac{1}{2}\sum_{ij}\mathbf{F}_{ij}\mathbf{r}_{ij}\int_0^1 d\epsilon\delta(\mathbf{r} - \mathbf{r}_j - \epsilon\mathbf{r}_{ij})\right]$$

The last term may be written as

$$\frac{1}{2}\sum_{ij}' \int d\mathbf{r}'\delta(\mathbf{r}' - \mathbf{r}_i)\int d\mathbf{r}''\delta(\mathbf{r}'' - \mathbf{r}_j)\mathbf{F}_{ij}\mathbf{r}_{ij}\int_0^1 d\epsilon\delta(\mathbf{r} - \mathbf{r}_j - \epsilon\mathbf{r}_{ij})$$

$$= \frac{1}{2}\int d\mathbf{r}' \int d\mathbf{r}''\mathbf{F}(\mathbf{r}' - \mathbf{r}'')(\mathbf{r}' - \mathbf{r}'')\int_0^1 d\epsilon\delta(\mathbf{r} - \mathbf{r}' - \epsilon(\mathbf{r}'' - \mathbf{r}'))\sum_{ij}' \delta(\mathbf{r}' - \mathbf{r}_j)\delta(\mathbf{r}'' - \mathbf{r}_i)$$

We now introduce the following pair correlation

$$g^{(2)}(\mathbf{r}', \mathbf{r}'') = \text{Tr}\left[\frac{1}{\Xi}\exp\left\{-\sum_i^N \beta(\mathbf{r}_i, t)\left(m_i\mathbf{u}_i\cdot\boldsymbol{\lambda}(\mathbf{r}_i, t) - m_i\mu(\mathbf{r}_i, t) + \frac{1}{2}\sum_j \phi_{ij}\right)\right\}\sum_{ij}' \delta(\mathbf{r}' - \mathbf{r}_j)\delta(\mathbf{r}'' - \mathbf{r}_i)\right]$$

Note that within the range of the interaction σ, for which $|\mathbf{r}' - \mathbf{r}''| < \sigma$ the conjugate variables $\beta(\mathbf{r}, t), \boldsymbol{\lambda}(\mathbf{r}, t), \mu(\mathbf{r}, t)$ do not change appreciably and we may approximate

$$g^{(2)}(\mathbf{r}', \mathbf{r}''|\beta, \boldsymbol{\lambda}, \mu) = \text{Tr}\left[\frac{1}{\Xi}\exp\left\{-\beta(\mathbf{r}', t)\left(\sum_i^N m_i \mathbf{u}_i \cdot \boldsymbol{\lambda}(\mathbf{r}', t) - mN\mu(\mathbf{r}, t) + \frac{1}{2}\sum_{ij}^N \phi_{ij}\right)\right\}\sum_{ij}' \delta(\mathbf{r}' - \mathbf{r}_j)\delta(\mathbf{r}'' - \mathbf{r}_i)\right]$$

In this way, we may write

$$\text{Tr}[\overline{\rho}_t^{\text{rest}}(z)\hat{\boldsymbol{\Sigma}}_{\mathbf{r}}] = \frac{1}{2}\int d\mathbf{r}' \int d\mathbf{r}'' \mathbf{F}(\mathbf{r}' - \mathbf{r}'')(\mathbf{r}' - \mathbf{r}'')\int_0^1 d\epsilon\,\delta(\mathbf{r} - \mathbf{r}' - \epsilon(\mathbf{r}'' - \mathbf{r}'))g^{(2)}(\mathbf{r}', \mathbf{r}''|\beta, \boldsymbol{\lambda}, \mu)$$

$$= \frac{1}{2}\int_0^1 d\epsilon\,\epsilon^2 \int d\mathbf{r}' \int d\mathbf{r}'' \mathbf{F}(\epsilon(\mathbf{r}' - \mathbf{r}''))\epsilon(\mathbf{r}' - \mathbf{r}'')\delta(\mathbf{r} - \frac{1}{\epsilon}\mathbf{r}' + (\mathbf{r}'' - \mathbf{r}'))g^{(2)}(\mathbf{r}', \mathbf{r}''|\beta, \boldsymbol{\lambda}, \mu)$$

18.15 Isothermal elasticity: $n_{\mathbf{r}}, \mathbf{g}_{\mathbf{r}}, \mathbf{d}_{\mathbf{r}}$

Route for study:

- Understand the derivation of the Goldstone theorem in classical statistical mechanics. This is for justifying that the displacement field is going to be a slow field. This involves, essentially that some correlation is long ranged and, therefore, Mori theory predicts that it will be slow.

- Requardt 1979 introduces the idea that it is the boundary terms that solve the paradox I have found in Das. I need to study the paper by Requardt and Wagner (1986) [?], that correct the problem I have found in the book by Das. **[Print the 1986 paper]**.

- Schofield and Henderson give an argument for computing the free energy of elasticity.

- Tsamados2009 [?] and Walz2010 [?] discuss microscopic definitions for the displacement field.

18.16 Appendix: A theorem

[Define the thermodynamic limit]

To fix ideas, consider a system in which a spherically symmetric hard core potential of radius a is placed at the origin. This potential may mimic the presence of a solid sphere in the system. We may model this potential as

$$V^{\text{ext}}(\mathbf{r}) = V_0\theta(a - r)$$

in the limit $V_0 \to \infty$ (in practice, $V_0 \gg k_B T$) and $\theta(x)$ is the Heaviside step function. The force produced by this potential is given by

$$\mathbf{F}^{\text{ext}}(\mathbf{r}) = \mathbf{n} V_0 \delta(a - r)$$

where $\mathbf{n} = \mathbf{r}/r$ is the unit outward vector.

It is obvious that we have rotational symmetry and, therefore, there may be space variations only in the radial direction. For example, the density field will depend only on the radial coordinate, this is $\rho^{\text{eq}}(\mathbf{r}) = \rho(r)$ and

$$\boldsymbol{\nabla} \rho^{\text{eq}}(\mathbf{r}) = \mathbf{n} \rho'(r)$$

where $\mathbf{n} = \mathbf{r}/r$ is the unit outward vector. Now take a sphere of radius $R' > a$ as the region $\mathscr{R}$, and the note the characteristic function of the interior of the sphere as $\chi_{R'}(\mathbf{r})$. The gradient of the characteristic function is

$$\boldsymbol{\nabla} \chi_{R'}(\mathbf{r}) = -\mathbf{n} \delta(r - R')$$

The theorem (18.1.1) now becomes

$$-\chi_{R'}(\mathbf{r}) \mathbf{n} \rho'_{\text{eq}}(r) = \beta \int_{\mathbb{R}^3} d\mathbf{r}' \mathbf{n}' \delta(R' - r') \langle \delta \hat{\rho}_{\mathbf{r}} \hat{\boldsymbol{\sigma}}_{\mathbf{r}'} \rangle^{\text{eq}} + \beta \left\langle \delta \hat{\rho}_{\mathbf{r}} \hat{\mathbf{F}}^{\text{ext}} \right\rangle^{\text{eq}}$$

Consider the density-density correlation function $\langle \delta \hat{\rho}_{\mathbf{r}} \hat{\rho}_{\mathbf{r}'} \rangle^{\text{eq}}$ that depends, in principle, on the two vectors $\mathbf{r}, \mathbf{r}'$. Because of the rotational symmetry, this correlation can only depend on the three scalars $r, r', \mathbf{r} \cdot \mathbf{r}'$ that can be formed from the two vectors $\mathbf{r}, \mathbf{r}'$.

We may write the above equation in the form

$$-\chi_{\mathscr{R}}(\mathbf{r}) \mathbf{n} \rho'_{\text{eq}}(r) - \beta \left\langle \delta \hat{\rho}_{\mathbf{r}} \hat{\mathbf{F}}^{\text{ext}} \right\rangle^{\text{eq}} = \beta \int_{\mathbb{R}^3} d\mathbf{r}' \mathbf{n}' \delta(R' - r') \langle \delta \hat{\rho}_{\mathbf{r}} \hat{\boldsymbol{\sigma}}_{\mathbf{r}'} \rangle^{\text{eq}}$$

I see no reason, and would find it very suspicious, that the left hand side would vanish exactly. Therefore, this implies that the left hand side is "long ranged".

Consider now the following operator

$$\frac{1}{4\pi R^2} \int_{\mathbb{R}^3} d\mathbf{r} \boldsymbol{\nabla} \chi_R(\mathbf{r}) \cdots = \frac{1}{4\pi R^2} \int_{\mathbb{R}^3} d\mathbf{r} \mathbf{n} \delta(r - R) \cdots$$

This operator is just a sort of averaging vector operator over angles at a constant value R of the radius. For example, if we apply this operator on a vector function of the form $\mathbf{n} f(r)$ we have

$$\frac{1}{4\pi R^2} \int_{\mathbb{R}^3} d\mathbf{r} \boldsymbol{\nabla} \chi_R(\mathbf{r}) \mathbf{n} f(r) = \frac{1}{4\pi R^2} \int_{\mathbb{R}^3} d\mathbf{r} \mathbf{n} \delta(r - R) \mathbf{n} f(r) = f(R)$$

By applying this operator on both sides of (18.16) we obtain

$$\chi_{R'}(R)\rho'(R) = \beta\frac{1}{4\pi R^2}\int_{\mathbb{R}^3} d\mathbf{r}\boldsymbol{\nabla}\chi_R(\mathbf{r})\cdot\int_{\mathbb{R}^3} d\mathbf{r}'\boldsymbol{\nabla}'\chi_{R'}(\mathbf{r}')\cdot\langle\hat{\boldsymbol{\sigma}}_{\mathbf{r}'}\delta\hat{\rho}_{\mathbf{r}}\rangle^{\mathrm{eq}} + \beta\frac{1}{4\pi R^2}\int_{\mathbb{R}^3} d\mathbf{r}\boldsymbol{\nabla}\chi_R(\mathbf{r})\cdot\left\langle\delta\hat{\rho}_{\mathbf{r}}\hat{\mathbf{F}}^{\mathrm{ext}}\right\rangle^{\mathrm{eq}}$$

We introduce now the following two vectors

$$\hat{\mathbf{F}}_{R'} \equiv \frac{1}{4\pi R'^2}\int_{\mathbb{R}^3} d\mathbf{r}'\boldsymbol{\nabla}'\chi_{R'}(\mathbf{r}')\cdot\hat{\boldsymbol{\sigma}}_{\mathbf{r}'} = \int_{\mathbb{R}^3} d\mathbf{r}'\frac{\delta(r'-R')}{4\pi R'^2}\mathbf{n}'\cdot\hat{\boldsymbol{\sigma}}_{\mathbf{r}'}$$

$$\hat{\boldsymbol{\rho}}_R \equiv \int_{\mathbb{R}^3} d\mathbf{r}\frac{\delta(r-R)}{4\pi R^2}\mathbf{n}\delta\hat{\rho}_{\mathbf{r}}$$

The vector $\hat{\boldsymbol{\rho}}_R$ has the physical meaning of giving a direction where there are more particles at the distance R. Note that being the average rotationally invariant we may forget about the δ.

We expect that these vectors do not diverge as $R, R' \to \infty$, in some sense. Therefore, (18.16) becomes

$$\chi_{R'}(R)\rho'(R) = \beta 4\pi R'^2\left\langle\hat{\mathbf{F}}_{R'}\cdot\hat{\boldsymbol{\rho}}_R\right\rangle^{\mathrm{eq}} + \beta\left\langle\hat{\mathbf{F}}^{\mathrm{ext}}\cdot\hat{\boldsymbol{\rho}}_R\right\rangle^{\mathrm{eq}}$$

This is a testable prediction in MD. It is a rigorous expression that makes use of the rotational symmetry of the external force. In principle, in MD one would use periodic boundary conditions. I imagine that in the present case it may be much better to use an spherical confining potential concentrical with the hard core.

By symmetry reasons, the correlation needs to have the following form

$$\left\langle\hat{\mathbf{F}}_{R'}\hat{\rho}_{\mathbf{r}}\right\rangle^{\mathrm{eq}} = \mathbf{n}C(R', r)$$

where

$$C(r, R') = \mathbf{n}\cdot\left\langle\hat{\mathbf{F}}_{R'}\hat{\rho}_{\mathbf{r}}\right\rangle^{\mathrm{eq}}$$

Obviously, if we average over angles on both sides by applying $\int_{\mathbb{R}^3} d\mathbf{r}\frac{\delta(r-R)}{4\pi R^2}\cdots$ we obtain

$$C(R, R') = \left\langle\hat{\mathbf{F}}_{R'}\cdot\hat{\boldsymbol{\rho}}_R\right\rangle^{\mathrm{eq}}$$

Therefore

$$\rho'(R) = \beta 4\pi R'^2 C(R, R')$$

[Consider directly the planar case] Imagine now that the solid sphere is very large ($a \to \infty$), in such a way that we may understand the sphere surface almost planar with normal $\mathbf{n}^z$ in the z direction. As opposed to the finite sphere case, this normal is a constant vector which is independent on the position. In the planar case, we may

substitute the angle averages by the following average

$$\int_{\mathbb{R}^3} d\mathbf{r} \frac{\delta(r-R)}{4\pi R^2} \mathbf{n} \cdots \rightarrow \mathbf{n}^z \int_{\mathbb{R}^3} d\mathbf{r} \frac{\delta(z-R)}{L_x L_y} \chi_{xy}(\mathbf{r}) \cdots$$

where $\chi_{xy}(\mathbf{r})$ is the characteristic function of a rectangular prism of basis $L_x L_y$.

In this manner, we have that the force (18.16) has the expression

$$\hat{\mathbf{F}}_R^\alpha = \hat{\boldsymbol{\sigma}}_\mu^{\alpha z}$$

and we have

$$C(r, R') = \langle \hat{\boldsymbol{\sigma}}_{R'}^{zz} \hat{\rho}_{\mathbf{r}} \rangle^{\text{eq}}$$

Eq. (18.16) leads finally to

$$\langle \hat{\boldsymbol{\sigma}}_{R'}^{zz} \hat{\rho}_{\mathbf{r}} \rangle^{\text{eq}} = \frac{\rho'(R)}{\beta 4\pi R'^2}$$

This shows that the correlation of the zz component of the stress tensor is long ranged in space, as it goes like R'^{-2}.

The case $\hat{\varphi}_{\mathbf{r}}(z) \rightarrow \hat{\boldsymbol{\sigma}}_{\mathbf{r}}(z)$

Consider now that $\hat{\varphi}_{\mathbf{r}}(z) \rightarrow \hat{\boldsymbol{\sigma}}_{\mathbf{r}}(z)$, where the stress tensor is given in (18.1.1) by

$$\hat{\boldsymbol{\sigma}}_{\mathbf{r}}^{\alpha\beta} = \hat{\mathbf{K}}_{\mathbf{r}}^{\alpha\beta} + \hat{\boldsymbol{\Pi}}_{\mathbf{r}}^{\alpha\beta} = \sum_i^N \mathbf{p}_i^\alpha \mathbf{v}_i^\beta \delta(\mathbf{r}-\mathbf{q}_i) + \frac{1}{2} \sum_{ij}^N \mathbf{q}_{ij}^\alpha \hat{\mathbf{F}}_{ij}^\beta \int_0^1 d\epsilon \,\delta(\mathbf{r}-\mathbf{q}_i+\epsilon\mathbf{q}_{ij})$$

$$\frac{\partial \hat{\boldsymbol{\sigma}}_{\mathbf{r}}^{\alpha\beta}}{\partial \mathbf{q}_i^\delta} = \sum_k^N \mathbf{p}_k^\alpha \mathbf{v}_k^\beta \frac{\partial}{\partial \mathbf{q}_i^\delta} \delta(\mathbf{r}-\mathbf{q}_k) + \frac{\partial}{\partial \mathbf{q}_i^\delta} \frac{1}{2} \sum_{jk}^N \mathbf{q}_{jk}^\alpha \hat{\mathbf{F}}_{jk}^\beta \int_0^1 d\epsilon \,\delta(\mathbf{r}-\mathbf{q}_j+\epsilon\mathbf{q}_{jk})$$

$$= -\mathbf{p}_i^\alpha \mathbf{v}_i^\beta \boldsymbol{\nabla}^\delta \delta(\mathbf{r}-\mathbf{q}_i) + \frac{\partial}{\partial \mathbf{q}_i^\delta} \frac{1}{2} \sum_{jk}^N \mathbf{q}_{jk}^\alpha \hat{\mathbf{F}}_{jk}^\beta \int_0^1 d\epsilon \,\delta(\mathbf{r}-\mathbf{q}_j+\epsilon\mathbf{q}_{jk})$$

$$\frac{\partial \hat{\boldsymbol{\sigma}}_{\mathbf{r}}^{\alpha\beta}}{\partial \mathbf{p}_i^\delta} = \sum_k^N \frac{\partial}{\partial \mathbf{p}_i^\delta} \mathbf{p}_k^\alpha \mathbf{v}_k^\beta \delta(\mathbf{r}-\mathbf{q}_k) = \left(\delta^{\alpha\delta} \mathbf{v}_i^\beta + \delta^{\beta\delta} \mathbf{v}_i^\alpha \right) \delta(\mathbf{r}-\mathbf{q}_i)$$

and

$$\frac{\partial \hat{\mathbf{P}}_{\mathscr{R}}^\gamma}{\partial \mathbf{q}_i^\delta} = \frac{\partial}{\partial \mathbf{q}_i^\delta} \sum_j \mathbf{p}_j^\gamma \chi_{\mathscr{R}}(\mathbf{q}_j) = \mathbf{p}_i^\gamma \boldsymbol{\nabla}^\delta \chi_{\mathscr{R}}(\mathbf{q}_i)$$

$$\frac{\partial \hat{\mathbf{P}}_{\mathscr{R}}^\gamma}{\partial \mathbf{p}_i^\delta} = \frac{\partial}{\partial \mathbf{p}_i^\delta} \sum_j \mathbf{p}_j^\gamma \chi_{\mathscr{R}}(\mathbf{q}_j) = \delta^{\gamma\delta} \chi_{\mathscr{R}}(\mathbf{q}_i)$$

Therefore

$$\sum_i^N \frac{\partial \hat{\boldsymbol{\sigma}}_\mathbf{r}^{\alpha\beta}}{\partial \mathbf{q}_i^\delta} \frac{\partial \hat{\mathbf{P}}_\mathscr{R}^\gamma}{\partial \mathbf{p}_i^\delta} = -\sum_i^N \delta^{\gamma\delta} \chi_\mathscr{R}(\mathbf{q}_i) \mathbf{p}_i^\alpha \mathbf{v}_i^\beta \boldsymbol{\nabla}^\delta \delta(\mathbf{r} - \mathbf{q}_i) + \sum_i^N \delta^{\gamma\delta} \chi_\mathscr{R}(\mathbf{q}_i) \frac{\partial}{\partial \mathbf{q}_i^\delta} \frac{1}{2} \sum_{jk}^N \mathbf{q}_{jk}^\alpha \hat{\mathbf{F}}_{jk}^\beta \int_0^1 d\epsilon \delta(\mathbf{r} - \mathbf{q}_j + \epsilon \mathbf{q}_{jk})$$

$$= -\sum_i^N \chi_\mathscr{R}(\mathbf{q}_i) \mathbf{p}_i^\alpha \mathbf{v}_i^\beta \boldsymbol{\nabla}^\gamma \delta(\mathbf{r} - \mathbf{q}_i) + \sum_i^N \chi_\mathscr{R}(\mathbf{q}_i) \frac{\partial}{\partial \mathbf{q}_i^\gamma} \frac{1}{2} \sum_{jk}^N \mathbf{q}_{jk}^\alpha \hat{\mathbf{F}}_{jk}^\beta \int_0^1 d\epsilon \delta(\mathbf{r} - \mathbf{q}_j + \epsilon \mathbf{q}_{jk})$$

$$= -\boldsymbol{\nabla}^\gamma \left(\chi_\mathscr{R}(\mathbf{r}) \hat{\mathbf{K}}_\mathbf{r}^{\alpha\beta}(z) \right) + \sum_i^N \chi_\mathscr{R}(\mathbf{q}_i) \frac{\partial}{\partial \mathbf{q}_i^\gamma} \hat{\boldsymbol{\Pi}}_\mathbf{r}^{\alpha\beta}(z)$$

and

$$\sum_i^N \frac{\partial \hat{\boldsymbol{\sigma}}_\mathbf{r}^{\alpha\beta}}{\partial \mathbf{p}_i^\delta} \frac{\partial \hat{\mathbf{P}}_\mathscr{R}^\gamma}{\partial \mathbf{q}_i^\delta} = \sum_i^N \left(\delta^{\alpha\delta} \mathbf{v}_i^\beta + \delta^{\beta\delta} \mathbf{v}_i^\alpha \right) \delta(\mathbf{r} - \mathbf{q}_i) \mathbf{p}_i^\gamma \boldsymbol{\nabla}^\delta \chi_\mathscr{R}(\mathbf{q}_i)$$

$$= \sum_i^N \left(\mathbf{v}_i^\beta \boldsymbol{\nabla}^\alpha \chi_\mathscr{R}(\mathbf{q}_i) + \mathbf{v}_i^\alpha \boldsymbol{\nabla}^\beta \chi_\mathscr{R}(\mathbf{q}_i) \right) \delta(\mathbf{r} - \mathbf{q}_i) \mathbf{p}_i^\gamma$$

$$= \hat{\mathbf{K}}_\mathbf{r}^{\beta\gamma} \boldsymbol{\nabla}^\alpha \chi_\mathscr{R}(\mathbf{r}) + \hat{\mathbf{K}}_\mathbf{r}^{\alpha\gamma} \boldsymbol{\nabla}^\beta \chi_\mathscr{R}(\mathbf{r})$$

In this case the conjugate field becomes the following third order tensor

$$\hat{\boldsymbol{\psi}}_\mathbf{r}^{\alpha\beta\gamma}(z) = \{\hat{\boldsymbol{\sigma}}_\mathbf{r}^{\alpha\beta}, \hat{\mathbf{P}}_\mathscr{R}^\gamma\} = \sum_i^N \left(\frac{\partial \hat{\boldsymbol{\sigma}}_\mathbf{r}^{\alpha\beta}}{\partial \mathbf{q}_i^\delta} \frac{\partial \hat{\mathbf{P}}_\mathscr{R}^\gamma}{\partial \mathbf{p}_i^\delta} - \frac{\partial \hat{\boldsymbol{\sigma}}_\mathbf{r}^{\alpha\beta}}{\partial \mathbf{p}_i^\delta} \frac{\partial \hat{\mathbf{P}}_\mathscr{R}^\gamma}{\partial \mathbf{q}_i^\delta} \right)$$

$$= -\hat{\mathbf{K}}_\mathbf{r}^{\beta\gamma} \boldsymbol{\nabla}^\alpha \chi_\mathscr{R}(\mathbf{r}) - \hat{\mathbf{K}}_\mathbf{r}^{\alpha\gamma} \boldsymbol{\nabla}^\beta \chi_\mathscr{R}(\mathbf{r}) - \hat{\mathbf{K}}_\mathbf{r}^{\alpha\beta}(z) \boldsymbol{\nabla}^\gamma \chi_\mathscr{R}(\mathbf{r}) - \chi_\mathscr{R}(\mathbf{r}) \boldsymbol{\nabla}^\gamma \hat{\mathbf{K}}_\mathbf{r}^{\alpha\beta}(z) - \sum_i^N \chi_\mathscr{R}(\mathbf{q}_i) \frac{\partial}{\partial \mathbf{q}_i^\gamma} \hat{\boldsymbol{\Pi}}_\mathbf{r}^{\alpha\beta}(z)$$

The theorem (**??**) now becomes, for the points $\mathbf{r}$ inside the region $\mathscr{R}$ for which the terms $\boldsymbol{\nabla}\chi_\mathscr{R}(\mathbf{r}) = 0$ and $\chi_\mathscr{R}(\mathbf{r}) = 1$

$$\left\langle \boldsymbol{\nabla}^\gamma \hat{\mathbf{K}}_\mathbf{r}^{\alpha\beta} \right\rangle^\text{eq} - \left\langle \sum_i^N \chi_\mathscr{R}(\mathbf{q}_i) \frac{\partial}{\partial \mathbf{q}_i^\gamma} \hat{\boldsymbol{\Pi}}_\mathbf{r}^{\alpha\beta} \right\rangle^\text{eq} = \int_{\mathbb{R}^3} d\mathbf{r}' \boldsymbol{\nabla}'^\delta \chi_\mathscr{R}(\mathbf{r}') \left\langle \hat{\boldsymbol{\sigma}}_{\mathbf{r}'}^{\delta\gamma} \hat{\boldsymbol{\sigma}}_\mathbf{r}^{\alpha\beta} \right\rangle^\text{eq}$$

Note that the left hand side does not vanish in general. For example, we have that

$$\left\langle \boldsymbol{\nabla}^\gamma \hat{\mathbf{K}}_\mathbf{r}^{\alpha\beta} \right\rangle^\text{eq} = \delta^{\alpha\beta} k_B T \boldsymbol{\nabla}^\gamma n^\text{eq}(\mathbf{r})$$

This term is different from zero near a solid wall, where there are gradients of the number density. As a consequence, the correlation of stress tensor is necessarily long ranged, at least for some components.

18.16.1   Static structure factor from the continuum

The equilibrium correlation of the fluctuations of the concentration is translationally invariant, which implies

$$\langle \delta c(\mathbf{r}, 0) \delta c(\mathbf{r}', 0) \rangle = S(\mathbf{r} - \mathbf{r}'),$$

for some function $S(\mathbf{r})$. We may obtain the Fourier transform of $S(\mathbf{r})$ as follows. The right hand side of (18.16.1)

$$\frac{1}{\mathcal{V}} \int_{\mathcal{V}} d\mathbf{r} \frac{1}{\mathcal{V}'} \int_{\mathcal{V}'} d\mathbf{r}' \, e^{-i\mathbf{k} \cdot \mathbf{r}} e^{-i\mathbf{k}' \cdot \mathbf{r}'} S(\mathbf{r} - \mathbf{r}')$$

$$= \frac{1}{\mathcal{V}} \int_{\mathcal{V}} d\mathbf{r} \frac{1}{\mathcal{V}'} \int_{\mathcal{V}'} d\mathbf{r}' \, e^{-i\mathbf{k} \cdot (\mathbf{r} - \mathbf{r}')} e^{-i(\mathbf{k}' + \mathbf{k}) \cdot \mathbf{r}'} S(\mathbf{r} - \mathbf{r}')$$

$$= \frac{1}{\mathcal{V}'} \int_{\mathcal{V}'} d\mathbf{r}' \, e^{-i(\mathbf{k}' + \mathbf{k}) \cdot \mathbf{r}'} \frac{1}{\mathcal{V}} \int_{\mathcal{V}} d\mathbf{r}'' \, e^{-i\mathbf{k} \cdot \mathbf{r}''} S(\mathbf{r}'')$$

$$= \delta_{\mathbf{k}, -\mathbf{k}'} S(\mathbf{k}).$$

Respectively, the left hand side of (18.16.1) in Fourier space is

$$\frac{1}{\mathcal{V}} \int_{\mathcal{V}} d\mathbf{r} \frac{1}{\mathcal{V}'} \int_{\mathcal{V}'} d\mathbf{r}' \, e^{-i\mathbf{k} \cdot \mathbf{r}} e^{-i\mathbf{k}' \cdot \mathbf{r}'} \langle \delta c(\mathbf{r}, 0) \delta c(\mathbf{r}', 0) \rangle$$

$$= \sum_{\mathbf{k}''\mathbf{k}'''} \frac{1}{\mathcal{V}} \int_{\mathcal{V}} d\mathbf{r} \frac{1}{\mathcal{V}'} \int_{\mathcal{V}'} d\mathbf{r}' \, e^{-i\mathbf{k} \cdot \mathbf{r}} e^{-i\mathbf{k}' \cdot \mathbf{r}'} e^{i\mathbf{k}'' \cdot \mathbf{r}} e^{i\mathbf{k}''' \cdot \mathbf{r}'} \langle \delta c(\mathbf{k}'', 0) \delta c(\mathbf{k}''', 0) \rangle$$

$$= \sum_{\mathbf{k}''\mathbf{k}'''} \delta_{\mathbf{k}''\mathbf{k}} \delta_{\mathbf{k}'''\mathbf{k}'} \langle \delta c(\mathbf{k}'', 0) \delta c(\mathbf{k}''', 0) \rangle$$

$$= \langle \delta c(\mathbf{k}, 0) \delta c(\mathbf{k}', 0) \rangle.$$

This results give an equivalent relation in the Fourier space from a translational invariant in the real space. The Fourier transform of $S(r)$

$$S(\mathbf{k}) \equiv \int d\mathbf{r} \, S(\mathbf{r}) e^{-i\mathbf{k} \cdot \mathbf{r}}$$

$$= \langle \delta c(\mathbf{k}, 0) \delta c(-\mathbf{k}, 0) \rangle,$$

is known as *structure factor*.

Note that $S(\mathbf{k}) = c_0^2 S_\phi(\mathbf{k})$, with $S_\phi(\mathbf{k}) = \langle \phi(\mathbf{k}, 0) \phi(-\mathbf{k}, 0) \rangle$, and $\phi(\mathbf{r})$ is the relative fluctuations of the concentration field. The static structure factor is the Fourier transform of the second moments of the functional probability $P[c] \sim \exp\{-\frac{1}{k_B T} \mathscr{F}[c]\}$. For a Gaussian probability we may compute the second moments in a straightforward manner. The probability functional with the model $\mathscr{F}^{GA+\sigma}[c]$ given in (??) can be written in operator notation as

$$P^{\mathrm{eq}}[c] \propto \exp\left\{ -\frac{1}{2} \int d\mathbf{r} \int d\mathbf{r}' \, \phi(\mathbf{r}) \mathcal{L}(\mathbf{r}, \mathbf{r}') \phi(\mathbf{r}') \right\},$$

where we have introduced the kernel

$$\mathcal{L}(\mathbf{r}, \mathbf{r}') = r_0 \delta(\mathbf{r} - \mathbf{r}') - K \nabla^2 \delta(\mathbf{r} - \mathbf{r}') \,.$$

The covariance of the Gaussian probability functional is given by

$$\langle \phi(\mathbf{r}) \phi(\mathbf{r}') \rangle = \mathcal{L}^{-1}(\mathbf{r}, \mathbf{r}') \,,$$

where $\mathcal{L}^{-1}(\mathbf{r}, \mathbf{r}')$ is the inverse of the operator $\mathcal{L}(\mathbf{r}, \mathbf{r}')$, satisfying

$$\int d\mathbf{r}' \, \mathcal{L}(\mathbf{r}, \mathbf{r}') \mathcal{L}^{-1}(\mathbf{r}', \mathbf{r}'') = \delta(\mathbf{r} - \mathbf{r}'') \,.$$

By inserting the form of the operator $\mathcal{L}(\mathbf{r}, \mathbf{r}')$ one recognizes that the inverse operator is just the Green's function $\mathcal{L}^{-1}(\mathbf{r}, \mathbf{r}') = S_\phi(\mathbf{r} - \mathbf{r}')$, which satisfies

$$r_0 S_\phi(\mathbf{r} - \mathbf{r}') - K \nabla^2 S_\phi(\mathbf{r} - \mathbf{r}') = \delta(\mathbf{r} - \mathbf{r}') \,.$$

The solution of this equation is obtained by going to Fourier space. We introduce the Fourier transform

$$\hat{S}_\phi(\mathbf{k}) = \int d\mathbf{r} \, e^{-i\mathbf{k} \cdot \mathbf{r}} S_\phi(\mathbf{r}) \,,$$

$$S_\phi(\mathbf{r}) = \int \frac{d\mathbf{k}}{(2\pi)^D} \, e^{i\mathbf{k} \cdot \mathbf{r}} \hat{S}_\phi(\mathbf{k}) \,.$$

In Fourier space, (18.16.1) becomes

$$r_0 \hat{S}_\phi(\mathbf{k}) + K k^2 \hat{S}_\phi(\mathbf{k}) = 1 \,,$$

which gives

$$\hat{S}_\phi(\mathbf{k}) = \frac{1}{r_0} \frac{1}{1 + k^2/k_0^2} \,,$$

where $k_0^2 = r_0/K$. Therefore, the Green function is

$$S_\phi(\mathbf{r}) = \int \frac{d^D \mathbf{k}}{(2\pi)^D} e^{i\mathbf{k} \cdot \mathbf{r}} \frac{1}{r_0} \frac{1}{1 + k^2/k_0^2} \,,$$

and the covariance, or correlation function, is given by

$$\langle \phi(\mathbf{r}) \phi(\mathbf{r}') \rangle = \int \frac{d^D \mathbf{k}}{(2\pi)^D} e^{i\mathbf{k} \cdot (\mathbf{r} - \mathbf{r}')} \frac{1}{r_0} \frac{1}{1 + k^2/k_0^2} \,.$$

For $D = 1$ this correlation takes the form

$$\langle \phi(x) \phi(x') \rangle = \frac{k_0}{2r_0} e^{-k_0 |x - x'|} \,.$$

For $D = 2$ the result is

$$\langle \phi(\mathbf{r})\phi(\mathbf{r}')\rangle = \frac{k_0^2}{4\pi r_0} K_0(k_0|\mathbf{r} - \mathbf{r}'|)\,.$$

where $K_0(x)$ is a Bessel function. Finally, in $3D$ the result is

$$\langle \phi(\mathbf{r})\phi(\mathbf{r}')\rangle = \frac{k_0^2}{4\pi r_0}\frac{e^{-k_0|\mathbf{r} - \mathbf{r}'|}}{|\mathbf{r} - \mathbf{r}'|}\,.$$

Note that the quantity $\langle \phi^2(\mathbf{r})\rangle$ that gives the normalized fluctuations of the concentration field at a given point of space does not diverge in $1D$ but it diverges in $2D$ and $3D$, a phenomenon known as the *ultraviolet catastrophe*. We shall conclude that the point-wise fluctuations are unbounded in dimensions higher than one. *Any particular realization of a Gaussian field in $D > 1$ is extremely rough.*

Nevertheless, physical observables like the number of particles in a finite region are well behaved. From a physical point of view this quantity should be independent of the resolution used to discretize the problem. The number of particles in a region V is given by

$$N_V = \int_V d\mathbf{r}\, c(\mathbf{r})\,,$$

and the relative fluctuations are given by

$$\phi_V \equiv \frac{N_V - Vc_0}{Vc_0} = \frac{1}{V}\int_V d\mathbf{r}\,\phi(\mathbf{r})\,.$$

The variance of this fluctuation is

$$\langle \phi_V^2\rangle = \frac{1}{V^2}\int_V d\mathbf{r}\int_V d\mathbf{r}'\,\langle \phi(\mathbf{r})\phi(\mathbf{r}')\rangle\,.$$

This quantity is finite for any finite volume but as the domain shrinks to a point it diverges in $2D$ logarithmic with the size of the domain, and in $3D$ inversely with the size of the domain, in agreement with (18.16.1).

[Anisotropic: Heat diffusion in anisotropic crystals: $e_\mathbf{r}$]

19

Electromagnetism and Electrokinetic flows

Maxwell stress tensor in the equations, ads a Lorentz force in momentum electrochemical potential, chemical potential that includes the potential

Nerts-Planck theory

Dielectric relaxation

20

Isothermal kinetic theory: $\hat{f}_{\mathbf{rp}}$

We present a generalization of the Density Functional Theory to distributions in *μ-space* rather than in configuration space. This equilibrium theory is the basic ingredient for constructing a dynamic theory with projection operators. The reversible part of the dynamics is computed exactly while the irreversible part is approximated with a fast momentum relaxation assumption. As a result the irreversible operator is given in terms of a viscosity tensor. We show that the kinetic equation has an H-theorem.

20.1   Introduction

Fluids display structure at short length scales and behave hydrodynamically at large scales. An unexpected outcome of early computer simulations was that the scales where hydrodynamics is already valid are in practice rather small [**?**]. In fact, a fluid starts to behave hydrodynamically at a few atomic distances. Given the recent interest in micro and nanofluidic devices, the description of the dynamics of structured fluids flowing in confined geometries deserves some attention, in particular because a simple application of Navier-Stokes equations for structureless fluids is doomed to fail. A powerful approach for the study of structural static equilibrium properties of classical fluids is through Density Functional Theory (DFT) [**?**, **?**]. The use of sophisticated non-local models [**?**, **?**] has allowed to investigate a number of interesting phenomena, ranging from wetting phase transitions, to solid-liquid transitions and highly structured fluids in micropores (see [**?**] for a recent survey). Unfortunately, only equilibrium situations can be investigated with DFT and there is clearly a need to extend the theory to non-equilibrium situations [**?**]. Phenomenological theories of the Ginzburg-Landau or Cahn-Hilliard type have been proposed to study non-equilibrium situations, but these theories are too coarse-grained to capture the ordered structures that occur at nanoscales in fluids. Attempts to generalize DFT to non-equilibrium situations have been taken in Refs. [**?**]-[**?**], and most notoriously in Ref. [**?**] where the theory has been validated through Brownian dynamics simulations [**?**]-[**?**]. However, the theory is valid only if the underlying dynamics is stochastic and the range of application is limited to colloidal and other mesoscopic systems. Of course, one would like to have a similar dynamic equation that would apply to simple fluids and not

only to colloidal systems. For simple fluids one expects to have a richer *hydrodynamic* phenomenology as compared to the purely diffusive dynamics of colloids. Very recently, DFT has been generalized to dynamic situations and hydrodynamics has been described through a Kohn-Sham approximation [**?**]. We propose in this paper an alternative approach. On intuitive grounds, one expects the momentum of the particles to play a role in a dynamic equation, and this suggests that one may focus on the one-particle distribution function in μ-space $f(\mathbf{r}, \mathbf{p})$ rather than on configuration space (i.e. rather than on the density $n(\mathbf{r})$. The classic Boltzmann's equation is just a kinetic equation governing the dynamics of $f(\mathbf{r}, \mathbf{p})$ which, unfortunately, only applies to dilute gases. Extensions to dense situations have been also considered in the Revised Enskog Theory [**?**]. RET is a very powerful theory valid for hard spheres only [**?**]. Yet, one could aim to incorporate the large amount of knowledge on static properties compiled in the DFT literature (and condensed in the form of the density functional) in such a kinetic equation.

In this chapter we formulate a Boltzmann functional theory which has two ingredients. The first one is a functional of $f(\mathbf{r}, \mathbf{p})$, which we call the Boltzmann free energy functional, that is the μ-space analog of the density functional. The second ingredient is a kinetic equation for $f(\mathbf{r}, \mathbf{p})$ that incorporates in a transparent way all the information provided by the equilibrium DFT. This kinetic equation is obtained through the standard time-dependent projection operator technique [**?**]. For this reason, we can show that it has a naturally built in H-theorem, where the H function is just the Boltzmann functional. The issue of a proper definition of the Boltzmann entropy satisfying an appropriate H-theorem is a subject of recent interest [**?**, **?**].

- Obtain the relevant ensemble.

- Obtain the entropy of the level of description.

- Compute the time derivatives of the CG variables.

- Compute the reversible drift. If the level of description is mesocanonical and if the energy is expressible in terms of the CG variables, then is usually helpful to consider the GENERIC structure.

- Compute the irreversible operator.

- Write down the transport equation.

- Approximate things according to your good taste and intuition.

20.2   The system and the CG variables

The system that we consider is a system of particles in the liquid state. They may be a gas, a dense gas, or a liquid. The Hamiltonian of the system is

$$\hat{H}(z) = \sum_{i=1}^{N} \left[\frac{\mathbf{p}_i^2}{2m_i} + V^{\text{ext}}(\mathbf{q}_i) \right] + \hat{U}(z)$$

where the last term is the potential of interaction between the particles, assumed to be of pair-wise form.

The CG variables that we choose are the total energy and the one particle distribution. Their averages computed with the real ensemble $\rho_t(z)$ which is the solution of the Liouville equation are denoted by

$$f(\mathbf{r}, \mathbf{p}, t) = \text{Tr}\left[\rho_t \hat{f}_{\mathbf{rp}}\right]$$

$$E = \text{Tr}\left[\rho_t \hat{H}\right]$$

Obviously the average energy E does not depend on time. These averages, by assumption, are also correctly reproduced with the relevant ensemble $\overline{\rho}_t$ obtained from the maximization of the Gibbs-Jaynes entropy subject to the restriction on the averages, this is

$$f(\mathbf{r}, \mathbf{p}, t) = \text{Tr}\left[\overline{\rho}_t \hat{f}_{\mathbf{rp}}\right]$$

$$E = \text{Tr}\left[\overline{\rho}_t \hat{H}\right]$$

The relevant ensemble in the present level of description has been obtained in (22.6) or (22.6). The relevant ensemble that reproduces the time-dependent averages (20.2) contains time dependent conjugate variables $\lambda_t(\mathbf{r}, \mathbf{p}), \beta_t$ and has the form

$$\overline{\rho}_t(z) = \frac{1}{Z[\lambda_t, \beta_t]} \rho_0^N \exp\left\{ -\beta_t \hat{H}(z) - \sum_i^N \lambda_t(\mathbf{q}_i, \mathbf{p}_i) \right\}$$

Note that there is a one to one correspondence between the averages $f(\mathbf{r}, \mathbf{p}, t), E$ and the conjugate variables $\lambda_t(\mathbf{r}, \mathbf{p}), \beta_t$. In principle, the conjugate variable β_t also depends on time. **[This poses some doubts on calling this level "isothermal".]** By using (22.6), we can express (22.6) in the form

$$\overline{\rho}_t(z) = \frac{1}{Z[\lambda_t, \beta_t]N!} \prod_{i=1}^N f(\mathbf{q}_i, \mathbf{p}_i, t) \exp\left\{ \sum_i^N c^{(1)}(\mathbf{q}_i, t) - \beta_t \hat{U}(z) \right\}$$

The time derivatives of the CG variables are

$$i\mathcal{L}\hat{f}_{\mathbf{rp}} = -\frac{\mathbf{p}}{m}\frac{\partial}{\partial \mathbf{r}}\hat{f}_{\mathbf{rp}} - \mathbf{F}^{\text{ext}}(\mathbf{r})\frac{\partial}{\partial \mathbf{p}}\hat{f}_{\mathbf{rp}} - \frac{\partial}{\partial \mathbf{p}}\int d\mathbf{r}'d\mathbf{p}'\mathbf{F}(\mathbf{r} - \mathbf{r}')\hat{f}_{\mathbf{rp}}\hat{f}_{\mathbf{r'p'}}$$

$$i\mathcal{L}\hat{H}(z) = 0$$

where $\mathbf{F}^{\text{ext}}(\mathbf{r})$ is the force on a particle at $\mathbf{r}$ due to the external potential $V^{\text{ext}}(\mathbf{r})$. We have assumed that the interaction between the particles is pair-wise and $\mathbf{F}(\mathbf{r} - \mathbf{r}')$ is the force that a particle at $\mathbf{r}'$ exerts on a particle at $\mathbf{r}$.

$$\text{Tr}[\overline{\rho}i\mathcal{L}\hat{f}_{\mathbf{rp}}] = -\frac{\mathbf{p}}{m}\cdot\frac{\partial f}{\partial \mathbf{r}} - \mathbf{F}^{\text{ext}}\cdot\frac{\partial f}{\partial \mathbf{p}} - k_B T\frac{\partial}{\partial \mathbf{p}}f\frac{\partial}{\partial \mathbf{r}}c^{(1)}$$

By using as relevant variable the microscopic operator $\hat{f}_{\mathbf{rp}}$, the translation of the general dynamic equation (2.5.17) with the Markovian approximation (3.5.2) of Ref. [**?**] to our particular problem is

$$\partial_t f(\mathbf{r}, \mathbf{p}) = v(\mathbf{r}, \mathbf{p}) - \int d\mathbf{r}' d\mathbf{p}' M(\mathbf{r}, \mathbf{p}, \mathbf{r}', \mathbf{p}') \frac{\delta \overline{\Phi}[f]}{\delta f(\mathbf{r}', \mathbf{p}')}$$

$$v(\mathbf{r}, \mathbf{p}) \equiv \mathrm{Tr}[\overline{\rho}_t i \mathcal{L} \hat{f}_{\mathbf{rp}}]$$

$$M(\mathbf{r}, \mathbf{p}, \mathbf{r}', \mathbf{p}') \equiv \frac{1}{k_B T} \int_0^\infty du \, \mathrm{Tr}\left[\overline{\rho}_t \mathcal{Q}_t i \mathcal{L} \hat{f}_{\mathbf{r}'\mathbf{p}'} \exp\{i\mathcal{L}\mathcal{Q}_t u\} \mathcal{Q}_t i \mathcal{L} \hat{f}_{\mathbf{rp}}\right]$$

$$\frac{\delta \overline{\Phi}[f]}{\delta f(\mathbf{r}', \mathbf{p}')} = k_B T \ln\left(\frac{f(\mathbf{r}', \mathbf{p}')}{f^{\mathrm{eq}}(\mathbf{r}', \mathbf{p}')}\right)$$

where the exact equilibrium distribution is given by

$$f^{\mathrm{eq}}(\mathbf{r}, \mathbf{p}) = \frac{1}{h} \exp\left\{-\beta\left(\frac{p^2}{2m} + V^{\mathrm{ext}} - \mu\right) + c^{(1)}\right\}$$

In Eqs. (20.2), $\mathrm{Tr}[\cdots]$ denotes an integral over phase space, the Liouville operator is $i\mathcal{L}$, and the operator $\mathcal{Q}_t$ is a projection operator satisfying $\mathcal{Q}_t \hat{f}_{\mathbf{rp}} = 0$ whose actual form can be found in Ref. [**?**] and it is not required in the present development.

20.2.1   Form of the projected current

The projected current has the form

$$Q_t i \mathcal{L} \hat{f}_{\mathbf{rp}} = i \mathcal{L} \hat{f}_{\mathbf{rp}} - \mathrm{Tr}[\overline{\rho} i \mathcal{L} \hat{f}_{\mathbf{rp}}] - \int d\mathbf{r}' d\mathbf{p}' \delta \hat{f}_{\mathbf{r}'\mathbf{p}'}(z) \frac{\delta}{\delta f(\mathbf{r}', \mathbf{p}')} \mathrm{Tr}[\overline{\rho} i \mathcal{L} \hat{f}_{\mathbf{rp}}]$$

where $\delta \hat{f}_{\mathbf{r}'\mathbf{p}'}(z) = \hat{f}_{\mathbf{r}'\mathbf{p}'}(z) - f(\mathbf{r}', \mathbf{p}'))$ and

$$i\mathcal{L}\hat{f}_{\mathbf{rp}} = -\frac{\mathbf{p}}{m}\frac{\partial}{\partial \mathbf{r}}\hat{f}_{\mathbf{rp}} - \mathbf{F}^{\mathrm{ext}}(\mathbf{r})\frac{\partial}{\partial \mathbf{p}}\hat{f}_{\mathbf{rp}} - \frac{\partial}{\partial \mathbf{p}}\int d\mathbf{r}' d\mathbf{p}' \mathbf{F}(\mathbf{r} - \mathbf{r}')\hat{f}_{\mathbf{rp}}\hat{f}_{\mathbf{r}'\mathbf{p}'}$$

$$\mathrm{Tr}[\overline{\rho} i \mathcal{L} \hat{f}_{\mathbf{rp}}] = -\frac{\mathbf{p}}{m}\cdot\frac{\partial f}{\partial \mathbf{r}} - \mathbf{F}^{\mathrm{ext}}\cdot\frac{\partial f}{\partial \mathbf{p}} - k_B T \frac{\partial}{\partial \mathbf{p}} f \frac{\partial}{\partial \mathbf{r}} c^{(1)}$$

The reversible drift (20.2.1) has the following derivative

$$\frac{\delta}{\delta f(\mathbf{r}', \mathbf{p}')} \mathrm{Tr}[\overline{\rho} i \mathcal{L} \hat{f}_{\mathbf{rp}}] \approx \frac{\delta}{\delta f(\mathbf{r}', \mathbf{p}')}\left[-\frac{\mathbf{p}}{m}\cdot\frac{\partial f}{\partial \mathbf{r}}(\mathbf{r}, \mathbf{p}) - \mathbf{F}^{\mathrm{ext}}\cdot\frac{\partial f}{\partial \mathbf{p}}(\mathbf{r}, \mathbf{p}) - k_B T \frac{\partial}{\partial \mathbf{p}} f(\mathbf{r}, \mathbf{p})\frac{\partial}{\partial \mathbf{r}} c^{(1)}(\mathbf{r})\right]$$

$$= -\frac{\mathbf{p}}{m}\cdot\frac{\partial}{\partial \mathbf{r}}\delta(\mathbf{r} - \mathbf{r}')\delta(\mathbf{p} - \mathbf{p}') - \mathbf{F}^{\mathrm{ext}}\cdot\frac{\partial}{\partial \mathbf{p}}\delta(\mathbf{r} - \mathbf{r}')\delta(\mathbf{p} - \mathbf{p}')$$

$$- k_B T \frac{\partial}{\partial \mathbf{p}}\delta(\mathbf{r} - \mathbf{r}')\delta(\mathbf{p} - \mathbf{p}')\frac{\partial}{\partial \mathbf{r}}c^{(1)}(\mathbf{r}) - k_B T \frac{\partial}{\partial \mathbf{p}}f(\mathbf{r}, \mathbf{p})\frac{\partial}{\partial \mathbf{r}}c^{(2)}(\mathbf{r}, \mathbf{r}')$$

where we have used that the functional derivative of the direct correlation function $c^{(1)}(\mathbf{r})$ is the direct two-point correlation function $c^{(2)}(\mathbf{r}, \mathbf{r}')$, which is momentum independent.

The last term in the projected current has the form

$$-\int d\mathbf{r}'d\mathbf{p}'\delta\hat{f}_{\mathbf{r}'\mathbf{p}'}(z)\frac{\delta}{\delta f(\mathbf{r}',\mathbf{p}')}\mathrm{Tr}[\overline{\rho}i\mathcal{L}\hat{f}_{\mathbf{r}\mathbf{p}}] = -\int d\mathbf{r}'d\mathbf{p}'\delta\hat{f}_{\mathbf{r}'\mathbf{p}'}(z)\left[\frac{\mathbf{p}}{m}\cdot\frac{\partial}{\partial\mathbf{r}}\delta(\mathbf{r}-\mathbf{r}')\delta(\mathbf{p}-\mathbf{p}') - \mathbf{F}^{\mathrm{ext}}\cdot\frac{\partial}{\partial\mathbf{p}}\delta(\mathbf{r}-\mathbf{r}')\delta(\mathbf{p}-\mathbf{p}')\right]$$

$$= \frac{\mathbf{p}}{m}\cdot\frac{\partial}{\partial\mathbf{r}}\delta\hat{f}_{\mathbf{r}\mathbf{p}}(z) + \mathbf{F}^{\mathrm{ext}}\cdot\frac{\partial}{\partial\mathbf{p}}\delta\hat{f}_{\mathbf{r}\mathbf{p}}(z)$$

$$+ k_B T\frac{\partial}{\partial\mathbf{p}}\delta\hat{f}_{\mathbf{r}\mathbf{p}}\frac{\partial}{\partial\mathbf{r}}c^{(1)}(\mathbf{r}) + k_B T\frac{\partial}{\partial\mathbf{p}}f(\mathbf{r},\mathbf{p})\int d\mathbf{r}'\delta\hat{n}_{\mathbf{r}}\frac{\partial}{\partial\mathbf{r}}c^{(2)}(\mathbf{r},\mathbf{r}')$$

Therefore

$$Q_t i\mathcal{L}\hat{f}_{\mathbf{r}\mathbf{p}} = -\frac{\partial}{\partial\mathbf{p}}\hat{f}_{\mathbf{r}\mathbf{p}}\left[\sum_i \mathbf{F}(\mathbf{r}-\mathbf{q}_i) - k_B T\frac{\partial}{\partial\mathbf{r}}c^{(1)}(\mathbf{r})\right] + k_B T\frac{\partial}{\partial\mathbf{p}}f(\mathbf{r},\mathbf{p})\int d\mathbf{r}'\delta\hat{n}_{\mathbf{r}'}\frac{\partial}{\partial\mathbf{r}}c^{(2)}(\mathbf{r},\mathbf{r}')$$

The first term has zero average with respect to the relevant ensemble, due to (22.6).

$$\beta\int d\mathbf{r}'d\mathbf{p}'\mathbf{F}(\mathbf{r}-\mathbf{r}')\langle\hat{f}_{\mathbf{r}\mathbf{p}}\hat{f}_{\mathbf{r}',\mathbf{p}'}\rangle^\lambda = f(\mathbf{r},\mathbf{p})\frac{\partial\mathscr{C}^{(1)}(\mathbf{r},\mathbf{p})}{\partial\mathbf{r}}$$

The second term involving the fluctuations of the density also has zero average because the density is the integral of $\hat{f}_{\mathbf{r}\mathbf{p}}$ which is relevant.

The term $v(\mathbf{r}, \mathbf{p}, t)$ in the kinetic Eq. (??) describes reversible transport, while the term involving the Green-Kubo operator $M(\mathbf{r}, \mathbf{p}, \mathbf{r}', \mathbf{p}')$ describes irreversible transport. The basic assumption behind Eq. (??) is that there exists a clear separation between the time scale of the evolution of $f(\mathbf{r}, \mathbf{p})$ and the time scale of the decay of the memory function in the Green-Kubo operator. There is no a priori guarantee that this Markovian approximation will hold, but we explore in this Letter the consequences of a Markovian theory. The Green-Kubo operator M is positive definite in the sense that $\int d\mathbf{r}d\mathbf{p}d\mathbf{r}'d\mathbf{p}'A(\mathbf{r},\mathbf{p})M(\mathbf{r},\mathbf{p},\mathbf{r}',\mathbf{p}')A(\mathbf{r}',\mathbf{p}') > 0$ for arbitrary A. This is a consequence of the Wiener-Kinchine theorem that states that the time integral of a stationary auto-correlation function is always positive [?]. Note that within the Markovian framework in which this theory is formulated, the relevant ensemble $\overline{\rho}_t$ hardly changes in the time scale of the decay of the autocorrelation, and the stationarity of the autocorrelation is ensured.

As it usually happens in the projection operator technique, the reversible part can be computed exactly. Consider the effect of the Liouville operator on the relevant variable,

$$i\mathcal{L}\hat{f}_{\mathbf{r}\mathbf{p}} = -\frac{\mathbf{p}}{m}\frac{\partial}{\partial\mathbf{r}}\hat{f}_{\mathbf{r}\mathbf{p}} + \mathbf{F}^{\mathrm{ext}}(\mathbf{r})\frac{\partial}{\partial\mathbf{p}}\hat{f}_{\mathbf{r}\mathbf{p}} + \frac{\partial}{\partial\mathbf{p}}\int d\mathbf{r}'d\mathbf{p}'\mathbf{F}(\mathbf{r}-\mathbf{r}')\hat{f}_{\mathbf{r}\mathbf{p}}\hat{f}_{\mathbf{r}'\mathbf{p}'}$$

where $\mathbf{F}^{\text{ext}}$ is the external force and $\mathbf{F}(\mathbf{r} - \mathbf{r}')$ is the pairwise force between particles. Therefore,

$$v(\mathbf{r}, \mathbf{p}, t) = -\frac{\mathbf{p}}{m} \cdot \frac{\partial f}{\partial \mathbf{r}} - \mathbf{F}^{\text{ext}} \cdot \frac{\partial f}{\partial \mathbf{p}} - k_B T \frac{\partial}{\partial \mathbf{p}} f \frac{\partial}{\partial \mathbf{r}} c^{(1)}$$

where we have used the exact sum rule (22.6). The last term in the reversible transport in Eq. (20.2.1) involving the direct correlation $c^{(1)}(\mathbf{r})$ in Eq. (20.2.1) is absent in the Boltzmann and revised Enskog kinetic theories. Note that $c^{(1)}$ is a functional of f and the reversible term is non-linear in general.

The irreversible transport is not as easy to compute, because it involves an autocorrelation of a function that evolves according to the microscopic (unknown) dynamics of the system. Therefore, we need to approximate the Green-Kubo operator in some way. One possibility is to assume that only two particles are present in the system. In this case, it is possible to compute the autocorrelation function and the result is the famous Boltzmann collision operator [?, ?], which by the very assumption involved is valid for dilute gases only. In this paper we propose a different approach in order to find an approximate expression for the Green-Kubo operator $M(\mathbf{r}, \mathbf{p}, \mathbf{r}', \mathbf{p}')$. First, we apply the projection operator $\mathcal{Q}_t$ on Eq. (20.2.1) and we obtain

$$Q_t i \mathcal{L} \hat{f}_{\mathbf{rp}}(z) = \frac{\partial}{\partial \mathbf{p}} Q_t \hat{f}_{\mathbf{rp}} \sum_i^N \mathbf{F}(\mathbf{r} - \mathbf{q}_i)$$

The approximation that we introduce assumes that the momentum relaxes much faster than the positions of the molecules towards the local equilibrium. If this is the case, we can substitute within (and only within) the kernel memory $\hat{f}_{\mathbf{rp}} \approx \phi(\mathbf{r}, \mathbf{p}) \hat{n}_{\mathbf{r}}$ where the local Maxwellian is

$$\phi(\mathbf{p}, \mathbf{r}) = \frac{1}{(2\pi m k_B T)^{3/2}} \exp\left(-\beta \frac{m}{2} \left(\frac{\mathbf{p}}{m} - \mathbf{v}(\mathbf{r})\right)^2\right)$$

The velocity field is defined as $mn(\mathbf{r})\mathbf{v}(\mathbf{r}) = \int d\mathbf{p} \mathbf{p} f(\mathbf{r}, \mathbf{p})$. With this relaxed momentum approximation we can write the projected current in Eq. (20.2.1) as

$$i\mathcal{L}\hat{f}_{\mathbf{rp}} = -\frac{\mathbf{p}}{m} \frac{\partial}{\partial \mathbf{r}} \hat{f}_{\mathbf{rp}} + \mathbf{F}^{\text{ext}}(\mathbf{r}) \frac{\partial}{\partial \mathbf{p}} \hat{f}_{\mathbf{rp}} + \frac{\partial}{\partial \mathbf{p}} \int d\mathbf{r}' d\mathbf{p}' \mathbf{F}(\mathbf{r} - \mathbf{r}') \hat{f}_{\mathbf{rp}} \hat{f}_{\mathbf{r}'\mathbf{p}'}$$

$$Q_t i \mathcal{L} \hat{f}_{\mathbf{rp}}(z) = \boldsymbol{\phi}(\mathbf{r}, \mathbf{p}) \frac{\partial}{\partial \mathbf{r}} : Q_t \hat{\boldsymbol{\sigma}}_{\mathbf{r}}$$

$$\boldsymbol{\phi}(\mathbf{r}, \mathbf{p}) \equiv \beta \left(\mathbf{v} - \mathbf{v}(\mathbf{r})\right) \phi(\mathbf{r}, \mathbf{p})$$

$$\hat{\boldsymbol{\sigma}}_{\mathbf{r}} \equiv -\frac{1}{2} \sum_{ij} \mathbf{F}_{ij} \mathbf{e}_{ij} \int_0^{r_{ij}} d\epsilon \delta(\mathbf{r} - \mathbf{q}_i + \epsilon \mathbf{e}_{ij})$$

where $\mathbf{q}_{ij} = \mathbf{q}_i - \mathbf{q}_j$, $\mathbf{e}_{ij} = \mathbf{q}_{ij}/r_{ij}$ with $r_{ij} = |\mathbf{r}_{ij}|$. The second order tensor $\hat{\boldsymbol{\sigma}}_{\mathbf{r}}$ is the

interaction part of the microscopic stress tensor [?]. Note that the usual kinetic part of the microscopic stress tensor, which is

$$\sum_i \frac{1}{m} \mathbf{p}_i \mathbf{p}_i \delta(\mathbf{r} - \mathbf{q}_i) = \int d\mathbf{p} \, \mathbf{p} \mathbf{p} \hat{f}_{\mathbf{r}\mathbf{p}}$$

being proportional to $\hat{f}_{\mathbf{r}\mathbf{p}}$, vanishes under the effect of the projection operator $\mathcal{Q}_t$.

After using Eq. (20.2.1) into (20.2) we obtain

$$M(\mathbf{r}, \mathbf{p}, \mathbf{r}', \mathbf{p}') = \phi(\mathbf{r}', \mathbf{p}') \frac{\partial}{\partial \mathbf{r}'} \phi(\mathbf{r}, \mathbf{p}) \frac{\partial}{\partial \mathbf{r}} :: \boldsymbol{Z}(\mathbf{r}, \mathbf{r}')$$

where the four dots :: indicate a contraction with each component of the fourth order tensor

$$\boldsymbol{Z}(\mathbf{r}, \mathbf{r}') = \frac{1}{k_B T} \int_0^\infty du \mathrm{Tr} \left[\overline{\rho}_t (Q_t \boldsymbol{\sigma}_{\mathbf{r}'}) \exp(i\mathcal{L}Q_u u) (Q_t \boldsymbol{\sigma}_{\mathbf{r}}) \right]$$

In principle, this fourth order tensor is a functional of $f(\mathbf{r}, \mathbf{p})$ and it is non-local in space in general. Its structure reminds strongly of the stress correlations involved in the Green-Kubo expressions for the viscosity coefficients in the Navier-Stokes equations [?], although $\boldsymbol{Z}(\mathbf{r}, \mathbf{r}')$ is a functional of $f(\mathbf{r}, \mathbf{p})$ while the corresponding tensor in a hydrodynamic theory depends on the hydrodynamic fields [?]. If non-local effects can be neglected, then $\boldsymbol{Z}(\mathbf{r}, \mathbf{r}') \approx \boldsymbol{\Theta}(\mathbf{r}) \delta(\mathbf{r} - \mathbf{r}')$. The tensor $\boldsymbol{\Theta}(\mathbf{r})$ can be named the viscosity tensor. Under this local assumption we obtain the following kinetic equation

$$\frac{\partial f}{\partial t} = -\frac{\mathbf{p}}{m} \cdot \frac{\partial f}{\partial \mathbf{r}} - \mathbf{F}^{\mathrm{ext}} \cdot \frac{\partial f}{\partial \mathbf{p}} - k_B T \frac{\partial}{\partial \mathbf{p}} f \frac{\partial}{\partial \mathbf{r}} c^{(1)} + k_B T \phi \frac{\partial}{\partial \mathbf{r}} : \boldsymbol{\Theta} : \frac{\partial}{\partial \mathbf{r}} \int d\mathbf{p}' \phi(\mathbf{r}, \mathbf{p}') \ln \left(\frac{f(\mathbf{r}, \mathbf{p}')}{f^{\mathrm{eq}}(\mathbf{r}, \mathbf{p}')} \right)$$

This kinetic equation is the main result of this paper. It is a kinetic equation for the one particle distribution function that has an exact reversible transport and an approximate irreversible transport that describes the relaxation, through viscous processes, towards the exact equilibrium. Actually, it can be easily shown that this kinetic equation satisfies an H-theorem where the H function is given by $\overline{\Phi}[f]$. Indeed, by using Eq. (??) we have

$$\partial_t \overline{\Phi}[f] = \int d\mathbf{r} d\mathbf{p} \frac{\delta \overline{\Phi}[f]}{\delta f(\mathbf{r}, \mathbf{p})} v(\mathbf{r}, \mathbf{p}) - \int d\mathbf{r} d\mathbf{p} d\mathbf{r}' d\mathbf{p}' \frac{\delta \overline{\Phi}[f]}{\delta f(\mathbf{r}, \mathbf{p})} M(\mathbf{r}, \mathbf{p}, \mathbf{r}', \mathbf{p}') \frac{\delta \overline{\Phi}[f]}{\delta f(\mathbf{r}', \mathbf{p}')}$$

By using the definition of $v(\mathbf{r}, \mathbf{p})$ in Eq. (20.2) we observe that the first term in Eq. (20.2.1) vanishes because it is equal to $\mathrm{Tr}[i\mathcal{L}\overline{\rho}_t] = 0$, thus justifying the name reversible for the $v(\mathbf{r}, \mathbf{p})$ transport. The positive definite character of the Green-Kubo kernel ensures then that $\partial_t \overline{\Phi}[f] \leq 0$, with the equality sign occurring at the minimum of the Boltzmann

free energy functional $\overline{\Phi}[f]$. The existence of an H-theorem has been a guiding principle for the rejection of unacceptable kinetic equations (as the Enskog equation) in favor of physically acceptable ones (like the revised Enskog equation) [?, ?]. As opposed to the conventional method of truncation of the BBGKY hierarchy in order to obtain closed kinetic equations, the projection operator method always produces kinetic equations which comply with the Second Law in a natural way, and it also specifies what is the corresponding H function. All the modeling effort in the theory must be directed, then, on finding accurate representations of the Green-Kubo operator.

The approximate irreversible transport that we propose is compatible with the Navier-Stokes equations. Consider the mass density $\rho(\mathbf{r}, t) = m \int d\mathbf{p} f(\mathbf{r}, \mathbf{p})$ and momentum density $\mathbf{g}(\mathbf{r}, t) = \int d\mathbf{p}\, \mathbf{p} f(\mathbf{r}, \mathbf{p})$. The time derivatives of these densities are easily obtained from Eq. (20.2.1). The mass density obeys the usual continuity equation, while the momentum satisfies

$$\frac{\partial}{\partial t}\mathbf{g}(\mathbf{r}) = -\frac{\partial}{\partial \mathbf{r}}\left[\frac{1}{m}\int d\mathbf{p}\, \mathbf{p}\, \mathbf{p} f - k_B T c^{(1)}(\mathbf{r})n(\mathbf{r})\right] - \frac{\partial}{\partial \mathbf{r}}\mathbf{\Theta}k_B T\frac{\partial}{\partial \mathbf{r}}\int d\mathbf{p}'\phi(\mathbf{p}')\ln\left(\frac{f(\mathbf{r},\mathbf{p}')}{f^{\mathrm{eq}}(\mathbf{p}')}\right) + \mathbf{F}^{\mathrm{ext}}n(\mathbf{r})$$

This equation is not closed for the hydrodynamic fields $\rho, \mathbf{g}$. In order to close the equation, we need to express the distribution function $f(\mathbf{r}, \mathbf{p})$ as a functional of the hydrodynamic fields. We expect that the distribution function relaxes in a short time scale towards the local equilibrium distribution $f_0(\mathbf{r}, \mathbf{p}) = n(\mathbf{r}, t)\exp\{-\beta\frac{m}{2}(\mathbf{v} - \mathbf{v}(\mathbf{r}, t)^2\}/(2\pi m k_B T)^{3/2}$ where $\mathbf{v} = \mathbf{p}/m$ is the particle's velocity. We do not have a proof of this conjecture, which is partially proved for the case of the Boltzmann equation and a subject of considerable difficulty [?]. However, if this is the case, we can substitute the local equilibrium distribution into Eq. (20.2.1) and we obtain a closed equation for the momentum density field $\partial_t\mathbf{g} = -\nabla\mathbf{g}\mathbf{v} - \nabla P + \nabla\mathbf{\Theta}\nabla\mathbf{v} + \mathbf{F}^{\mathrm{ex}}n$ where the pressure field is given by $P(\mathbf{r}, t) = k_B T[n(\mathbf{r}, t) - c^1(\mathbf{r}, t)n(\mathbf{r}, t)]$. In principle, the viscosity tensor $\mathbf{\Theta}(\mathbf{r})$ reflects the symmetries of the confining volume. For situations in which isotropy may be assumed, the resulting momentum equation turns out to be equal to the Navier-Stokes equation. In fact, for isotropic situations we have

$$\mathbf{\Theta}^{\mu\nu\mu'\nu'} \approx \left(a\left[\delta^{\mu\mu'}\delta^{\nu\nu'} + \delta^{\mu\nu'}\delta^{\nu\mu'}\right] + b\delta^{\mu\nu}\delta^{\mu'\nu'}\right)$$

which allows, after substitution of this expression into the momentum equation to identify the coefficients a, b introduced in Eq. (20.2.1) in terms of the shear η and bulk ζ viscosities in the form $a = \eta$ and $b = \zeta - 2\eta/3$. Near planar walls, symmetry arguments show that new viscosity coefficients appear that take into account the viscous effects along and perpendicular to the wall. In principle, these viscosity coefficients depend on the distance to the wall.

In summary, we have derived a kinetic equation for $f(\mathbf{r}, \mathbf{p}, t)$ that (i) has an exact reversible dynamics and an approximate irreversible dynamics (ii) has an H-theorem describing relaxation towards global equilibrium, with an H function given by the Boltzmann free energy functional, (iii) the global equilibrium state is the *exact* one and may describe structured fluids, and (iv) the irreversible relaxation towards equilibrium occurs through viscous processes. The kinetic equation relies on three main assumptions:

locality in time (i.e. a Markovian assumption), locality in space, and fast momentum relaxation. The basic ingredient describing the structure of the fluid that appears in the kinetic equation is the direct correlation function $c^{(1)}(\mathbf{r})$, which is evaluated at the time-dependent density field $n(\mathbf{r}, t)$. One can use some of the most popular approximations to model the functional dependence of $c^{(1)}(\mathbf{r})$. Transport is governed by a viscous tensor that may reflect anisotropies due to confining walls. The present kinetic equation describes situations where both, fluid structure and hydrodynamics are important.

20.3   The Boltzmann equation

We compute explicitly the Green-Kubo formula with binary collisions. It must be possible to compute from Green-Kubo the "elementary kinetic theory" calculation of transport coefficients. En este apéndice presentaremos la forma explícita de la matriz M para el caso en que la parte de interacción del funcional de la densidad sea nulo, es decir

$$\overline{\Phi}^{int}[f] = 0$$

y por tanto, las funciones de correlación serán

$$C^{(1)}(\mathbf{r}) = 0$$

$$C^{(2)}(\mathbf{r}, \mathbf{r}') = 0$$

Esto significa que la escala de evolución temporal de $f(\mathbf{r}, \mathbf{p})$ y de la fuerza entre pares $\mathbf{F}(\mathbf{r} - \mathbf{r}')$ está claramente diferenciada, en concreto sabemos que la función de correlación y la fuerza se relacionan a través de

$$\beta \int d\mathbf{r}' d\mathbf{p}' \mathbf{F}(\mathbf{r} - \mathbf{r}') \left\langle \hat{f}_{\mathbf{r}, \mathbf{p}} \hat{f}_{\mathbf{r}', \mathbf{p}'} \right\rangle^{\lambda} = f(\mathbf{r}, \mathbf{p}) \frac{\partial C^{(1)}(\mathbf{r})}{\partial \mathbf{r}}$$

y que por tanto en nuestra aproximación

$$\int d\mathbf{r}' d\mathbf{p}' \mathbf{F}(\mathbf{r} - \mathbf{r}') \left\langle \hat{f}_{\mathbf{r}, \mathbf{p}} \hat{f}_{\mathbf{r}', \mathbf{p}'} \right\rangle^{\lambda} = 0$$

La densidad relevante tiene la forma

$$\overline{\rho}(z) = \frac{1}{N^N} \prod_{j=1}^{N} f(\mathbf{r}_j, \mathbf{p}_j) \exp \left\{ C^{(1)}(\mathbf{r}_j) - \beta V_j \right\}$$

que bajo la aproximación (20.3) queda

$$\overline{\rho}(z) = \frac{1}{N^N} \prod_{j=1}^{N} f(\mathbf{r}_j, \mathbf{p}_j)$$

Podemos calcular los siguientes momentos de manera exacta

$$\left\langle \hat{f}_{\mathbf{r}, \mathbf{p}} \hat{f}_{\mathbf{r}', \mathbf{p}'} \right\rangle^{\lambda} = \delta(\mathbf{r} - \mathbf{r}') \delta(\mathbf{p} - \mathbf{p}') f(\mathbf{r}, \mathbf{p}) + \frac{N(N-1)}{N^2} f(\mathbf{r}, \mathbf{p}) f(\mathbf{r}', \mathbf{p}')$$

Así, la integral (20.3) queda como

$$\int d\mathbf{r}' d\mathbf{p}' \mathbf{F}(\mathbf{r} - \mathbf{r}') \left[\delta(\mathbf{r} - \mathbf{r}') \delta(\mathbf{p} - \mathbf{p}') f(\mathbf{r}, \mathbf{p}) + \frac{N(N-1)}{N^2} f(\mathbf{r}, \mathbf{p}) f(\mathbf{r}', \mathbf{p}') \right] = 0$$

La integral sobre la delta se anula pues $\mathbf{F}(0) = 0$. The second integral gives a result to be used later

$$\int d\mathbf{r}' d\mathbf{p}' \mathbf{F}(\mathbf{r} - \mathbf{r}') f(\mathbf{r}', \mathbf{p}') = 0$$

20.3.1   Binary collisions from a dilute assumption

Utilizaremos la definición de la matriz M

$$M(\mathbf{r}, \mathbf{p}, \mathbf{r}', \mathbf{p}', t) = \frac{1}{k_B} \int_0^\tau du \, Tr \left[\overline{\rho}(t) Q_t i\mathcal{L} \hat{f}_{\mathbf{r}'\mathbf{p}'} \exp(i\mathcal{L}Q_u u) Q_t i\mathcal{L} \hat{f}_{\mathbf{r}\mathbf{p}} \right]$$

Re-do with new projected current Si introducimos el operador de proyección en la matriz M, obtenemos

$$M(\mathbf{r}, \mathbf{p}, \mathbf{r}', \mathbf{p}') = \frac{1}{k_B} \frac{\partial}{\partial \mathbf{p}'} \frac{\partial}{\partial \mathbf{p}} \int_0^\tau du \int \overline{\rho}(z) \sum_i \hat{f}_{\mathbf{r}', \mathbf{p}'}(z) \mathbf{F}(\mathbf{r}' - \mathbf{q}_i) \exp(i\mathcal{L}Q_u u) \sum_j \mathbf{F}(\mathbf{r} - \mathbf{r}_j) \hat{f}_{\mathbf{r}\mathbf{p}} d^{6N}z$$

Por definición de

$$\hat{f}_{\mathbf{r}\mathbf{p}}(z) = \sum_i \delta(\mathbf{r} - \mathbf{r}_i) \delta(\mathbf{p} - \mathbf{p}_i)$$

$$M(\mathbf{r}, \mathbf{p}, \mathbf{r}', \mathbf{p}') = \frac{1}{k_B} \frac{\partial}{\partial \mathbf{p}'} \frac{\partial}{\partial \mathbf{p}} \int_0^\tau du \int \overline{\rho}(z) \sum_{ik} \delta(\mathbf{r}' - \mathbf{r}_k) \delta(\mathbf{p}' - \mathbf{p}_k) \mathbf{F}(\mathbf{r}' - \mathbf{q}_i)$$
$$\times \exp(i\mathcal{L}Q_u u) \sum_{jl} \mathbf{F}(\mathbf{r} - \mathbf{r}_j) \delta(\mathbf{r} - \mathbf{r}_l) \delta(\mathbf{p} - \mathbf{p}_l) d^{6N}z$$

Nos podemos concentrar en el siguiente sumatorio

$$\sum_i \sum_k \sum_j \sum_l \mathbf{F}(\mathbf{r}_k - \mathbf{r}_i) \mathbf{F}(\mathbf{r}_l - \mathbf{r}_j(u)) \dots$$

donde hemos aplicado el operador temporal. La aproximación diluida supone que la contribución de las configuraciones donde se producen multicolisiones es despreciable frente a la que corresponde a las colisiones binarias. Es decir, si k debe ser distinto de i, sólo nos quedan dos alternativas, $k = l$ e $i = j$, o $k = j$ e $i = l$. Esto provoca que sobrevivan solo N^2 parejas y la ecuación (20.3.1) quede como

$$M\left(\mathbf{r},\mathbf{p},\mathbf{r}',\mathbf{p}'\right) =$$

$$+\frac{N^2}{k_B}\frac{\partial}{\partial\mathbf{p}'}\frac{\partial}{\partial\mathbf{p}}\int_0^\tau du\int\overline{\rho}(z)\mathbf{F}\left(\mathbf{r}'-\mathbf{r}_2\right)\delta\left(\mathbf{r}'-\mathbf{r}_1\right)\delta\left(\mathbf{p}'-\mathbf{p}_1\right)\exp\left(i\mathcal{L}Q_u u\right)\mathbf{F}\left(\mathbf{r}-\mathbf{r}_1\right)\delta\left(\mathbf{r}-\mathbf{r}_2\right)\delta\left(\mathbf{p}-\mathbf{p}_2\right)d^{6N}z$$

$$+\frac{N^2}{k_B}\frac{\partial}{\partial\mathbf{p}'}\frac{\partial}{\partial\mathbf{p}}\int_0^\tau du\int\overline{\rho}(z)\mathbf{F}\left(\mathbf{r}'-\mathbf{r}_2\right)\delta\left(\mathbf{r}'-\mathbf{r}_1\right)\delta\left(\mathbf{p}'-\mathbf{p}_1\right)\exp\left(i\mathcal{L}Q_u u\right)\mathbf{F}\left(\mathbf{r}-\mathbf{r}_2\right)\delta\left(\mathbf{r}-\mathbf{r}_1\right)\delta\left(\mathbf{p}-\mathbf{p}_1\right)d^{6N}z$$

$$+\frac{N^2}{k_B}\frac{\partial}{\partial\mathbf{p}'}\frac{\partial}{\partial\mathbf{p}}\int_0^\tau du\int\overline{\rho}(z)\mathbf{F}\left(\mathbf{r}'-\mathbf{r}_1\right)\delta\left(\mathbf{r}'-\mathbf{r}_2\right)\delta\left(\mathbf{p}'-\mathbf{p}_2\right)\exp\left(i\mathcal{L}Q_u u\right)\mathbf{F}\left(\mathbf{r}-\mathbf{r}_1\right)\delta\left(\mathbf{r}-\mathbf{r}_2\right)\delta\left(\mathbf{p}-\mathbf{p}_2\right)d^{6N}z$$

$$+\frac{N^2}{k_B}\frac{\partial}{\partial\mathbf{p}'}\frac{\partial}{\partial\mathbf{p}}\int_0^\tau du\int\overline{\rho}(z)\mathbf{F}\left(\mathbf{r}'-\mathbf{r}_1\right)\delta\left(\mathbf{r}'-\mathbf{r}_2\right)\delta\left(\mathbf{p}'-\mathbf{p}_2\right)\exp\left(i\mathcal{L}Q_u u\right)\mathbf{F}\left(\mathbf{r}-\mathbf{r}_2\right)\delta\left(\mathbf{r}-\mathbf{r}_1\right)\delta\left(\mathbf{p}-\mathbf{p}_1\right)d^{6N}z$$

Introduciendo la expresión (20.3) en M podemos hacer todas las integrales excepto $\mathbf{r}_2$ y $\mathbf{r}_1$, En la aproximación diluida la partícula 1 "ve" la partícula 2 e interacciona colisionando, pero no colisionan con otras partículas. Esto obviamente nos lleva a la conclusión de que la posición de la partícula 1 solo depende de ella misma y de la de su pareja 2, así $\mathbf{r}_1(t) = \mathbf{R}_1\left(\mathbf{r}_1,\mathbf{r}_2,t\right)$ o $\mathbf{r}_2(t) = \mathbf{R}_2\left(\mathbf{r}_1,\mathbf{r}_2,t\right)$

$$M\left(\mathbf{r},\mathbf{p},\mathbf{r}',\mathbf{p}',t\right) = \frac{1}{k_B}\frac{\partial}{\partial\mathbf{p}'}\frac{\partial}{\partial\mathbf{p}}\int_0^\tau du\int\frac{1}{4}f(\mathbf{r}_1,\mathbf{p}_1)f(\mathbf{r}_2,\mathbf{p}_2)\left[\begin{array}{c}\delta\left(\mathbf{r}'-\mathbf{r}_1\right)\delta\left(\mathbf{p}'-\mathbf{p}_1\right)\mathbf{F}\left(\mathbf{r}'-\mathbf{r}_2\right)\\+\delta\left(\mathbf{r}'-\mathbf{r}_2\right)\delta\left(\mathbf{p}'-\mathbf{p}_2\right)\mathbf{F}\left(\mathbf{r}'-\mathbf{r}_1\right)\end{array}\right]$$
$$\times\exp\left(Q_\tau i\mathcal{L}u\right)\left[\begin{array}{c}\delta\left(\mathbf{r}-\mathbf{r}_1\right)\delta\left(\mathbf{p}-\mathbf{p}_1\right)\mathbf{F}\left(\mathbf{r}-\mathbf{r}_2\right)\\+\delta\left(\mathbf{r}-\mathbf{r}_2\right)\delta\left(\mathbf{p}-\mathbf{p}_2\right)\mathbf{F}\left(\mathbf{r}-\mathbf{r}_1\right)\end{array}\right]d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{p}_1 d\mathbf{p}_2$$

La conclusión es que podemos realizar el cálculo de la matriz M de manera explícita para dos partículas, y el resultado obtenido será valido para un sistema de N partículas en la aproximación diluida donde sólo hay colisiones binarias.

Agrupando términos semejantes en (20.3.1) obtenemos

$$M\left(\mathbf{r},\mathbf{p},\mathbf{r}',\mathbf{p}',t\right) = \frac{1}{k_B}\frac{\partial}{\partial\mathbf{p}'}\frac{\partial}{\partial\mathbf{p}}\int_0^\tau du\int\frac{1}{2}f(\mathbf{r}_1,\mathbf{p}_1)f(\mathbf{r}_2,\mathbf{p}_2)\left[\begin{array}{c}\delta\left(\mathbf{r}'-\mathbf{r}_1\right)\delta\left(\mathbf{p}'-\mathbf{p}_1\right)\mathbf{F}\left(\mathbf{r}'-\mathbf{r}_2\right)\\+\delta\left(\mathbf{r}'-\mathbf{r}_2\right)\delta\left(\mathbf{p}'-\mathbf{p}_2\right)\mathbf{F}\left(\mathbf{r}'-\mathbf{r}_1\right)\end{array}\right]$$
$$\times\left[\delta\left(\mathbf{r}-\mathbf{r}_1\right)\delta\left(\mathbf{p}-\mathbf{p}_1(u)\right)\mathbf{F}\left(\mathbf{r}_1(u)-\mathbf{r}_2(u)\right)\right]d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{p}_1 d\mathbf{p}_2$$

Para comenzar el cálculo podemos realizar con facilidad la integral temporal en u usando la regla de la cadena

$$\frac{\partial}{\partial\mathbf{p}}\int_0^\tau du\,\delta\left(\mathbf{p}-\mathbf{p}_1(u)\right)\mathbf{F}\left(\mathbf{r}_1(u)-\mathbf{r}_2(u)\right) = -\int_0^\tau du\frac{d}{du}\delta\left(\mathbf{p}-\mathbf{p}_1(u)\right)$$
$$= -\delta\left(\mathbf{p}-\mathbf{p}_1(\tau)\right) + \delta\left(\mathbf{p}-\mathbf{p}_1\right)$$

$$M\left(\mathbf{r}, \mathbf{p}, \mathbf{r}', \mathbf{p}', t\right) = \frac{1}{k_B} \frac{\partial}{\partial \mathbf{p}'} \int \frac{1}{2} f(\mathbf{r}_1, \mathbf{p}_1) f(\mathbf{r}_2, \mathbf{p}_2) \left[\begin{array}{c} \delta\left(\mathbf{r}' - \mathbf{r}_1\right) \delta\left(\mathbf{p}' - \mathbf{p}_1\right) \mathbf{F}\left(\mathbf{r}' - \mathbf{r}_2\right) \\ +\delta\left(\mathbf{r}' - \mathbf{r}_2\right) \delta\left(\mathbf{p}' - \mathbf{p}_2\right) \mathbf{F}\left(\mathbf{r}' - \mathbf{r}_1\right) \end{array} \right]$$
$$\times \left[-\delta\left(\mathbf{p} - \mathbf{p}_1(\tau)\right) + \delta\left(\mathbf{p} - \mathbf{p}_1\right)\right] \delta\left(\mathbf{r} - \mathbf{r}_1\right) d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{p}_1 d\mathbf{p}_2$$

esta integral se divide en dos partes

$$M_1\left(\mathbf{r}, \mathbf{p}, \mathbf{r}', \mathbf{p}', t\right) = -\frac{1}{k_B} \frac{\partial}{\partial \mathbf{p}'} \int \frac{1}{2} f(\mathbf{r}_1, \mathbf{p}_1) f(\mathbf{r}_2, \mathbf{p}_2) \left[\begin{array}{c} \delta\left(\mathbf{r}' - \mathbf{r}_1\right) \delta\left(\mathbf{p}' - \mathbf{p}_1\right) \mathbf{F}\left(\mathbf{r}' - \mathbf{r}_2\right) \\ +\delta\left(\mathbf{r}' - \mathbf{r}_2\right) \delta\left(\mathbf{p}' - \mathbf{p}_2\right) \mathbf{F}\left(\mathbf{r}' - \mathbf{r}_1\right) \end{array} \right]$$
$$\times \delta\left(\mathbf{p} - \mathbf{p}_1(\tau)\right) \delta\left(\mathbf{r} - \mathbf{r}_1\right) d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{p}_1 d\mathbf{p}_2$$

y

$$M_2\left(\mathbf{r}, \mathbf{p}, \mathbf{r}', \mathbf{p}', t\right) = \frac{1}{k_B} \frac{\partial}{\partial \mathbf{p}'} \int \frac{1}{2} f(\mathbf{r}_1, \mathbf{p}_1) f(\mathbf{r}_2, \mathbf{p}_2) \left[\begin{array}{c} \delta\left(\mathbf{r}' - \mathbf{r}_1\right) \delta\left(\mathbf{p}' - \mathbf{p}_1\right) \mathbf{F}\left(\mathbf{r}' - \mathbf{r}_2\right) \\ +\delta\left(\mathbf{r}' - \mathbf{r}_2\right) \delta\left(\mathbf{p}' - \mathbf{p}_2\right) \mathbf{F}\left(\mathbf{r}' - \mathbf{r}_1\right) \end{array} \right]$$
$$\times \delta\left(\mathbf{p} - \mathbf{p}_1\right) \delta\left(\mathbf{r} - \mathbf{r}_1\right) d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{p}_1 d\mathbf{p}_2$$

Esta última contribución va a ser nula por la ecuación (20.3). Veámoslo,

$$M_2\left(\mathbf{r}, \mathbf{p}, \mathbf{r}', \mathbf{p}', t\right) = \frac{1}{k_B} \frac{\partial}{\partial \mathbf{p}'} \int \frac{1}{2} f(\mathbf{r}, \mathbf{p}) f(\mathbf{r}_2, \mathbf{p}_2) \left[\begin{array}{c} \delta\left(\mathbf{r}' - \mathbf{r}\right) \delta\left(\mathbf{p}' - \mathbf{p}\right) \mathbf{F}\left(\mathbf{r}' - \mathbf{r}_2\right) \\ +\delta\left(\mathbf{r}' - \mathbf{r}_2\right) \delta\left(\mathbf{p}' - \mathbf{p}_2\right) \mathbf{F}\left(\mathbf{r}' - \mathbf{r}\right) \end{array} \right] d\mathbf{r}_2 d\mathbf{p}_2$$
$$= \frac{1}{k_B} \frac{\partial}{\partial \mathbf{p}'} \frac{1}{2} f(\mathbf{r}, \mathbf{p}) \delta\left(\mathbf{r}' - \mathbf{r}\right) \delta\left(\mathbf{p}' - \mathbf{p}\right) \int f(\mathbf{r}_2, \mathbf{p}_2) \mathbf{F}\left(\mathbf{r}' - \mathbf{r}_2\right) d\mathbf{r}_2 d\mathbf{p}_2$$
$$+ \frac{1}{k_B} \frac{\partial}{\partial \mathbf{p}'} \frac{1}{2} f(\mathbf{r}, \mathbf{p}) \int f(\mathbf{r}_2, \mathbf{p}_2) \delta\left(\mathbf{r}' - \mathbf{r}_2\right) \delta\left(\mathbf{p}' - \mathbf{p}_2\right) \mathbf{F}\left(\mathbf{r}' - \mathbf{r}\right) d\mathbf{r}_2 d\mathbf{p}_2$$
$$= +\frac{1}{k_B} \frac{\partial}{\partial \mathbf{p}'} \frac{1}{2} f(\mathbf{r}, \mathbf{p}) f(\mathbf{r}', \mathbf{p}') \mathbf{F}\left(\mathbf{r}' - \mathbf{r}\right)$$

Al considerar el término irreversible que proviene de esta contribución de M, tenemos

$$M \frac{\delta S}{\delta x} = \int d\mathbf{r}' d\mathbf{p}' M(\mathbf{r}, \mathbf{p}, \mathbf{r}', \mathbf{p}') \frac{\delta S[f]}{\delta f\left(\mathbf{r}', \mathbf{p}'\right)}$$

con

$$\frac{\delta S[f]}{\delta f\left(\mathbf{r}', \mathbf{p}'\right)} = -k_B \ln f\left(\mathbf{r}', \mathbf{p}'\right)$$

Sustituyendo (20.3.1) en (20.3.1),

$$M_2 \frac{\delta S}{\delta x} = -\frac{1}{2} f(\mathbf{r}, \mathbf{p}) \int d\mathbf{r}' d\mathbf{p}' \frac{\partial}{\partial \mathbf{p}'} f(\mathbf{r}', \mathbf{p}') \mathbf{F}\left(\mathbf{r}' - \mathbf{r}\right) \ln f\left(\mathbf{r}', \mathbf{p}'\right)$$

Integrando por partes

$$M_2 \frac{\delta S}{\delta x} = \frac{1}{2} f(\mathbf{r}, \mathbf{p}) \int d\mathbf{r}' d\mathbf{p}' \frac{\partial}{\partial \mathbf{p}'} f(\mathbf{r}', \mathbf{p}') \mathbf{F} (\mathbf{r}' - \mathbf{r})$$

supondremos que en la escala del rango de la fuerza la función $\frac{\partial}{\partial \mathbf{p}'} f(\mathbf{r}', \mathbf{p}')$ apenas varia con lo cual podemos aproximar

$$M_2 \frac{\delta S}{\delta x} = \frac{1}{2} f(\mathbf{r}, \mathbf{p}) \frac{\partial}{\partial \mathbf{p}'} f(\mathbf{r}, \mathbf{p}) \int d\mathbf{r}' d\mathbf{p}' \mathbf{F} (\mathbf{r}' - \mathbf{r})$$

que es nula por isotropía de la fuerza.

Así la matriz M queda reducida a calcular

$$M \frac{\delta S}{\delta x} = M_1 \frac{\delta S}{\delta x} = \int d\mathbf{r}' d\mathbf{p}' \frac{\partial}{\partial \mathbf{p}'} \frac{1}{2} f(\mathbf{r}_1, \mathbf{p}_1) f(\mathbf{r}_2, \mathbf{p}_2) \left[\begin{array}{c} \delta \left(\mathbf{r}' - \mathbf{r}_1 \right) \delta \left(\mathbf{p}' - \mathbf{p}_1 \right) \mathbf{F} \left(\mathbf{r}' - \mathbf{r}_2 \right) \\ + \delta \left(\mathbf{r}' - \mathbf{r}_2 \right) \delta \left(\mathbf{p}' - \mathbf{p}_2 \right) \mathbf{F} \left(\mathbf{r}' - \mathbf{r}_1 \right) \end{array} \right]$$
$$\times \delta \left(\mathbf{p} - \mathbf{p}_1(\tau) \right) \delta \left(\mathbf{r} - \mathbf{r}_1 \right) \ln f \left(\mathbf{r}', \mathbf{p}' \right) d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{p}_1 d\mathbf{p}_2$$

Integro pues en $\mathbf{r}_1, \mathbf{p}_1$ en la primera parte y en $\mathbf{r}_2, \mathbf{p}_2$ en la segunda

$$M \frac{\delta S}{\delta x} = \frac{1}{2} \int d\mathbf{r}' d\mathbf{p}' \frac{\partial}{\partial \mathbf{p}'} f \left(\mathbf{r}', \mathbf{p}' \right) f(\mathbf{r}_2, \mathbf{p}_2) \mathbf{F} \left(\mathbf{r}' - \mathbf{r}_2 \right) \delta \left(\mathbf{p} - \mathbf{p}_1(\mathbf{r}', \mathbf{p}', \mathbf{r}_2, \mathbf{p}_2, \tau) \right) \delta \left(\mathbf{r} - \mathbf{r}' \right) \ln f \left(\mathbf{r}', \mathbf{p}' \right) d\mathbf{r}_2 d\mathbf{p}_2$$
$$+ \frac{1}{2} \int d\mathbf{r}' d\mathbf{p}' \frac{\partial}{\partial \mathbf{p}'} f(\mathbf{r}_1, \mathbf{p}_1) f \left(\mathbf{r}', \mathbf{p}' \right) \mathbf{F} \left(\mathbf{r}' - \mathbf{r}_1 \right) \delta \left(\mathbf{p} - \mathbf{p}_1(\mathbf{r}_1, \mathbf{p}_1, \mathbf{r}', \mathbf{p}', \tau) \right) \delta \left(\mathbf{r} - \mathbf{r}_1 \right) \ln f \left(\mathbf{r}', \mathbf{p}' \right) d\mathbf{r}_1 d\mathbf{p}_1$$

Integramos por partes

$$M \frac{\delta S}{\delta x} = \frac{1}{2} \int d\mathbf{r}' d\mathbf{p}' \frac{\partial}{\partial \mathbf{p}'} \left(f \left(\mathbf{r}', \mathbf{p}' \right) \right) f(\mathbf{r}_2, \mathbf{p}_2) \mathbf{F} \left(\mathbf{r}' - \mathbf{r}_2 \right) \delta \left(\mathbf{p} - \mathbf{p}_1(\mathbf{r}', \mathbf{p}', \mathbf{r}_2, \mathbf{p}_2, \tau) \right) \delta \left(\mathbf{r} - \mathbf{r}' \right) d\mathbf{r}_2 d\mathbf{p}_2$$
$$+ \frac{1}{2} \int d\mathbf{r}' d\mathbf{p}' \frac{\partial}{\partial \mathbf{p}'} \left(f \left(\mathbf{r}', \mathbf{p}' \right) \right) f(\mathbf{r}_1, \mathbf{p}_1) \mathbf{F} \left(\mathbf{r}' - \mathbf{r}_1 \right) \delta \left(\mathbf{p} - \mathbf{p}_1(\mathbf{r}_1, \mathbf{p}_1, \mathbf{r}', \mathbf{p}', \tau) \right) \delta \left(\mathbf{r} - \mathbf{r}_1 \right) d\mathbf{r}_1 d\mathbf{p}_1$$

Integramos por partes de nuevo

$$M \frac{\delta S}{\delta x} = \frac{1}{2} \int d\mathbf{r}' d\mathbf{p}' f \left(\mathbf{r}', \mathbf{p}' \right) f(\mathbf{r}_2, \mathbf{p}_2) \mathbf{F} \left(\mathbf{r}' - \mathbf{r}_2 \right) \frac{\partial}{\partial \mathbf{p}'} \delta \left(\mathbf{p} - \mathbf{p}_1(\mathbf{r}', \mathbf{p}', \mathbf{r}_2, \mathbf{p}_2, \tau) \right) \delta \left(\mathbf{r} - \mathbf{r}' \right) d\mathbf{r}_2 d\mathbf{p}_2$$
$$+ \frac{1}{2} \int d\mathbf{r}' d\mathbf{p}' f \left(\mathbf{r}', \mathbf{p}' \right) f(\mathbf{r}_1, \mathbf{p}_1) \mathbf{F} \left(\mathbf{r}' - \mathbf{r}_1 \right) \frac{\partial}{\partial \mathbf{p}'} \delta \left(\mathbf{p} - \mathbf{p}_1(\mathbf{r}_1, \mathbf{p}_1, \mathbf{r}', \mathbf{p}', \tau) \right) \delta \left(\mathbf{r} - \mathbf{r}_1 \right) d\mathbf{r}_1 d\mathbf{p}_1$$

Podemos simplificar la notación si en lugar de primas utilizamos el subíndice correspon-

diente a la colisión, de modo que se obtiene

$$M\frac{\delta S}{\delta x} = \frac{1}{2}\int d\mathbf{r}_1 d\mathbf{p}_1 f(\mathbf{r}_1,\mathbf{p}_1) f(\mathbf{r}_2,\mathbf{p}_2)\mathbf{F}(\mathbf{r}_1-\mathbf{r}_2)\frac{\partial}{\partial\mathbf{p}_1}\delta(\mathbf{p}-\mathbf{p}_1(\mathbf{r}_1,\mathbf{p}_1,\mathbf{r}_2,\mathbf{p}_2,\tau))\,\delta(\mathbf{r}-\mathbf{r}_1)\,d\mathbf{r}_2 d\mathbf{p}_2$$
$$+\frac{1}{2}\int d\mathbf{r}_2 d\mathbf{p}_2 f(\mathbf{r}_2,\mathbf{p}_2) f(\mathbf{r}_1,\mathbf{p}_1)\mathbf{F}(\mathbf{r}_2-\mathbf{r}_1)\frac{\partial}{\partial\mathbf{p}_2}\delta(\mathbf{p}-\mathbf{p}_1(\mathbf{r}_1,\mathbf{p}_1,\mathbf{r}_2,\mathbf{p}_2,\tau))\,\delta(\mathbf{r}-\mathbf{r}_1)\,d\mathbf{r}_1 d\mathbf{p}_1$$

o lo que es igual

$$M\frac{\delta S}{\delta x} = \frac{1}{2}\int d\mathbf{r}_1 d\mathbf{p}_1 d\mathbf{r}_2 d\mathbf{p}_2 f(\mathbf{r}_1,\mathbf{p}_1) f(\mathbf{r}_2,\mathbf{p}_2)\mathbf{F}(\mathbf{r}_1-\mathbf{r}_2)$$
$$\times [\frac{\partial}{\partial\mathbf{p}_1}\delta(\mathbf{p}-\mathbf{p}_1(\mathbf{r}_1,\mathbf{p}_1,\mathbf{r}_2,\mathbf{p}_2,\tau)) - \frac{\partial}{\partial\mathbf{p}_2}\delta(\mathbf{p}-\mathbf{p}_1(\mathbf{r}_1,\mathbf{p}_1,\mathbf{r}_2,\mathbf{p}_2,\tau))]\delta(\mathbf{r}-\mathbf{r}_1)$$

En una colisión binaria de partículas de igual masa, la forma funcional del momento después de la colisión es

$$\mathbf{p}_1(\mathbf{r}_1,\mathbf{p}_1,\mathbf{r}_2,\mathbf{p}_2,\tau) = \mathbf{p}_1 - \epsilon(\epsilon(\mathbf{p}_1-\mathbf{p}_2))$$
$$\mathbf{p}_2(\mathbf{r}_1,\mathbf{p}_1,\mathbf{r}_2,\mathbf{p}_2,\tau) = \mathbf{p}_2 + \epsilon(\epsilon(\mathbf{p}_1-\mathbf{p}_2))$$

donde ϵ es el vector unitario que va de 1 a 2. De la misma manera

$$\mathbf{p}_1(\mathbf{r}_2,\mathbf{p}_2,\mathbf{r}_1,\mathbf{p}_1,\tau) = \mathbf{p}_2 - \epsilon(\epsilon(\mathbf{p}_2-\mathbf{p}_1))$$
$$\mathbf{p}_2(\mathbf{r}_2,\mathbf{p}_2,\mathbf{r}_1,\mathbf{p}_1,\tau) = \mathbf{p}_1 + \epsilon(\epsilon(\mathbf{p}_2-\mathbf{p}_1))$$

En realidad, los momentos cambian en un tiempo de colisión muy corto debido a la fuerza $\mathbf{F}(\mathbf{r}_1-\mathbf{r}_2)$ entre las partículas. Esta fuerza es distinta de cero sólo cuando $\mathbf{r}_1 + a\epsilon = \mathbf{r}_2$ donde a es la distancia entre el centro de ambas partículas. Podemos escribir esta distancia como $a = \epsilon(\mathbf{v}_1-\mathbf{v}_2)t$ donde ϵ es el vector unitario que cumple $\epsilon(\mathbf{v}_1-\mathbf{v}_2) > 0$, es decir, en la dirección del centro de la partícula 1 a la 2. Esto permite realizar un cambio de variable que exprese las integrales en función de ϵ y t.

Por ejemplo, supongamos una función arbitraria $\mathbf{F}(\mathbf{r})$, que queremos integrar a todo el espacio

$$\int d\mathbf{r}\mathbf{F}(\mathbf{r})$$

Si realizamos el cambio de variable de $\mathbf{r} = r\epsilon$ donde ϵ es el correspondiente vector unitario en la dirección de $\mathbf{r}$, la integral de nuestra función arbitraria sobre la superficie de radio ϵ se puede escribir como

$$\int_S d\epsilon\mathbf{F}(r\epsilon) = \int d\mathbf{r}\delta(r-1)\mathbf{F}(\mathbf{r})$$

entonces

$$\int_o^\infty dr \int d\epsilon \mathbf{F}\left(r\epsilon\right) = \int d\mathbf{r} \mathbf{F}\left(\mathbf{r}\right)$$

Vamos a realizar el cambio de variable definido por $\mathbf{r}_1 = \mathbf{r}_2 - a\epsilon = \mathbf{r}_2 - \epsilon\left(\mathbf{v}_1 - \mathbf{v}_2\right)t\epsilon$ en la ecuación (20.3.1).

$$M\frac{\delta S}{\delta x} = -\frac{1}{2}\int d\mathbf{r}_2 d\mathbf{p}_2 d\epsilon dt d\mathbf{p}_1 f\left(\mathbf{r}_2 - a\epsilon, \mathbf{p}_1\right) f(\mathbf{r}_2, \mathbf{p}_2)\mathbf{F}\left(-\epsilon\left(\mathbf{v}_1 - \mathbf{v}_2\right)t\epsilon\right)\epsilon\left(\mathbf{v}_1 - \mathbf{v}_2\right)$$

$$\times \left[\frac{\partial}{\partial \mathbf{p}_1}\delta\left(\mathbf{p} - \mathbf{p}_1(\mathbf{r}_2 - a\epsilon, \mathbf{p}_1, \mathbf{r}_2, \mathbf{p}_2, \tau)\right) - \frac{\partial}{\partial \mathbf{p}_2}\delta\left(\mathbf{p} - \mathbf{p}_1(\mathbf{r}_2 - a\epsilon, \mathbf{p}_1, \mathbf{r}_2, \mathbf{p}_2, \tau)\right)\right]\delta\left(\mathbf{r} - \mathbf{r}_2 + a\epsilon\right)$$

Consideremos la integral temporal siguiente

$$\int dt \mathbf{F}\left(-\epsilon\left(\mathbf{v}_1 - \mathbf{v}_2\right)\epsilon t\right)\left[\frac{\partial}{\partial \mathbf{p}_1}\delta\left(\mathbf{p} - \mathbf{p}_1(\mathbf{r}_2 - a\epsilon, \mathbf{p}_1, \mathbf{r}_2, \mathbf{p}_2, t)\right) - \frac{\partial}{\partial \mathbf{p}_2}\delta\left(\mathbf{p} - \mathbf{p}_1(\mathbf{r}_2 - a\epsilon, \mathbf{p}_1, \mathbf{r}_2, \mathbf{p}_2, t)\right)\right]$$

Como $\mathbf{F}$ representa la fuerza entre pares, podemos concluir que el cambio del momento producido en la colisión es únicamente debido a esta fuerza, es decir

$$\frac{d}{dt}\delta\left(\mathbf{p} - \mathbf{p}_1(\mathbf{r}_2 - a\epsilon, \mathbf{p}_1, \mathbf{r}_2, \mathbf{p}_2, t)\right) = \frac{\partial}{\partial \mathbf{p}_1}\delta\left(\mathbf{p} - \mathbf{p}_1(\mathbf{r}_2 - a\epsilon, \mathbf{p}_1, \mathbf{r}_2, \mathbf{p}_2, t)\right)\frac{d}{dt}\mathbf{p}_1(\mathbf{r}_2 - a\epsilon, \mathbf{p}_1, \mathbf{r}_2, \mathbf{p}_2, t)$$

$$= \frac{\partial}{\partial \mathbf{p}_1}\delta\left(\mathbf{p} - \mathbf{p}_1(\mathbf{r}_2 - a\epsilon, \mathbf{p}_1, \mathbf{r}_2, \mathbf{p}_2, t)\right)\mathbf{F}\left(-\epsilon\left(\mathbf{v}_1 - \mathbf{v}_2\right)\epsilon t\right)$$

de modo que la integral temporal se puede hacer fácilmente como

$$\int dt \mathbf{F}\left(-\epsilon\left(\mathbf{v}_1 - \mathbf{v}_2\right)\epsilon t\right)\frac{\partial}{\partial \mathbf{p}_1}\delta\left(\mathbf{p} - \mathbf{p}_1(\mathbf{r}_2 - a\epsilon, \mathbf{p}_1, \mathbf{r}_2, \mathbf{p}_2, t)\right) = \int dt \frac{d}{dt}\delta\left(\mathbf{p} - \mathbf{p}_1(\mathbf{r}_2 - a\epsilon, \mathbf{p}_1, \mathbf{r}_2, \mathbf{p}_2, t)\right)$$

$$= \delta\left(\mathbf{p} - \mathbf{p}_1(\mathbf{r}_2 - a\epsilon, \mathbf{p}_1, \mathbf{r}_2, \mathbf{p}_2, \tau)\right) - \delta\left(\mathbf{p} - \mathbf{p}_1\right)$$

Utilizando el mismo razonamiento para la otra contribución

$$\int dt \mathbf{F}\left(-\epsilon\left(\mathbf{v}_1 - \mathbf{v}_2\right)\epsilon t\right)\frac{\partial}{\partial \mathbf{p}_2}\delta\left(\mathbf{p} - \mathbf{p}_1(\mathbf{r}_2 - a\epsilon, \mathbf{p}_1, \mathbf{r}_2, \mathbf{p}_2, t)\right) = -\int dt \frac{d}{dt}\delta\left(\mathbf{p} - \mathbf{p}_1(\mathbf{r}_2 - a\epsilon, \mathbf{p}_1, \mathbf{r}_2, \mathbf{p}_2, t)\right)$$

$$= -\delta\left(\mathbf{p} - \mathbf{p}_1(\mathbf{r}_2 - a\epsilon, \mathbf{p}_1, \mathbf{r}_2, \mathbf{p}_2, \tau)\right) + \delta\left(\mathbf{p} - \mathbf{p}_1\right)$$

Introduciendo estos resultados en la ecuación (20.3.1) obtenemos

$$M\frac{\delta S}{\delta x} = -\frac{1}{2}\int d\mathbf{r}_2 d\mathbf{p}_2 d\epsilon d\mathbf{p}_1 f\left(\mathbf{r}_2 - a\epsilon, \mathbf{p}_1\right) f(\mathbf{r}_2, \mathbf{p}_2)$$
$$\times \left[2\delta\left(\mathbf{p} - \mathbf{p}_1(\mathbf{r}_2 - a\epsilon, \mathbf{p}_1, \mathbf{r}_2, \mathbf{p}_2, \tau)\right) - 2\delta\left(\mathbf{p} - \mathbf{p}_1\right)\right]\epsilon\left(\mathbf{v}_1 - \mathbf{v}_2\right)\delta\left(\mathbf{r} - \mathbf{r}_2 + a\epsilon\right)$$

o lo que es igual

$$M\frac{\delta S}{\delta x} = \int d\mathbf{r}_2 d\mathbf{p}_2 d\epsilon d\mathbf{p}_1 f\left(\mathbf{r}_2 - a\epsilon, \mathbf{p}_1\right) f(\mathbf{r}_2, \mathbf{p}_2)$$
$$\times \left[\delta\left(\mathbf{p} - \mathbf{p}_1\right) - \delta\left(\mathbf{p} - \mathbf{p}_1 + \epsilon\left(\epsilon\left(\mathbf{p}_1 - \mathbf{p}_2\right)\right)\right)\right]\epsilon\left(\mathbf{v}_1 - \mathbf{v}_2\right)\delta\left(\mathbf{r} - \mathbf{r}_2 + a\epsilon\right)$$

Nos gustaría poder integrar en $\mathbf{p}_2$ o en $\mathbf{p}_1$, pero es complicado integrar en estas variables la segunda contribución. Definamos entonces

$$\mathbf{p}_a = \mathbf{p}_1 + \mathbf{p}_2$$
$$\mathbf{p}_b = \frac{\mathbf{p}_2 - \mathbf{p}_1}{2}$$

con lo cual

$$\mathbf{p}_1 = \mathbf{p}_b + \frac{\mathbf{p}_a}{2}$$
$$\mathbf{p}_2 = -\mathbf{p}_b + \frac{\mathbf{p}_a}{2}$$

El jacobiano de esta transformación es la unidad. Nos queda

$$M\frac{\delta S}{\delta x} = -\int d\mathbf{r}_2 d\mathbf{p}_a d\epsilon d\mathbf{p}_b f\left(\mathbf{r}_2 - a\epsilon, -\mathbf{p}_b + \frac{\mathbf{p}_a}{2}\right) f(\mathbf{r}_2, \mathbf{p}_b + \frac{\mathbf{p}_a}{2})$$
$$\times \left[\delta\left(\mathbf{p} + \mathbf{p}_b - \frac{\mathbf{p}_a}{2}\right) - \delta\left(\mathbf{p} + \mathbf{p}_b - \frac{\mathbf{p}_a}{2} - 2\epsilon\left(\epsilon\mathbf{p}_b\right)\right)\right]2\epsilon\mathbf{v}_b\delta\left(\mathbf{r} - \mathbf{r}_2 + a\epsilon\right)$$

Ahora podemos integrar sobre $\mathbf{p}_a$

$$M\frac{\delta S}{\delta x} = -\int d\mathbf{r}_2 d\epsilon d\mathbf{p}_b \{f\left(\mathbf{r}_2 - a\epsilon, \mathbf{p}\right) f\left(\mathbf{r}_2, 2\mathbf{p}_b + \mathbf{p}\right) - f\left(\mathbf{r}_2 - a\epsilon, \mathbf{p} - 2\epsilon\left(\epsilon\mathbf{p}_b\right) f\left(\mathbf{r}_2, 2\mathbf{p}_b + \mathbf{p} - 2\epsilon\left(\epsilon\mathbf{p}_b\right)\right)\right\}$$
$$\times 2\epsilon\mathbf{v}_b\delta\left(\mathbf{r} - \mathbf{r}_2 + a\epsilon\right)$$

Podemos deshacer el cambio de variables en la ecuación (20.3.1), es decir

$$\frac{\mathbf{p}_a}{2} = \mathbf{p} + \mathbf{p}_b - 2\epsilon\left(\epsilon\mathbf{p}_b\right)$$

De donde, por definición

$$\mathbf{p} = \mathbf{p}_1\left(\mathbf{r}_1, \mathbf{p}_1, \mathbf{r}_2, \mathbf{p}_2, \tau\right)$$

y por conservación del momento

$$2\mathbf{p}_b + \mathbf{p} = \mathbf{p}_2(\mathbf{r}_1, \mathbf{p}_1, \mathbf{r}_2, \mathbf{p}_2, \tau)$$

con lo cual

$$\mathbf{p} - 2\epsilon\,(\epsilon\mathbf{p}_b) = \mathbf{p}_1$$
$$2\mathbf{p}_b + \mathbf{p} - 2\epsilon\,(\epsilon\mathbf{p}_b) = \mathbf{p}_2$$

El resultado de deshacer el cambio de variable en la ecuación (20.3.1) es

$$M\frac{\delta S}{\delta x} = -\frac{1}{2}\int d\mathbf{r}_2 d\mathbf{p}_1 d\epsilon\, f\left(\mathbf{r}_2 - a\epsilon, \mathbf{p}_1(\mathbf{r}_2 - a\epsilon, \mathbf{p}_1, \mathbf{r}_2, \mathbf{p}_2, \tau)\right) f(\mathbf{r}_2, \mathbf{p}_2(\mathbf{r}_2 - a\epsilon, \mathbf{p}_1, \mathbf{r}_2, \mathbf{p}_2, \tau))\epsilon\left(\mathbf{v}_1 - \mathbf{v}_2\right)\delta\left(\mathbf{r} - \mathbf{r}_2 + a\epsilon\right)$$

$$+ \frac{1}{2}\int d\mathbf{r}_2 d\mathbf{p}_2 d\epsilon\, f\left(\mathbf{r}_2 - a\epsilon, \mathbf{p}_1(\mathbf{r}_2 - a\epsilon, \mathbf{p}_1, \mathbf{r}_2, \mathbf{p}_2, \tau)\right) f(\mathbf{r}_2, \mathbf{p}_2(\mathbf{r}_2 - a\epsilon, \mathbf{p}_1, \mathbf{r}_2, \mathbf{p}_2, \tau))\epsilon\left(\mathbf{v}_1 - \mathbf{v}_2\right)\delta\left(\mathbf{r} - \mathbf{r}_2 + a\epsilon\right)$$

$$+ \frac{1}{2}\int d\mathbf{r}_2 d\mathbf{p}_1 d\epsilon\, f\left(\mathbf{r}_2 - a\epsilon, \mathbf{p}_1\right) f(\mathbf{r}_2, \mathbf{p}_2)\epsilon\left(\mathbf{v}_1 - \mathbf{v}_2\right)\delta\left(\mathbf{r} - \mathbf{r}_2 + a\epsilon\right)$$

$$- \frac{1}{2}\int d\mathbf{r}_2 d\mathbf{p}_2 d\epsilon\, f\left(\mathbf{r}_2 - a\epsilon, \mathbf{p}_1\right) f(\mathbf{r}_2, \mathbf{p}_2)\epsilon\left(\mathbf{v}_1 - \mathbf{v}_2\right)\delta\left(\mathbf{r} - \mathbf{r}_2 + a\epsilon\right)$$

integrando sobre $\mathbf{r}_2$, y nombrando $\mathbf{r} = \mathbf{r}_1$ obtenemos

$$M\frac{\delta S}{\delta x} = -\frac{1}{2}\int d\mathbf{p}_1 d\epsilon\, f\left(\mathbf{r}_1, \mathbf{p}_1(\mathbf{r}_1, \mathbf{p}_1, \mathbf{r}_2, \mathbf{p}_2, \tau)\right) f(\mathbf{r}_2, \mathbf{p}_2(\mathbf{r}_1, \mathbf{p}_1, \mathbf{r}_2, \mathbf{p}_2, \tau))\epsilon\left(\mathbf{v}_1 - \mathbf{v}_2\right)$$

$$+ \frac{1}{2}\int d\mathbf{p}_2 d\epsilon\, f\left(\mathbf{r}_1, \mathbf{p}_1(\mathbf{r}_1, \mathbf{p}_1, \mathbf{r}_2, \mathbf{p}_2, \tau)\right) f(\mathbf{r}_2, \mathbf{p}_2(\mathbf{r}_1, \mathbf{p}_1, \mathbf{r}_2, \mathbf{p}_2, \tau))\epsilon\left(\mathbf{v}_1 - \mathbf{v}_2\right)$$

$$+ \frac{1}{2}\int d\mathbf{p}_1 d\epsilon\, f\left(\mathbf{r}_1, \mathbf{p}_1\right) f(\mathbf{r}_2, \mathbf{p}_2)\epsilon\left(\mathbf{v}_1 - \mathbf{v}_2\right)$$

$$- \frac{1}{2}\int d\mathbf{p}_2 d\epsilon\, f\left(\mathbf{r}_1, \mathbf{p}_1\right) f(\mathbf{r}_2, \mathbf{p}_2)\epsilon\left(\mathbf{v}_1 - \mathbf{v}_2\right)$$

podemos agrupar los términos cambiando los subíndices de la primera y tercera integral
y recordando que por definición

$$\mathbf{p}_1(\mathbf{r}_1, \mathbf{p}_1, \mathbf{r}_2, \mathbf{p}_2, \tau) = \mathbf{p}_2(\mathbf{r}_2, \mathbf{p}_2, \mathbf{r}_1, \mathbf{p}_1, \tau)$$

$$\mathbf{p}_2(\mathbf{r}_1, \mathbf{p}_1, \mathbf{r}_2, \mathbf{p}_2, \tau) = \mathbf{p}_1(\mathbf{r}_2, \mathbf{p}_2, \mathbf{r}_1, \mathbf{p}_1, \tau)$$

obtenemos

$$M\frac{\delta S}{\delta x} = \int d\mathbf{p}_2 d\epsilon [f\left(\mathbf{r}_1, \mathbf{p}_1(\mathbf{r}_1, \mathbf{p}_1, \mathbf{r}_2, \mathbf{p}_2, \tau)\right) f(\mathbf{r}_2, \mathbf{p}_2(\mathbf{r}_1, \mathbf{p}_1, \mathbf{r}_2, \mathbf{p}_2, \tau)) - f\left(\mathbf{r}_1, \mathbf{p}_1\right) f(\mathbf{r}_2, \mathbf{p}_2)]\epsilon\left(\mathbf{v}_1 - \mathbf{v}_2\right)$$

que como resultado es la ecuación de Boltzmann, para un sistema ideal (20.3) y colisiones
binarias, que no es más que el resultado obtenido por Ottinger. Si queremos recuperar

el resultado de Polewczak basta no hacer la integral sobre $\mathbf{r}_2$ en la ecuación (20.3.1)

$$
\begin{aligned}
M\frac{\delta S}{\delta x} = \int d\mathbf{p}_2 d\mathbf{r}_2 d\epsilon \{ & f\left(\mathbf{r}_1, \mathbf{p}_1(\mathbf{r}_1, \mathbf{p}_1, \mathbf{r}_2, \mathbf{p}_2, \tau)\right) f(\mathbf{r}_2, \mathbf{p}_2(\mathbf{r}_1, \mathbf{p}_1, \mathbf{r}_2, \mathbf{p}_2, \tau)) \\
& - f\left(\mathbf{r}_1, \mathbf{p}_1\right) f(\mathbf{r}_2, \mathbf{p}_2) \} \epsilon \left(\mathbf{v}_1 - \mathbf{v}_2\right) \delta \left(\mathbf{r}_1 - \mathbf{r}_2 + a\epsilon\right)
\end{aligned}
$$

que utilizando de nuevo (20.3.1) y (20.3.1) se obtiene

$$
\begin{aligned}
M\frac{\delta S}{\delta x} = \int d\mathbf{p}_2 d\mathbf{r}_2 d\epsilon \{ & f\left(\mathbf{r}_1, \mathbf{p}_1(\mathbf{r}_1, \mathbf{p}_1, \mathbf{r}_2, \mathbf{p}_2, \tau)\right) f(\mathbf{r}_2, \mathbf{p}_2(\mathbf{r}_1, \mathbf{p}_1, \mathbf{r}_2, \mathbf{p}_2, \tau)) \delta \left(\mathbf{r}_1 - \mathbf{r}_2 - a\epsilon\right) \\
& - f\left(\mathbf{r}_1, \mathbf{p}_1\right) f(\mathbf{r}_2, \mathbf{p}_2) \delta \left(\mathbf{r}_1 - \mathbf{r}_2 + a\epsilon\right) \} \epsilon \left(\mathbf{v}_1 - \mathbf{v}_2\right)
\end{aligned}
$$

que es el resultado de Polewczak

21

Non-Isothermal kinetic theory: $f_{\mathbf{rp},\,e_{\mathbf{r}}}$ vs. $f_{\mathbf{r},\mathbf{p},e}$

Part I

Appendices

22

Field theories and the entropy

22.1 Introduction

When an atomic liquid is near a solid wall, the atoms organize themselves into layers near the wall. Typically, the width of the layer is of the order of the atomic radius. This layering can be described with the one-particle probability that gives the probability of finding an atom near a particular position of space. Far from the wall, this probability becomes constant, because an atom of a liquid in the bulk can be equally well in any point of space.

The Hamiltonian

The microscopic Hamiltonian of an atomic liquid is given by

$$\hat{H}(z) = \sum_i^N \frac{\mathbf{p}_i^2}{2m_i} + U_N(q)$$

where the potential energy of interaction U_N between the particles *includes any external field* $V^{\text{ext}}(\mathbf{r})$. Usually, we will assume that the interatomic potential is of the pair-wise form, although this is not essential in the following development. Therefore, the potential energy of interaction is given by

$$U_N(q) = \frac{1}{2} \sum_{ij}^N \phi(r_{ij}) + \sum_i^N V^{\text{ext}}(\mathbf{q}_i)$$

Note that our isolated system is made of only the atoms of the liquid. Therefore, we should confine this liquid with some confining potential. The potential describes in an idealized way the interaction with a solid wall. We will discuss in **??** how to deal with walls made of actual atoms in a solid state.

22.2   Levels of description

We talk about fields because the CG variables are of the form of a sum of Dirac delta functions. The prototypical field is the number density, which is defined as

$$\hat{n}_{\mathbf{r}}(z) = \sum_{i}^{N} \delta(\mathbf{r} - \mathbf{q}_i)$$

For this type of variables, only evolution equations for the *averages* make sense. As it has been explained in Sec. **??**, it makes no sense to give "the probability that the phase function $\hat{n}_{\mathbf{r}}(z)$ take a value $n(\mathbf{r})$" because this probability would be zero except for fields $n(\mathbf{r})$ that are as spiky as (22.2).

As we have already discussed when introducing the mesocanonical flavor, it makes no sense to ask about the probability that the phase function (22.3) takes particular values. Therefore, the macroscopic information that will be retained in this level of description will be the average of the total energy and the density field. We will, therefore, consider the averages flavor for this level of description and refer the reader to the summary in Sec. 1.11.

There are several different levels of description that may be employed. The ones that we consider are the following

- MTS: Macroscopic ThermoStatics $\overline{N}, \overline{E}$.

- DFT: Density Functional Theory $n(\mathbf{r}), \overline{E}$.

- HCT: Heat Conduction Theory $\overline{N}, e(\mathbf{r})$.

- FTD: Functional Thermodynamics $n(\mathbf{r}), e(\mathbf{r})$.

- FHD: Functional Hydrodynamics $n(\mathbf{r}), \mathbf{g}(\mathbf{r}), e(\mathbf{r})$.

- IKT: Isothermal Kinetic Theory $f(\mathbf{r}, \mathbf{p}), \overline{E}$.

- TKT: Thermal Kinetic Theory $f(\mathbf{r}, \mathbf{p}), e(\mathbf{r})$.

- TKT: Thermal Kinetic Theory $f(\mathbf{r}, \mathbf{p}, e)$.

The density variable is is particularly useful when we are interested in how the particles of the liquid distribute themselves in space. I believe that the only levels that make sense physically are Thermostatics, Heat Conduction, Functional Hydrodynamics, Isothermal Kinetic Theory, and Non-isothermal Kinetic Theory. Density Functional theory and Functional Thermodynamics do not really make sense because if density changes in time is because the atoms themselves move, implying that the momentum density should be included in the description. However, both levels of description are useful because they allow to discuss the construction of the entropy functional of the Functional Hydrodynamic theory itself.

Up to now, the only approximation that we have taken is the Markovian approximation implicit in the use of the transport equation (1.11.1). This assumption relies on the possibility that the density field evolves in a time scale much larger than the current

correlation function. This is, indeed a very strong assumption that only in very particular circumstances is expected to be satisfied by an atomic fluid. Situations in which the density evolves slowly as compared with the current may arise near liquid-solid phase transitions. In liquid phase states, we expect that the fluid moves and that changes in the density are always accompanied by currents that evolve in the same time scales. We will discuss in Chapter **??** a level of description in which, in addition to the density field, we also include the momentum field (closely related to the current of particles).

22.3   Density Functional Theory: $\hat{n}_{\mathbf{r}}, \hat{H}$

The level of description that we consider in this section is known as Density Functional Theory (DFT). This name should be further qualified as *classical* and *equilibrium* in order to distinguish this theory from the electronic structure calculation that uses quantum mechanics, and to emphasize that the results of DFT apply only at equilibrium. In this level of description, the CG variables are the **number density field** also known as the one particle distribution function $\hat{n}_{\mathbf{r}}(z)$ and the dynamic invariants of the system. The number density field is defined microscopically as the following phase function

$$\hat{n}_{\mathbf{r}}(z) \equiv \sum_{i=1}^{N} \delta(\mathbf{r} - \mathbf{q}_i) \tag{22.3.0}$$

The ensemble average of this function is denoted as

$$n(\mathbf{r}) = \mathrm{Tr}[\overline{\rho}\hat{n}_{\mathbf{r}}]$$

The field $n(\mathbf{r})$ gives the probability of finding any one atom in the vicinity of $\mathbf{r}$, given the microscopic probability $\rho(z)$. Note that we have the obvious identity

$$\int d\mathbf{r}\,\hat{n}_{\mathbf{r}}(z) = \mathscr{N}(z)$$

Therefore, the information about the average $n(\mathbf{r})$ already informs us about the value of the average of the number of particles $\overline{N}$. We have a case of redundant information as discussed in Sec. **??**. For this reason, we will exclude $\hat{N}(z)$ from the list of CG variables. As we will have external fields that usually break the translational and rotational invariance of the Hamiltonian, we will assume that the only dynamical invariant is given by the Hamiltonian $\hat{H}(z)$ whose ensemble average will be denoted by

$$\overline{E} = \mathrm{Tr}[\rho\hat{H}]$$

We do not include any relevant variable to describe the state of the container of the fluid. This container will be assumed to be well-described by the external potential $V^{\mathrm{ext}}(\mathbf{r})$. We will discuss in Chapter 21 more realistic situations in which the solid walls of the container are described in a coarse-grained way.

The relevant ensemble in the canonical flavor is given by (1.11.3). The relevant variable (22.3) is, in fact, a collection of phase functions that are indexed with the continuum subindex $\mathbf{r}$. For the selected CG variables (22.3), we will have a conjugate

variable $\alpha(\mathbf{r})$, i.e. a value of α for each value of $\mathbf{r}$. The relevant ensemble (1.11.3) becomes

$$\bar{\rho}(z_N) = \frac{\rho_N^0}{Z[\alpha, \beta]} \exp\left\{ -\int d\mathbf{r}\alpha(\mathbf{r})\hat{n}_{\mathbf{r}}(z_N) - \beta\hat{H}(z_N) \right\}$$

$$Z[\alpha, \beta] = \sum_{N=0}^{\infty} \frac{1}{N!} \int \frac{dz_N}{h^{3N}} \exp\left\{ -\sum_{i=1}^{N} \alpha(\mathbf{q}_i) - \beta\hat{H}(z_N) \right\}$$

The grand potential of this level of description is

$$\Phi[\alpha, \beta] = -\ln Z[\alpha, \beta]$$

The conjugate variables and the average of the CG variables are related by (1.11.7) that in the present case becomes

$$\frac{\delta\Phi}{\delta\alpha(\mathbf{r})}[\alpha, \beta] = n(\mathbf{r})$$
$$\frac{\partial\Phi}{\partial\beta}[\alpha, \beta] = \overline{E}$$

The first equation in Eqs. (22.3) involves a functional derivative with respect to the field $\alpha(\mathbf{r})$ whereas the last equation involves a partial derivative with respect to β. One way to solve these equations is by assuming in the first equation that β is a fixed parameter, allowing to solve $\alpha(\mathbf{r})$ as a functional of $n(\mathbf{r})$ that depends parametrically on β. By substituting this functional into the second equation, we obtain an implicit equation between β and $\overline{E}$. Because we do not have redundant information (see Sec. **??**) the connection between the variables $n(\mathbf{r}), \overline{E}$ and $\alpha(\mathbf{r}), \beta$ is one to one. This means that for a given equilibrium state determined by $\overline{E}$ and for a given density field there exists a unique value of the conjugate variable $\alpha(\mathbf{r})$. This is one of the statements of an important theorem due to Mermin [**?**], which is at the foundation of classic Density Functional Theory.

The next step is to obtain the entropy for this level of description. The entropy of this level of description is obtained by substituting the relevant ensemble (22.3) into the Gibbs-Jaynes functional (**??**), with the result

$$S[n, \overline{E}] = -\Phi[\alpha, \beta] + \int d\mathbf{r}\alpha(\mathbf{r})n(\mathbf{r}) + \beta\overline{E}$$

In this expression, $\alpha(\mathbf{r}), \beta$ are understood as functions of the averages $n, \overline{E}$. We may write the entropy in the following form

$$S[n, \overline{E}] = -F[n, \beta] + \beta\overline{E}$$

where

$$F[n, \beta] = \Phi[\alpha, \beta] - \int d\mathbf{r}\alpha(\mathbf{r})n(\mathbf{r}),$$

is a function of the number density $n(\mathbf{r})$ and the conjugate variable β. We name this functional as the **dimensionless free energy functional** or simply **the density functional** and plays a fundamental role in modelling the entropy functional. We do not include a usual factor of $k_B T$ in front of the free energy as we are dealing with dimensionless quantities. The free energy functional $F[n, \beta]$ is the partial Legendre transform of the grand potential with respect to the density field. The functional derivative of the free energy functional is

$$\frac{\delta F}{\delta n(\mathbf{r})}[n, \beta] = -\alpha(\mathbf{r})$$

where, here, $\alpha(\mathbf{r})$ is a functional of $n(\mathbf{r}), \beta$ (not of $n(\mathbf{r}), \overline{E}$). In this way, the derivative of the free energy with respect to β gives, by use of the chain rule,

$$\frac{\partial F}{\partial \beta}[n, \beta] = \frac{\partial}{\partial \beta} \Phi[\alpha(n, \beta), \beta] - \frac{\partial}{\partial \beta} \int d\mathbf{r} \alpha(\mathbf{r}) n(\mathbf{r})$$

$$= \int d\mathbf{r} \frac{\delta \Phi}{\delta \alpha(\mathbf{r})}[\alpha(n, \beta), \beta] \frac{\partial \alpha(\mathbf{r})}{\partial \beta} + \frac{\partial \Phi}{\partial \beta}[\alpha(n, \beta), \beta] - \int d\mathbf{r} \frac{\partial \alpha(\mathbf{r})}{\partial \beta} n(\mathbf{r})$$

By using (22.3) we have the simple expression

$$\frac{\partial F}{\partial \beta}[n, \beta] = \overline{E}$$

Given a model for the free energy $F[n, \beta]$, the Eq. (22.6) allows to obtain the functional $\overline{E}[n, \beta]$ that can be, at least in principle, inverted to give $\beta[n, \overline{E}]$. With this functional $\beta[n, \overline{E}]$ in the expression (22.3) we may recover the entropy functional of the DFT level of description.

In principle, $S[n, \overline{E}]$, $F[n, \beta]$ and $\Phi[\alpha, \beta]$ contain exactly the same information, as they are (partial) Legendre transforms of each other. However, it appears much easier to find approximations for the free energy functional $F[n, \beta]$ than for the grand potential $\Phi[\alpha, \beta]$, or the entropy function $S[n, \overline{E}]$.

22.3.1 Models for the DFT level of description

For the sake of completeness, we review some standard result of Classical Equilibrium Density Functional Theory [?]. The entropy functional or, equivalently, its Legendre transform, the grand potential are not easy to compute explicitly. The grand potential involves computing the partition function (22.3) that contains highly multidimensional integrals over phase space with complicated potential energy functions. However, for the case of non-interacting particles, the solution is straightforward. This is the ideal gas model for which the Hamiltonian reduces to the kinetic energy term and external potential terms. As we will see, the ideal gas model is the basis for developing models for interacting systems.

Ideal gas model

In this case, the thermodynamic potential can be explicitly computed with the result

$$\Phi^{\text{id}}[\alpha, \beta] = -\int \frac{d\mathbf{r}}{\Lambda^3(\beta)} \exp\{-\alpha(\mathbf{r}) - \beta V^{\text{ext}}(\mathbf{r})\} \tag{22.3.-4}$$

where $\Lambda(\beta)$ is the thermal wavelength introduced in (**??**) and $V^{\text{ext}}(\mathbf{r})$ is the external potential. Eq. (22.3) becomes now

$$n(\mathbf{r}) = \frac{\delta \Phi^{\text{id}}[\phi]}{\delta \alpha(\mathbf{r})} = \frac{1}{\Lambda^3} \exp\{-\alpha(\mathbf{r}) - \beta V^{\text{ext}}(\mathbf{r})\}$$

$$\overline{E} = \frac{\partial \Phi^{\text{id}}}{\partial \beta} = \frac{3\overline{N}}{2\beta} + \int d\mathbf{r} n(\mathbf{r}) V^{\text{ext}}(\mathbf{r})$$

The conjugate variables may be easily obtained from this equations

$$\alpha(\mathbf{r}) = -\ln \Lambda^3(\beta) n(\mathbf{r}) - \beta V^{\text{ext}}(\mathbf{r})$$

$$\beta = \frac{3\overline{N}}{2\overline{K}}$$

where we have introduced the kinetic energy

$$\overline{K} = \overline{E} - \int d\mathbf{r} n(\mathbf{r}) V^{\text{ext}}(\mathbf{r})$$

The parameter β is, therefore, proportional to the inverse kinetic energy per particle. According to the **equipartition theorem** the average kinetic energy is related to the temperature according to

$$\overline{K} = \frac{3}{2}\overline{N} k_B T$$

this is, for each degree of freedom we have a contribution of $k_B T/2$ to the kinetic energy. Therefore, the interpretation of the parameter β is that of the inverse temperature. Note that this parameter β depends, in general, not only on the average total energy $\overline{E}$ but also on the actual value of the average of the density field $n(\mathbf{r})$.

The ideal gas entropy functional is given by

$$S^{\text{id}}_{\text{DFT}}[n, E] = -\int d\mathbf{r} n(\mathbf{r}) \left[\ln\{\Lambda^3(\beta[E, n]) n(\mathbf{r})\} - 1\right] + \beta E$$

where β is the function of $n, \overline{E}$ given in (22.3.1). The density functional (22.3) for the ideal gas is given by

$$F^{\text{id}}[n, \beta] = \int d\mathbf{r} n(\mathbf{r})[\ln(\Lambda^3(\beta) n(\mathbf{r})) - 1] \tag{22.3.-6}$$

Non-ideal gas models

When the particles in the fluid interact with each other, we can no longer neglect the interaction potential energy $\hat{U} \neq 0$. The partition function now does not decouple in a product of one particle integrals. Instead of modelling the grand potential or the entropy functional, it turns out to be more easy to model the free energy density $F[n, \beta]$. The idea is to write down the free energy functional as the sum of an ideal part $F^{\mathrm{id}}[n, \beta]$ and an interaction or excess over ideal part $F^{\mathrm{int}}[n, \beta]$

$$F[n, \beta] = F^{\mathrm{id}}[n, \beta] + F^{\mathrm{int}}[n, \beta]$$

The functional derivative with respect to the number density is

$$\frac{\delta F}{\delta n(\mathbf{r})}[n, \beta] = \ln \Lambda^3(\beta) n(\mathbf{r}) - c^{(1)}(\mathbf{r})$$

where we have introduced the first member of the set of **direct correlation functions** defined as

$$c^{(n)}(\mathbf{r}_1, \cdots, \mathbf{r}_n) \equiv -\frac{\delta F^{\mathrm{int}}}{\delta n(\mathbf{r}_1) \cdots \delta n(\mathbf{r}_n)}[n, \beta]$$

Usually a factor β is introduced in the definition of the direct correlations but, consistently with the definition of the free energy in (22.3) in a dimensionless fashion (without factor of $k_B T$), we do not include such a factor β.

Equations (22.3.1) and (22.3) give the following result for the number density

$$n(\mathbf{r}) = \frac{1}{\Lambda^3(\beta)} \exp\left\{-\alpha(\mathbf{r}) + c^{(1)}(\mathbf{r})\right\}$$

one introduces an interacting part $S^{\mathrm{int}}[n, \overline{E}]$ to the entropy functional,

$$\begin{aligned} S_{\mathrm{DFT}}[n, \overline{E}] &= S^{id}[n, \overline{E}] + S^{\mathrm{int}}[n, \overline{E}] \\ &= -\int d\mathbf{r} n(\mathbf{r}) \left[\ln\{\Lambda^3 n(\mathbf{r})\} - 1\right] + S^{\mathrm{int}}[n, \overline{E}] + \beta E \end{aligned}$$

The interaction part is sometimes referred to the *excess* (over ideal) part. The functional derivative is

$$\frac{\delta S_{\mathrm{DFT}}[n, \overline{E}]}{\delta n(\mathbf{r})} = -\ln\{\Lambda^3 n(\mathbf{r})\} + c^{(1)}(\mathbf{r})$$

where the **direct correlations** are defined as functional derivatives of the interaction part

$$c^{(n)}(\mathbf{r}_1, \cdots, \mathbf{r}_n) \equiv \frac{\delta^n S^{\mathrm{int}}[n, \overline{E}]}{\delta n(\mathbf{r}_1) \cdots \delta n(\mathbf{r}_n)}$$

From Eqs. (22.3.1), (22.3.1), (22.3.1) one easily obtains the following identities

$$n(\mathbf{r}) = \frac{1}{\Lambda^3} \exp\{-\alpha(\mathbf{r}) + c^{(1)}(\mathbf{r})\}$$

$$n(\mathbf{r})\nabla \frac{\delta S_{\mathrm{DFT}}[n, \overline{E}]}{\delta n(\mathbf{r})} = -\nabla n(\mathbf{r}) + n(\mathbf{r})\nabla c(\mathbf{r})$$

On the other hand, if we take the second derivatives of $S_{\mathrm{DFT}}[n, \overline{E}]$

$$\frac{\delta^2 S_{\mathrm{DFT}}[n, \overline{E}]}{\delta n(\mathbf{r}')\delta n(\mathbf{r})} = \frac{\delta\alpha(\mathbf{r})}{\delta n(\mathbf{r}')} = -\frac{\delta(\mathbf{r} - \mathbf{r}')}{n(\mathbf{r})} + c^{(2)}(\mathbf{r}, \mathbf{r}')$$

Now we use (12.2) because

$$\frac{\partial^2 \Phi_{\mathrm{DFT}}[\alpha, (\beta)]}{\partial\alpha(\mathbf{r})\partial\alpha(\mathbf{r}')} = \frac{\delta n(\mathbf{r})}{\delta\alpha(\mathbf{r}')} = -\langle\delta\hat{n}_\mathbf{r}\delta\hat{n}_{\mathbf{r}'}\rangle^{\mu,\beta}$$

$$= -\langle\hat{n}_\mathbf{r}\hat{n}_{\mathbf{r}'}\rangle^{\mu,\beta} + n(\mathbf{r})n(\mathbf{r}')$$

$$= -n^{(2)}(\mathbf{r}, \mathbf{r}') - n(\mathbf{r})\delta(\mathbf{r} - \mathbf{r}') + n(\mathbf{r})n(\mathbf{r}')$$

but $S_{\mathrm{DFT}}[n, \overline{E}]$ and $\Phi_{\mathrm{DFT}}[\alpha, (\beta)]$ are Legendre transform, therefore

$$\int d\mathbf{r}'' \Phi_{\mathbf{r}\mathbf{r}''}^{\alpha\alpha} S_{\mathbf{r}''\mathbf{r}'}^{nn} = \delta(\mathbf{r} - \mathbf{r}')$$

Substituting (22.3.1) and (22.3.1) in (22.3.1)

$$-\frac{1}{n(\mathbf{r}')}\frac{\delta n(\mathbf{r})}{\delta\alpha(\mathbf{r}')} + \int d\mathbf{r}'' \frac{\delta n(\mathbf{r})}{\delta\alpha(\mathbf{r}'')} c^{(2)}(\mathbf{r}'', \mathbf{r}') = \delta(\mathbf{r} - \mathbf{r}')$$

or

$$n^{(2)}(\mathbf{r}, \mathbf{r}') - n(\mathbf{r})n(\mathbf{r}') - c^{(2)}(\mathbf{r}, \mathbf{r}')n(\mathbf{r})n(\mathbf{r}') = n(\mathbf{r}') \int d\mathbf{r}'' c^{(2)}(\mathbf{r}'', \mathbf{r}') \left[n^{(2)}(\mathbf{r}, \mathbf{r}'') - n(\mathbf{r})n(\mathbf{r}'')\right]$$

For a uniform fluid of density n_0, $c^{(2)}(\mathbf{r}, \mathbf{r}') \equiv c^{(2)}(r)$ and $n^{(2)}(\mathbf{r}, \mathbf{r}') \equiv n_0^2 g(r)$ where $g(r)$ is the radial distribution function

$$g(r) - 1 = c^{(2)}(r) + n_0 \int d\mathbf{r}' c^{(2)}(|\mathbf{r} - \mathbf{r}'|) [g(r') - 1]$$

This equation is known as **the Ornstein-Zernike equation**. Note that the entropy functional or the density functional in principle captures the full microstructure of the fluid. Near walls, for example, allows to describe the equilibrium density field showing layering of the atoms.

The hard sphere model

[Write a particularly useful hard sphere model, to fix ideas.]

22.4   FTD: Functional Thermodynamics $\hat{n}_\mathbf{r}, \hat{e}_\mathbf{r}$

The next level of description that we consider is a more detailed one in which the CG variables are the density field and the energy density field, which are defined as

$$\hat{n}_\mathbf{r}(z) = \sum_i^N \delta(\mathbf{r} - \mathbf{q}_i)$$

$$\hat{e}_\mathbf{r}(z) = \sum_i^N e_i \delta(\mathbf{r} - \mathbf{q}_i)$$

Here, e_i is the energy of particle i, which is defined as

$$e_i = \frac{\mathbf{p}_i^2}{2m_i} + \frac{1}{2}\sum_j \phi(r_{ij}) + V^{\text{ext}}(\mathbf{q}_i)$$

where $\phi(r)$ is the (pair-wise) interparticle potential and $V^{\text{ext}}(\mathbf{r})$ is any external potential acting on the particles. The averages of these phase functions with respect to the relevant distribution in the macrocanonical phase space are denoted by

$$n(\mathbf{r}) = \sum_{N=0}^{\infty} \int dz_N \overline{\rho}(z_N) \hat{n}_\mathbf{r}(z_N)$$

$$e(\mathbf{r}) = \sum_{N=0}^{\infty} \int dz_N \overline{\rho}(z_N) \hat{e}_\mathbf{r}(z_N)$$

In this level of description the two dynamic invariants $\hat{N}(z), \hat{H}(z)$ are given in terms of the CG variables $\hat{n}_\mathbf{r}(z), \hat{e}_\mathbf{r}(z)$ in the form

$$\hat{N}(z) = \int d\mathbf{r}\, \hat{n}_\mathbf{r}(z)$$

$$\hat{H}(z) = \int d\mathbf{r}\, \hat{e}_\mathbf{r}(z)$$

Therefore, these dynamic invariants are not included in the list of CG variables, in order to not have redundant information.

The relevant ensemble (1.2.4) has the form in this level of description

$$\overline{\rho}(z_N) = \frac{\rho_N^0}{Z[\alpha, \beta]} \exp\left\{ -\int d\mathbf{r}\, (\alpha(\mathbf{r})\hat{n}_\mathbf{r}(z) + \beta(\mathbf{r})\hat{e}_\mathbf{r}(z)) \right\}$$

Here, $\alpha(\mathbf{r})$ and $\beta(\mathbf{r})$ are the Lagrange multipliers associated to each constrain in (22.4).

The normalization factor is the dimensionless partition function defined as

$$Z[\alpha, \beta] = \sum_{N=0}^{\infty} \frac{1}{N!} \int \frac{dz_N}{h^{3N}} \exp\left\{-\sum_{i=1}^{N} (\alpha(\mathbf{r}_i) + \beta(\mathbf{q}_i)e_i)\right\}$$

This partition function is a functional of both fields α, β which are the conjugate fields of the number density and energy density, respectively. By inserting (22.4) into (22.4) we may find the connection between the Lagrange multipliers $\alpha(\mathbf{r}), \beta(\mathbf{r})$ and the averages $n(\mathbf{r}), e(\mathbf{r})$. This connections can be expressed as

$$\frac{\delta \Phi_{\mathrm{FTD}}[\alpha, \beta]}{\delta \alpha(\mathbf{r})} = n(\mathbf{r})$$

$$\frac{\delta \Phi_{\mathrm{FTD}}[\alpha, \beta]}{\delta \beta(\mathbf{r})} = e(\mathbf{r})$$

where the dimensionless thermodynamic potential of the functional thermodynamics level of description is given by

$$\Phi_{\mathrm{FTD}}[\alpha, \beta] \equiv -\ln Z[\alpha, \beta]$$

The entropy at the Functional Thermodynamics level is defined as the result of evaluating the entropy functional (12.2) at the relevant ensemble (22.4). By inserting the relevant ensemble Eq. (22.4) in (12.2), we obtain the *entropy functional* of the Functional Thermodynamics level of description

$$S_{\mathrm{FTD}}[n, e] = -\Phi_{\mathrm{FTD}}[\alpha, \beta] + \int d\mathbf{r} \left[\alpha(\mathbf{r})n(\mathbf{r}) + \beta(\mathbf{r})e(\mathbf{r})\right]$$

The functional derivatives of the FTD entropy functional satisfies the following relationships,

$$\frac{\delta S_{\mathrm{FTD}}[n, e]}{\delta n(\mathbf{r})} = \alpha(\mathbf{r})$$

$$\frac{\delta S_{\mathrm{FTD}}[n, e]}{\delta e(\mathbf{r})} = \beta(\mathbf{r})$$

At this point, it proves convenient to perform the momenta integrals in the partition function (22.4), with the result

$$Z[\alpha, \beta] = \sum_{N=0}^{\infty} \frac{1}{N!} \int \prod_{i=0}^{N} \frac{d\mathbf{q}_i}{\Lambda^3(\mathbf{q}_i)} \exp\left\{-\sum_{j=1}^{N} [\alpha(\mathbf{q}_j) + \beta(\mathbf{q}_j)\phi_j]\right\}$$

where the **local thermal wavelength** is defined as

$$\Lambda(\mathbf{r}) \equiv \left(\frac{h^2 \beta(\mathbf{r})}{2m\pi} \right)^{\frac{1}{2}}$$

The functional derivative in (22.4) becomes now

$$e(\mathbf{r}) = \frac{3n(\mathbf{r})}{2\beta(\mathbf{r})} + \phi(\mathbf{r})$$

where we have introduced the average potential energy field as

$$\phi(\mathbf{r}) = \mathrm{Tr} \left[\overline{\rho} \sum_{i=0}^{N} \phi_i \delta(\mathbf{r} - \mathbf{q}_i) \right]$$

It is natural to define the average kinetic energy field as $k(\mathbf{r}) = e(\mathbf{r}) - \phi(\mathbf{r})$, in such a way that the physical meaning of the Lagrange multiplier $\beta(\mathbf{r})$ becomes transparent as proportional to the inverse of the kinetic energy field. Note that we may introduce the microscopic kinetic density field as

$$\hat{k}_{\mathbf{r}}(z) = \sum_{i}^{N} \frac{\mathbf{p}_i^2}{2m_i} \delta(\mathbf{r} - \mathbf{q}_i)$$

and, therefore,

$$k(\mathbf{r}) = \langle \hat{k}_{\mathbf{r}} \rangle^{\alpha\beta} = \frac{3n(\mathbf{r})}{2\beta(\mathbf{r})}$$

By defining the temperature field $T(\mathbf{r})$ as $2/3$ of the kinetic energy per particle divided by the Boltzmann constant, we have the interpretation of the field $\beta(\mathbf{r})$ as proportional to the inverse of the temperature field, this is $\beta(\mathbf{r}) = 1/k_B T(\mathbf{r})$.

22.4.1   Models for the FTD entropy

The functional form of the entropy at the FTD level contains all the information about the equilibrium profiles of number and energy densities and also, of the correlations of these variables. The problem here is identical to that faced by DFT in that one has to cook appropriate models for the density functional. Different approches have been considered in DFT, ranging from the Local Density Approximation (LDA), the Square Gradient Approximation (SGA), the Weighted density approximation (WDA), Taylor expansions around a reference system, up to the modern models based on the Fundamental Measure Theory. While similar schemes may be developed at the FTD level, we restrict to two models that admit exact (or almost exact) evaluation of the functional. These two models are the ideal gas and the hard sphere models. The ideal gas model entropy functional can be explicitly computed whereas the hard sphere model can be computed in terms of the free energy density of the DFT level of description, for which very good models already exists.

Ideal Gas

In the case of ideal gas the grand partition function Eq. (22.4) is

$$Z_{FTD}^{\mathrm{id}}[\alpha, \beta] = \sum_{N=0}^{\infty} \frac{1}{N! h^{3N}} \left[\int d\mathbf{r} \left(\frac{2m\pi}{\beta(\mathbf{r})} \right)^{\frac{3}{2}} \exp\left\{ -\alpha(\mathbf{r}) - \beta(\mathbf{r}) V(\mathbf{r}) \right\} \right]^{N}$$

$$= \exp\left\{ \int \frac{d\mathbf{r}}{\Lambda^3(\mathbf{r})} \exp\left\{ -\alpha(\mathbf{r}) - \beta(\mathbf{r}) V(\mathbf{r}) \right\} \right\}$$

where the *local thermal wavelength* is defined as

$$\Lambda(\mathbf{r}) \equiv \left(\frac{h^2 \beta(\mathbf{r})}{2m\pi} \right)^{\frac{1}{2}}$$

The dimensionles grand potential is

$$\Phi_{FTD}^{\mathrm{id}}[\alpha, \beta] = -\int \frac{d\mathbf{r}}{\Lambda^3(\mathbf{r})} \exp\left\{ -\alpha(\mathbf{r}) - \beta(\mathbf{r}) V(\mathbf{r}) \right\}$$

The functional derivatives respect to α and β are

$$\frac{\delta \Phi_{FTD}^{\mathrm{id}}[\alpha, \beta]}{\delta \alpha(\mathbf{r})} = \frac{1}{\Lambda^3(\mathbf{r})} \exp\left\{ -\alpha(\mathbf{r}) - \beta(\mathbf{r}) V(\mathbf{r}) \right\}$$

$$\frac{\delta \Phi_{FTD}^{\mathrm{id}}[\alpha, \beta]}{\delta \beta(\mathbf{r})} = \frac{1}{\Lambda^3(\mathbf{r})} \exp\left\{ -\alpha(\mathbf{r}) - \beta(\mathbf{r}) V(\mathbf{r}) \right\} \left[\frac{3}{2\beta(\mathbf{r})} + V(\mathbf{r}) \right]$$

Because of (22.4) we have

$$\frac{1}{\Lambda^3(\mathbf{r})} \exp\left\{ -\alpha(\mathbf{r}) - \beta(\mathbf{r}) V(\mathbf{r}) \right\} = n(\mathbf{r})$$

$$\frac{3n(\mathbf{r})}{2\beta(\mathbf{r})} + n(\mathbf{r}) V(\mathbf{r}) = e(\mathbf{r})$$

Therefore, we may obtain the conjugate variables in explicit form

$$\beta(\mathbf{r}) = \frac{3}{2} \frac{n(\mathbf{r})}{e(\mathbf{r}) - n(\mathbf{r}) V(\mathbf{r})}$$

$$\alpha(\mathbf{r}) = -\frac{3}{2} \frac{n(\mathbf{r}) V(\mathbf{r})}{e(\mathbf{r}) - n(\mathbf{r}) V(\mathbf{r})} - \ln[\Lambda^3(\mathbf{r}) n(\mathbf{r})]$$

With these results we may now simply compute the entropy (22.4) for the ideal gas, with the final result

$$S_{FTD}^{\mathrm{id}}[n, e] = -\int d\mathbf{r} \, n(\mathbf{r}) \left[\ln[\Lambda^3(\mathbf{r}) n(\mathbf{r})] - \frac{5}{2} \right]$$

Here, the thermal wavelength $\Lambda(\mathbf{r})$ given in Eq. (22.4.1) is a function of the fields n, e through β.

Hard sphere

A system of hard spheres is characterized by the fact that its total energy is fully kinetic, a fact also refered as the hard sphere system being *athermal*. There are many good approximations for the hard sphere free energy functional at the DFT level []. For this reason, we would like to use this DFT information in order to formulate the entropy functional of a hard sphere system at the level of FTD. This is actually possible precisely because the system is athermal.

In DFT we have from (**??**), after integrating over momenta

$$
\begin{aligned}
Z_{DFT}^{\mathrm{hs}}[\alpha, (\beta)] &= \sum_{N=0}^{\infty} \int dz_N \exp\left\{ -\sum_{i=1}^{N} \alpha(\mathbf{q}_i) - \beta\hat{H} \right\} \\
&= \sum_{N=0}^{\infty} \frac{1}{N!} \int \prod_i^N d\mathbf{q}_i \left(\frac{2m\pi h^2}{\beta} \right)^{\frac{3}{2}} \exp\left\{ -\sum_{i=1}^{N} \left(\alpha(\mathbf{q}_i) + \beta V(\mathbf{q}_i) + \beta\frac{1}{2}\sum_j \phi_{ij}^{\mathrm{hs}} \right) \right\}
\end{aligned}
$$

whereas in FTD we have from (22.4), after integrating over momenta

$$
\begin{aligned}
Z_{FTD}^{\mathrm{hs}}[\alpha, \beta] &= \sum_{N=0}^{\infty} \int dz_N \exp\left\{ -\sum_{i=1}^{N} (\alpha(\mathbf{r}_i) + \beta(\mathbf{q}_i)e_i) \right\} \\
&= \sum_{N=0}^{\infty} \frac{1}{N!} \int \prod_i^N d\mathbf{q}_i \left(\frac{2m\pi h^2}{\beta^{\mathrm{id}}(\mathbf{r}_i)} \right)^{\frac{3}{2}} \exp\left\{ -\sum_{i=1}^{N} \left(\alpha(\mathbf{q}_i) + \beta(\mathbf{q}_i)V(\mathbf{q}_i) + \beta(\mathbf{q}_i)\frac{1}{2}\sum_j \phi_{ij}^{\mathrm{hs}} \right) \right\} \\
&= \sum_{N=0}^{\infty} \frac{1}{N!} \int \prod_i^N d\mathbf{q}_i \left(\frac{2m\pi h^2}{\beta} \right)^{\frac{3}{2}} \exp\left\{ -\sum_{i=1}^{N} (\alpha(\mathbf{q}_i) + \beta(\mathbf{q}_i)V(\mathbf{q}_i)) \right\} f(\mathbf{r}_1, \cdots, \mathbf{r}_N)
\end{aligned}
$$

where we have introduced the function (related to the Meyer function)

$$
f(\mathbf{r}_1, \cdots, \mathbf{r}_N) \equiv \exp\left\{ -\sum_{i=1}^{N} \beta(\mathbf{q}_i)\frac{1}{2}\sum_j \phi_{ij}^{\mathrm{hs}} \right\}
$$

It is obvious that (22.4.1) is obtained from (22.4.1) by taking in the later a constant value for the field $\beta(\mathbf{r}) = \beta$. In the above expressions ϕ_{ij}^{hs} is the hard sphere potential for particles i, j. This potential is zero if the spheres do not overlap and infinite if they overlap. As a consequence, $f(\mathbf{r}_1, \cdots, \mathbf{r}_N)$ is zero if any two spheres overlap and 1

otherwise, *irrespective of the value of* $\beta(\mathbf{r})$. Therefore, we have at the DFT level

$$Z_{DFT}^{\text{hs}}[\alpha, (\beta)] = \sum_{N=0}^{\infty} \int dz_N \exp\left\{-\sum_{i=1}^{N} \alpha(\mathbf{q}_i) - \beta \hat{H}\right\}$$

$$= \sum_{N=0}^{\infty} \frac{1}{N!} \int \prod_i^N d\mathbf{q}_i \left(\frac{2m\pi h^2}{\beta}\right)^{\frac{3}{2}} \exp\left\{-\sum_{i=1}^{N} (\alpha(\mathbf{q}_i) + \beta V(\mathbf{q}_i))\right\} f(\mathbf{r}_1, \cdots, \mathbf{r}_N)$$

whereas at the FTD level

$$Z_{FTD}^{\text{hs}}[\alpha, \beta] = \sum_{N=0}^{\infty} \frac{1}{N!} \int \prod_i^N d\mathbf{q}_i \left(\frac{2m\pi h^2}{\beta(\mathbf{r}_i)}\right)^{\frac{3}{2}} \exp\left\{-\sum_{i=1}^{N} (\alpha(\mathbf{q}_i) + \beta(\mathbf{q}_i)V(\mathbf{q}_i))\right\} f(\mathbf{r}_1, \cdots, \mathbf{r}_N)$$

$$= \sum_{N=0}^{\infty} \frac{1}{N!} \int \prod_i^N d\mathbf{q}_i \left(\frac{2m\pi h^2}{\beta_0}\right)^{\frac{3}{2}} \exp\left\{-\sum_{i=1}^{N} \left(\alpha(\mathbf{q}_i) + \beta(\mathbf{q}_i)V(\mathbf{q}_i) + \frac{3}{2}\ln\frac{\beta(\mathbf{q}_i)}{\beta_0}\right)\right\} f(\mathbf{r}_1, \cdots, \mathbf{r}_N)$$

$$= Z_{DFT}^{\text{hs}}\left[\alpha + (\beta - \beta_0)V + \frac{3}{2}\ln\frac{\beta}{\beta_0}, (\beta_0)\right]$$

In this way, if we know the functional form of $Z_{DFT}^{\text{hs}}[\alpha, (\beta)]$ for a hard sphere system at the DFT level of description, then we automatically know the functional form of $Z_{FTD}^{\text{hs}}[\alpha, \beta]$ at the FTD level. The dimensionless grand canonical potential at both levels, DFT and FTD, are also related as

$$\Phi_{\text{FTD}}^{\text{hs}}[\alpha, \beta] = \Phi_{\text{DFT}}^{\text{hs}}\left[\alpha + (\beta - \beta_0)V + \frac{3}{2}\ln\frac{\beta}{\beta_0}, (\beta_0)\right]$$

Now, from Eqs. (22.4) we readily obtain the result

$$n(\mathbf{r}) = \frac{\delta\Phi_{DFT}^{\text{hs}}}{\delta\alpha(\mathbf{r})}\left[\alpha + (\beta - \beta_0)V + \frac{3}{2}\ln\frac{\beta}{\beta_0}, (\beta_0)\right]$$

$$e(\mathbf{r}) = \frac{3n(\mathbf{r})}{2\beta(\mathbf{r})} + n(\mathbf{r})V(\mathbf{r})$$

The last identity is a reflection that the hard sphere has only kinetic energy.

The value of the parameter β_0 seems to be irrelevant in the previous argument because we could choose an arbitrary value for β_0 and the identity (22.4.1) would hold true. This means that the right hand side of (22.4.1) is actually independent of β_0. By taking the partial derivative with respect to β_0 and using the chain rule we obtain

$$0 = -\int d\mathbf{r} \frac{\delta\Phi_{\text{DFT}}^{\text{hs}}}{\delta\alpha(\mathbf{r})}\left[\alpha + \frac{3}{2}\ln\frac{\beta}{\beta_0}, (\beta_0)\right]\left[V(\mathbf{r}) + \frac{3}{2\beta_0}\right] + \frac{\partial\Phi_{\text{DFT}}^{\text{hs}}}{\partial\beta_0}\left[\alpha + \frac{3}{2}\ln\frac{\beta}{\beta_0}, (\beta_0)\right]$$

By using (22.3) we have simply

$$0 = -\int d\mathbf{r} n(\mathbf{r}) \left[V(\mathbf{r}) + \frac{3}{2\beta_0} \right] + E$$

In this expression, we should keep in mind that both $n(\mathbf{r})$ and E are actually functionals of the form

$$n(\mathbf{r}) \left[\alpha + \frac{3}{2} \ln \frac{\beta}{\beta_0}, (\beta_0) \right]$$

$$E \left[\alpha + \frac{3}{2} \ln \frac{\beta}{\beta_0}, (\beta_0) \right]$$

and Eq. (22.4.1) is just an implicit equation for β_0 that could be solved in order to get β_0 as a functional of $\alpha(\mathbf{r}), \beta(\mathbf{r})$. Now, if we assume that what is known is not the conjugate variables $\alpha(\mathbf{r}), \beta(\mathbf{r})$ but rather the CG variables $n(\mathbf{r}), e(\mathbf{r})$ (and, therefore, their space integrals N, E), then Eq. (22.4.1) gives the explicit value that β_0 should have for consistency, which is

$$\beta_0[n, e] = \frac{3}{2} \frac{\int d\mathbf{r} n(\mathbf{r})}{\int d\mathbf{r} \left[e(\mathbf{r}) - n(\mathbf{r}) V(\mathbf{r}) \right]}$$

Let us assume that we know the functional form of the free energy density functional $F_{DFT}^{\text{hs}}[n, (\beta)]$ introduced in (**??**) for the case of a hard sphere. We also know the functional derivative

$$\frac{\delta F_{DFT}^{\text{hs}}[n, (\beta)]}{\delta n(\mathbf{r})} = \alpha[n, (\beta)](\mathbf{r})$$

that can be formally inverted in order to get $n[\alpha, (\beta)](\mathbf{r})$ as a functional of $\alpha(\mathbf{r})$. With this input information we can obtain the grand potential through Eq. (**??**) as

$$\Phi_{DFT}^{\text{hs}}[\alpha, (\beta)] \equiv F_{DFT}^{\text{hs}}[n[\alpha, (\beta)], (\beta)] + \int d\mathbf{r} \alpha(\mathbf{r}) n[\alpha, (\beta)](\mathbf{r})$$

Then, Eq. (22.4.1) allows us to obtain

$$\Phi_{\text{FTD}}^{\text{hs}}[\alpha, \beta] = \Phi_{\text{DFT}}^{\text{hs}} \left[\alpha + (\beta - \beta_0)V + \frac{3}{2} \ln \frac{\beta}{\beta_0}, (\beta_0) \right]$$

$$= F_{DFT} \left[n \left[\alpha + (\beta - \beta_0)V + \frac{3}{2} \ln \frac{\beta}{\beta_0} \right], (\beta_0) \right]$$

$$+ \int d\mathbf{r} \left(\alpha(\mathbf{r}) + (\beta - \beta_0)V + \frac{3}{2} \ln \frac{\beta(\mathbf{r})}{\beta_0} \right) n \left[\alpha + (\beta - \beta_0)V + \frac{3}{2} \ln \frac{\beta}{\beta_0}, (\beta_0) \right] (\mathbf{r})$$

Finally, we need to take the Legendre transform of this in order to obtain the entropy

functional, according to Eq. (22.4), this is

$$
\begin{aligned}
S_{\text{FTD}}^{\text{hs}}[n, e] &= -\Phi_{\text{FTD}}^{\text{hs}}[\alpha, \beta] + \int d\mathbf{r}\, [\alpha(\mathbf{r})n(\mathbf{r}) + \beta(\mathbf{r})e(\mathbf{r})] \\
&= F_{DFT}^{\text{hs}}[n, (\beta_0)] - \int d\mathbf{r} \left(\alpha(\mathbf{r}) + (\beta - \beta_0)V + \frac{3}{2}\ln\frac{\beta(\mathbf{r})}{\beta_0} \right) n(\mathbf{r}) + \int d\mathbf{r}\, [\alpha(\mathbf{r})n(\mathbf{r}) + \beta(\mathbf{r})e(\mathbf{r})] \\
&= -F_{DFT}^{\text{hs}}[n, (\beta_0)] - \int d\mathbf{r}\frac{3}{2}n(\mathbf{r})\ln\frac{\beta(\mathbf{r})}{\beta_0} - \int d\mathbf{r}(\beta(\mathbf{r}) - \beta_0)V(\mathbf{r})n(\mathbf{r}) + \int d\mathbf{r}\beta(\mathbf{r})e(\mathbf{r}) \\
&= -F_{DFT}^{\text{hs}}[n, (\beta_0)] + \beta_0\int d\mathbf{r}V(\mathbf{r})n(\mathbf{r}) - \int d\mathbf{r}\frac{3}{2}n(\mathbf{r})\left[\ln\frac{\beta(\mathbf{r})}{\beta_0} - 1\right]
\end{aligned}
$$

This gives the explicit exact form of the entropy functional $S_{\text{FTD}}^{\text{hs}}[n, e]$ of a hard sphere system, provided that the free energy functional $F_{DFT}^{\text{hs}}[n, (\beta_0)]$ of the hard sphere is known. Note that in this expression $F_{DFT}^{\text{hs}}[n, (\beta_0)]$ is the free energy density *in the presence of the external field* and therefore

$$
F_{DFT}^{\text{0hs}}[n, (\beta_0)] \equiv F_{DFT}^{\text{hs}}[n, (\beta_0)] - \beta_0\int d\mathbf{r}V(\mathbf{r})n(\mathbf{r})
$$

is the intrinsinc (zero external field) free energy of the hard sphere system. Finally, we end up with the following remarkably simple and exact result for the entropy functional of the hard sphere system

$$
S_{\text{FTD}}^{\text{hs}}[n, e] = F_{DFT}^{\text{0hs}}[n, (\beta_0)] + \int d\mathbf{r}\frac{3}{2}n(\mathbf{r})\left[\ln\frac{\beta(\mathbf{r})}{\beta_0} - 1\right]
$$

where $\beta(\mathbf{r})$ is, from (22.4.1) the following function of $n(\mathbf{r}), e(\mathbf{r})$

$$
\beta(\mathbf{r}) = \frac{3}{2}\frac{n(\mathbf{r})}{e(\mathbf{r}) - n(\mathbf{r})V(\mathbf{r})}
$$

Use Theorem (22.9) to obtain the DFT entropy starting from this, just to check that everything is consistent. One check that we may perform on this expression is the ideal gas limit. In the limit that the radius of the hard sphere vanish, we have that the free energy $F_{DFT}^{\text{0hs}}[n, (\beta_0)]$ of the hard sphere is just the dimensionless free energy of the ideal gas, which is

$$
F_{DFT}^{\text{id}}[n, (\beta_0)] = \int d\mathbf{r}n(\mathbf{r})\left[\ln\Lambda_0^3 n(\mathbf{r}) - 1\right]
$$

If we substitute this free energy functional into (22.4.1) we end up with the correct ideal gas result (22.4.1) for the entropy functional.

22.5 Functional Hydrodynamics

The next level of description that we will consider is characterized by the set of CG variables

$$\hat{\rho}_{\mathbf{r}}(z) = \sum_i^N m_i \delta(\mathbf{r} - \mathbf{q}_i)$$

$$\hat{\mathbf{g}}_{\mathbf{r}}(z) = \sum_i^N \mathbf{p}_i \delta(\mathbf{r} - \mathbf{q}_i)$$

$$\hat{e}_{\mathbf{r}}(z) = \sum_i^N e_i \delta(\mathbf{r} - \mathbf{q}_i)$$

In which, as compared with the FTD level of description, we use the mass density field $\hat{\rho}_{\mathbf{r}}$ instead of the number density $\hat{n}_{\mathbf{r}}$, and include also the momentum density field $\hat{\mathbf{g}}_{\mathbf{r}}(z)$ as relevant variable. We will consider simple fluids made of identical particles with mass $m_i = m$ and, therefore, the mass density and the number density fields are just proportional to each other, this is $\hat{\rho}_{\mathbf{r}}(z) = m\hat{n}_{\mathbf{r}}(z)$. We do not consider in the list of variables the dynamic invariants of the system, which are the the total mass, momentum, and energy. The reason is that these dynamic invariants can be fully expressible in terms of the variables (22.4) and we would have redundant information otherwise.

The relevant ensemble (1.11.3) now becomes

$$\overline{\rho}(z) = \frac{\rho_N^0}{Z[\lambda, \mathbf{v}, \beta]} \exp\left\{ -\int d\mathbf{r} \left[\lambda(\mathbf{r})\hat{\rho}_{\mathbf{r}}(z) - \beta(\mathbf{r})\mathbf{v}(\mathbf{r})\hat{\mathbf{g}}_{\mathbf{r}}(z) + \beta(\mathbf{r})\hat{e}_{\mathbf{r}}(z) \right] \right\}$$

For reasons that will become aparent soon, it proves convenient to introduce the conjugate variable $\mathbf{v}(\mathbf{r})$ with the prefactor $\beta(\mathbf{r})$ as the Lagrange multiplier associated to the momentum density field. Also, we have introduced the Lagrange multiplier $\lambda(\mathbf{r})$ (with units of inverse of mass) associated to the mass density field $\rho(\mathbf{r})$, in order to distinguish it from the dimensionless conjugate field $\alpha(\mathbf{r})$ that is associated to the number density $n(\mathbf{r})$.

The normalization factor is the partition function defined as

$$Z[\lambda, \mathbf{v}, \beta] \equiv \sum_{N=0}^{\infty} \frac{1}{N!} \int \frac{dz_N}{h^{3N}} \exp\left\{ -\sum_{i=1}^N \left[\lambda(\mathbf{q}_i)m - \beta(\mathbf{q}_i)\mathbf{v}(\mathbf{q}_i)\cdot\mathbf{p}_i + \beta(\mathbf{q}_i)e_i \right] \right\}$$

Here, $\lambda, \mathbf{v}, \beta$ are the conjugate fields of the mass, momentum, and energy density, respectively, which are fixed by the condition that the averages of the CG variables (22.4) with the relevant ensemble coincide with the averages $\rho(\mathbf{r}), \mathbf{g}(\mathbf{r}), e(\mathbf{r})$. This condition can be

expressed as in Eqs. (**??**) as

$$\rho(\mathbf{r}) = \frac{\delta \Phi[\lambda, \mathbf{v}, \beta]}{\delta \lambda(\mathbf{r})}$$

$$\mathbf{g}(\mathbf{r}) = -\frac{\delta \Phi[\lambda, \mathbf{v}, \beta]}{\delta \beta \mathbf{v}(\mathbf{r})}$$

$$e(\mathbf{r}) = \frac{\delta \Phi[\lambda, \mathbf{v}, \beta]}{\delta \beta(\mathbf{r})}$$

where the grand potential of the present level of description is

$$\Phi[\lambda, \mathbf{v}, \beta] \equiv -\ln Z[\lambda, \mathbf{v}, \beta]$$

Because $\lambda, \mathbf{v}, \beta$ are the conjugate variables of $\rho, \mathbf{g}, e$, there is a one to one connection between these fields. Therefore, the functionals $\lambda[\rho, \mathbf{g}, e]$, $\mathbf{v}[\rho, \mathbf{g}, e]$, and $\beta[\rho, \mathbf{g}, e]$ exist and are unique for a given value $\rho, \mathbf{g}, e$ of the CG variables.

The entropy functional of the hydrodynamic level of description is given by using the relevant ensemble (22.5) in the Gibbs-Jaynes entropy functional (**??**). The result is

$$S[\rho, \mathbf{g}, e] = -\Phi[\lambda, \mathbf{v}, \beta] + \int d\mathbf{r} \lambda(\mathbf{r})\rho(\mathbf{r}) - \int d\mathbf{r}\beta(\mathbf{r})\mathbf{v}(\mathbf{r})\cdot\mathbf{g}(\mathbf{r}) + \int d\mathbf{r}\beta(\mathbf{r})e(\mathbf{r})$$

where here the conjugate variables $\lambda, \mathbf{v}, \beta$ are understood as functionals of the CG variables $\rho, \mathbf{g}, e$. The entropy is related to the Legendre transform of the grand potential (up to some signs) and, therefore, we have the relations conjugate to (22.5)

$$\lambda(\mathbf{r}) = \frac{\delta S[\rho, \mathbf{g}, e]}{\delta \rho(\mathbf{r})}$$

$$\beta(\mathbf{r})\mathbf{v}(\mathbf{r}) = -\frac{\delta S[\rho, \mathbf{g}]}{\delta \mathbf{g}(\mathbf{r})}$$

$$\beta(\mathbf{r}) = \frac{\delta S[\rho, \mathbf{g}]}{\delta e(\mathbf{r})}$$

In fact, it is possible to find an *explicit* expression of $\mathbf{v}$ as a function of $\rho, \mathbf{g}$. Perform the momentum integrals in Eq. (22.5) and obtain

$$\Phi[\lambda, \mathbf{v}, \beta] = -\ln \sum_{N=0}^{\infty} \frac{1}{N!} \int \prod_{i=0}^{N} \frac{d\mathbf{q}_i}{\Lambda^3(\mathbf{q}_i)} \exp\left\{ -\sum_{j=1}^{N} \left[\lambda(\mathbf{q}_j)m + \beta(\mathbf{q}_j)\phi_j - \frac{m}{2}\mathbf{v}^2(\mathbf{q}_j) \right] \right\}$$

where the *local thermal wavelength* is defined as

$$\Lambda(\mathbf{q}_i) \equiv \left(\frac{h^2 \beta(\mathbf{r}_i)}{2m\pi} \right)^{\frac{1}{2}}$$

Then take the functional derivative of Eq. (18.4) with respect to the conjugate field $\mathbf{v}(\mathbf{r})$.

Together with Eqs. (22.5), (22.5), this leads directly to the explicit form of the conjugate field $\mathbf{v}(\mathbf{r})$

$$\mathbf{v}(\mathbf{r}, t) = \frac{\mathbf{g}(\mathbf{r}, t)}{\rho(\mathbf{r}, t)}$$

and allows one to interpret the conjugate field $\mathbf{v}(\mathbf{r}, t)$ as the velocity field. Note that because of Eq. (18.4), we have

$$\Phi[\lambda, \mathbf{v}, \beta] = \Phi_{\text{FTD}}\left[m\lambda - \frac{m}{2}\mathbf{v}^2, \beta\right]$$

where the right hand side of this equation is the thermodynamic of the FTD level of description with a redefined conjugate variable $\lambda'(\mathbf{r})$ given by

$$\lambda'(\mathbf{r}) = m\lambda(\mathbf{r}) - \frac{m}{2}\mathbf{v}^2(\mathbf{r})$$

Therefore, *the level of description of Functional Hydrodynamics (FHD) has a grand potential which is entirely determined by the grand potential of the Functional Thermodynamics (FTD) level of description.*

With this Eq. (22.5) inserted in Eq. (10) we obtain

$$F[\rho, \mathbf{g}] = \Phi\left[m\lambda[\rho, \mathbf{g}] - \frac{m}{2}\mathbf{v}^2[\rho, \mathbf{g}]\right] - \int d\mathbf{r}\rho(\mathbf{r})\lambda(\mathbf{r})[\rho, \mathbf{g}] + \int d\mathbf{r}\frac{\mathbf{g}^2(\mathbf{r})}{\rho(\mathbf{r})}$$

$$= \Phi\left[\lambda'[\rho, \mathbf{g}]\right] - \int d\mathbf{r}\rho(\mathbf{r})\frac{1}{m}\lambda'(\mathbf{r})[\rho, \mathbf{g}] + \int d\mathbf{r}\frac{\mathbf{g}^2(\mathbf{r})}{2\rho(\mathbf{r})}$$

We may take the functional derivative with respect to $\mathbf{g}(\mathbf{r}, t)$ of both sides of this equation and use Eqs. (22.5), (22.5) in order to show that the first two terms in Eq. (22.5) form a functional that is, in fact, independent of the momentum density $\mathbf{g}(\mathbf{r})$. Indeed, these two terms are just the Legendre transform of the grand-canonical potential, which is the density functional $\Phi[n]$. Therefore, we have

$$S_{\text{FHD}}[\rho, \mathbf{g}, e] = S_{\text{FTD}}\left[\frac{\rho}{m}, e\right] - \int d\mathbf{r}\frac{\mathbf{g}^2(\mathbf{r})}{2\rho(\mathbf{r})}$$

This is the explicit *exact* form for the entropy at the Functional Hydrodynamic level of description. It is a non-trivial result that has a very appealing simplicity. Note that if we have good expressions for the entropy functional $S_{\text{FTD}}[n, e]$, this information can be transferred directly to the hydrodynamic level. The hydrodynamic aspects of the hydrodynamic functional are simply encoded into a kinetic energy term.

The functional derivatives of Eq. (22.5) leads to

$$\lambda(\mathbf{r}, t) = -\frac{\delta\Phi^H[\rho, \mathbf{g}]}{\delta\rho(\mathbf{r}, t)} = -\frac{1}{m}\frac{\delta\Phi[n]}{\delta n(\mathbf{r}, t)} + \frac{\mathbf{v}^2(\mathbf{r}, t)}{2}$$

$$\equiv -\mu(\mathbf{r}, t) + \frac{\mathbf{v}^2(\mathbf{r}, t)}{2}$$

and to the second Eq. (22.4), as it should. We have introduced the chemical potential per unit mass in the last equation (22.5).

22.6   IKT: Isothermal Kinetic Theory $\hat{f}_{\mathbf{rp}}, \hat{H}$.

The one particle distribution is defined microscopically as

$$\hat{f}_{\mathbf{rp}}(z) = \sum_{i=1}^{N} \delta(\mathbf{r} - \mathbf{q}_i)\delta(\mathbf{p} - \mathbf{p}_i)$$

The ensemble averages are denoted by

$$f(\mathbf{r}, \mathbf{p}) = \mathrm{Tr}\left[\overline{\rho}\hat{f}_{\mathbf{rp}}\right]$$

$$\overline{E} = \mathrm{Tr}\left[\overline{\rho}\hat{H}\right]$$

The one particle distribution satisfies

$$\int d\mathbf{r} d\mathbf{p}\, \hat{f}_{\mathbf{rp}}(z) = \hat{N}(z)$$

Therefore, the knowledge of the average $f(\mathbf{r}, \mathbf{p})$ already informs us about the average value $\overline{N}$ of the number of particles. Therefore, in order to not have redundant information, we will not include the number of particles $\hat{N}(z)$ as relevant variable.

The relevant ensemble (1.11.3) is now

$$\overline{\rho}(z) = \frac{1}{Z[\beta, \lambda]} \rho_0^N \exp\left\{-\beta\hat{H}(z) - \int d\mathbf{r} d\mathbf{p}\, \lambda(\mathbf{r}, \mathbf{p})\hat{f}_{\mathbf{rp}}(z)\right\}$$

Here, $\lambda(\mathbf{r}, \mathbf{p})$ and β are the conjugate variables of the averages $f(\mathbf{r}, \mathbf{p})$, $\overline{E}$ of the CG variables. The partition function is defined as

$$Z[\beta, \lambda] = \sum_{N=0}^{\infty} \frac{1}{N! h^{3N}} \int d\mathbf{r}_1 d\mathbf{p}_1 \cdots d\mathbf{r}_N d\mathbf{p}_N \exp\left\{-\beta\hat{H}(z) - \sum_i \lambda(\mathbf{q}_i, \mathbf{p}_i)\right\}$$

and the dimensionless grand potential as

$$\Phi[\beta, \lambda] \equiv -\ln Z[\beta, \lambda]$$

Functional derivatives of the grand potential with respect to the conjugate variable give the averages

$$\frac{\delta\Phi[\beta, \lambda]}{\delta\lambda(\mathbf{r}, \mathbf{p})} = \langle\hat{f}_{\mathbf{rp}}\rangle^{\lambda\beta} = f(\mathbf{r}, \mathbf{p})$$

$$\frac{\partial\Phi[\beta, \lambda]}{\partial\beta} = \langle\hat{H}\rangle^{\lambda\beta} = \overline{E}$$

where $\langle\cdots\rangle^{\lambda\beta}$ denotes an average with the relevant ensemble (22.6).

The entropy of this level of description is obtained by evaluating the Gibbs-Jaynes

entropy at the relevant ensemble (22.6). The result is

$$S[f, \overline{E}] = -\Phi[\beta, \lambda] + \int d\mathbf{r}d\mathbf{p}\lambda(\mathbf{r}, \mathbf{p})f(\mathbf{r}, \mathbf{p}) + \beta\overline{E}$$

whose derivatives give the conjugate variables

$$\frac{\delta S}{\delta f(\mathbf{r}, \mathbf{p})}[f, \overline{E}] = \lambda(\mathbf{r}, \mathbf{p})$$

$$\frac{\partial S}{\partial E}[f, \overline{E}] = \beta$$

By analogy with the DFT level of description, we write the entropy functional (22.6) in the form of a partial Legendre transform

$$S[f, \overline{E}] = -F[f, \beta] + \beta\overline{E}$$

where the **dimensionless free energy functional** of the IKT level of description is defined as

$$F[f, \beta] \equiv \Phi[\beta, \lambda] - \int d\mathbf{r}d\mathbf{p}\lambda(\mathbf{r}, \mathbf{p})f(\mathbf{r}, \mathbf{p})$$

The functional derivative of this functional with respect to the one particle distribution is

$$\frac{\delta F}{\delta f(\mathbf{r}, \mathbf{p})}[f, \beta] = -\lambda(\mathbf{r}, \mathbf{p})$$

where here, as oposed to (22.6), $\lambda(\mathbf{r}, \mathbf{p})$ is a functional of $f(\mathbf{r}, \mathbf{p})$ and a function of β (and not $\overline{E}$). The derivative of the free energy with respect to β gives, by use of the chain rule, and in a similar way as in (22.6)

$$\frac{\partial}{\partial\beta}F[f, \beta] = \overline{E}$$

This expression gives the average energy as a functional of $f(\mathbf{r}, \mathbf{p})$ and a function of β. This relationship may be inverted, at least in principle, in order to produce $\beta[f, \overline{E}]$. By inserting this functional $\beta[f, \overline{E}]$ into the expression (22.6) we recover the entropy functional as a functional of $f(\mathbf{r}, \mathbf{p})$ and a function of $\overline{E}$.

The ideal gas

When $\hat{U}(z) = 0$ we have a system of non-interacting particles. In this case, the Hamiltonian can be expressed entirely in terms of the one particle function

$$\hat{H}(z) = \int d\mathbf{r}d\mathbf{p} \left[\frac{\mathbf{p}^2}{2m_i} + V^{\text{ext}}(\mathbf{r}) \right] \hat{f}_{\mathbf{rp}}(z)$$

The Hamiltonian becomes a linear functional of the one particle distribution function. In this case, we have redundant information. Nevertheless, in this example, we keep the Hamiltonian as relevant variable, because when we will consider the non-ideal gas, the Hamiltonian can no longer be expressed in terms of the one particle distribution function and, then, we need to include the Hamiltonian as an independent variable.

For the ideal gas, we may compute explicitly the partition function (22.6) with the result

$$Z^{\text{id}}[\beta, \lambda] = \sum_{N=0}^{\infty} \frac{1}{N!h^{3N}} \left[\int d\mathbf{r}d\mathbf{p} \exp\left\{ -\beta \left[\frac{\mathbf{p}^2}{2m} + V^{\text{ext}}(\mathbf{r}) \right] - \lambda(\mathbf{r}, \mathbf{p}) \right\} \right]^N$$

$$= \exp\left\{ \int \frac{d\mathbf{r}d\mathbf{p}}{h^3} \exp\left\{ -\beta \left[\frac{\mathbf{p}^2}{2m} + V^{\text{ext}}(\mathbf{r}) \right] - \lambda(\mathbf{r}, \mathbf{p}) \right\} \right\}$$

The corresponding grand potential is

$$\Phi^{\text{id}}[\beta, \lambda] = -\ln Z^{\text{id}}[\beta, \lambda] = -\int \frac{d\mathbf{r}d\mathbf{p}}{h^3} \exp\left\{ -\beta \left[\frac{\mathbf{p}^2}{2m} + V^{\text{ext}}(\mathbf{r}) \right] - \lambda(\mathbf{r}, \mathbf{p}) \right\}$$

Note that the conjugate variables appear in the combination $\lambda + \beta\Pi$, see Eq. (**??**), which in this case takes the form

$$\mu(\mathbf{r}, \mathbf{p}) = \lambda(\mathbf{r}, \mathbf{p}) + \beta \left[\frac{\mathbf{p}^2}{2m} + V^{\text{ext}}(\mathbf{r}) \right]$$

Note that the grand potential suffers from the symmetry (**??**) that, in the present case, takes the form

$$\Phi^{\text{id}} \left[\lambda + \beta_0 \left[\frac{\mathbf{p}^2}{2m} + V^{\text{ext}}(\mathbf{r}) \right], \beta + \beta_0 \right] = \Phi^{\text{id}} [\lambda, \beta]$$

The first equation in (22.6) now takes the form

$$f(\mathbf{r}, \mathbf{p}) = \frac{\delta}{\delta\lambda(\mathbf{r}, \mathbf{p})} \Phi^{\text{id}}[\beta, \lambda] = \frac{1}{h^3} \exp\left\{ -\beta \left[\frac{\mathbf{p}^2}{2m} + V^{\text{ext}}(\mathbf{r}) \right] - \lambda(\mathbf{r}, \mathbf{p}) \right\} = \frac{1}{h^3} \exp\left\{ -\mu(\mathbf{r}, \mathbf{p}) \right\}$$

Note that there is a one to one conection between $f(\mathbf{r}, \mathbf{p})$ and $\mu(\mathbf{r}, \mathbf{p})$.

The second equation (22.6) now becomes

$$\overline{E} = \frac{\partial}{\partial \beta} \Phi^{\mathrm{id}}[\beta, \lambda] = \int \frac{d\mathbf{r}d\mathbf{p}}{h^3} \left[\frac{\mathbf{p}^2}{2m} + V^{\mathrm{ext}}(\mathbf{r}) \right] \exp\left\{ -\beta \left[\frac{\mathbf{p}^2}{2m} + V^{\mathrm{ext}}(\mathbf{r}) \right] - \lambda(\mathbf{r}, \mathbf{p}) \right\}$$

$$= \int d\mathbf{r}d\mathbf{p} \left[\frac{\mathbf{p}^2}{2m} + V^{\mathrm{ext}}(\mathbf{r}) \right] f(\mathbf{r}, \mathbf{p})$$

which is, consistently, the average version of (22.6). The conjugate variable is given by inverting (22.6)

$$\lambda(\mathbf{r}, \mathbf{p}) = -\ln h^3 f(\mathbf{r}, \mathbf{p}) - \beta \left[\frac{\mathbf{p}^2}{2m} + V^{\mathrm{ext}}(\mathbf{r}) \right]$$

We may ask what is the explicit form of $\beta[f, \overline{E}]$. Unfortunatelly, it is simply not possible to obtain this functional form because there is not a one to one correspondence between $f, \overline{E}$ and λ, β, due to the degeneracy described by the symmetry (22.6).

The thermodynamic potential (22.6), once we use (22.6), takes the simple form

$$\Phi[\beta, \lambda] = \int d\mathbf{r}d\mathbf{p} f(\mathbf{r}, \mathbf{p})$$

and the entropy (22.6) is given by

$$S^{\mathrm{id}}[f, \overline{E}] = -\int d\mathbf{r}d\mathbf{p} f(\mathbf{r}, \mathbf{p}) \left(\ln h^3 f(\mathbf{r}, \mathbf{p}) - 1 \right) + \beta \overline{E} - \beta \int d\mathbf{r}d\mathbf{p} f(\mathbf{r}, \mathbf{p}) \left[\frac{\mathbf{p}^2}{2m} + V^{\mathrm{ext}}(\mathbf{r}) \right]$$

$$= -\int d\mathbf{r}d\mathbf{p} f(\mathbf{r}, \mathbf{p}) \left(\ln h^3 f(\mathbf{r}, \mathbf{p}) - 1 \right)$$

where we have used (22.6). Note that the ideal gas entropy does not depend explicitly on the average energy and we can write simply $S^{\mathrm{id}}[f]$.

The free energy functional (22.6) for the ideal gas in this level of description is given by

$$F^{\mathrm{id}}[f, \beta] = \int d\mathbf{r}d\mathbf{p} f(\mathbf{r}, \mathbf{p}) \left(\ln h^3 f(\mathbf{r}, \mathbf{p}) - 1 \right) + \beta \int d\mathbf{r}d\mathbf{p} f(\mathbf{r}, \mathbf{p}) \left[\frac{\mathbf{p}^2}{2m} + V^{\mathrm{ext}}(\mathbf{r}) \right]$$

Note that we may obtain the average energy $\overline{E}$ from this expression and Eq. (22.6). The result is again (22.6) that shows that the average energy $\overline{E}[f, \beta]$ does not depend on the parameter β at all. This means that we cannot invert this equation to obtain $\beta[f, \overline{E}]$, which is just a reflection that, for the ideal gas, the parameter β is redundant.

The relevant ensemble can be written in the simple form

$$\overline{\rho}(z_N) = \frac{e^{-\overline{N}}}{N!} \prod_{i=1}^{N} f(\mathbf{q}_i, \mathbf{p}_i)$$

where we recall that $\overline{N} = \int d\mathbf{r}d\mathbf{p}f(\mathbf{r}, \mathbf{p})$ is the average number of particles in the system. Recall that the relevant ensemble is normalized such that it gives the probability of having N particles in the system, i.e.

$$P(N) = \int dz_N \rho(z_N) = \frac{e^{-\overline{N}}\overline{N}^N}{N!}$$

which is a Poisson distribution with average $\overline{N}$.

The very weakly interacting gas

We have seen that the ideal gas is somewhat degenerate at the IKT level of description because the Hamiltonian becomes a linear functional of the one particle distribution when there are no interactions between the particles. When this happens, we have a problem of redundant information and we cannot use the variable β conjugate to the average energy $\overline{E}$. This poses a problem when we want to consider the ideal gas as a reference system for treating interactions, as we did for the DFT level of description. For this reason, we will consider here another model that corresponds to a system in which the particles interact with a *very weak* pair-wise potential. In this way, we may associate a dimensionless parameter ϵ to the total interaction energy potential $\hat{U}(z) \to \epsilon\hat{U}(z)$ and consider first order perturbation theory with respect to this parameter, assumed to be very small $\epsilon \simeq 0$. **[I hope to be able to show at the end that the expansion in ϵ is also an expansion in low density.]** The resulting model, very close to the ideal gas model, will no longer have the problematic behaviour due to redundant information.**[The final outcome of this calculation should be the relevant ensemble and the entropy, because these are the objects that are required in the calculation of the transport equation.]**

The relevant ensemble (22.6) can be written as

$$\overline{\rho}(z_N) = \frac{1}{Z[\beta, \lambda]} \exp\left\{-\sum_i^N \mu(\mathbf{q}_i, \mathbf{p}_i) - \beta\epsilon\hat{U}(z_N)\right\}$$

where we introduce for notational convenience the redefined conjugate variable

$$\mu(\mathbf{r}, \mathbf{p}) = \lambda(\mathbf{r}, \mathbf{p}) + \beta\left[\frac{\mathbf{p}^2}{2m} + V^{\text{ext}}(\mathbf{r})\right]$$

We may write this ensemble as

$$\overline{\rho}(z_N) = \overline{\rho}^{\text{id}}(z_N) \exp\left\{-\beta\epsilon\hat{U}(z_N) + \Phi[\beta, \lambda] - \Phi^{\text{id}}[\beta, \lambda]\right\}$$

where we have introduced the ideal relevant ensemble

$$\overline{\rho}^{\text{id}}(z_N) = \frac{1}{Z^{\text{id}}[\beta, \lambda]} \exp\left\{-\sum_i^N \mu(\mathbf{q}_i, \mathbf{p}_i)\right\}$$

with ideal partition function is given by

$$Z^{\text{id}}[\beta, \lambda] \equiv \sum_{N=0}^{\infty} \frac{1}{N!h^{3N}} \int dz_N \exp\left\{-\sum_i^N \mu(\mathbf{q}_i, \mathbf{p}_i)\right\} = \exp\left\{\int \frac{d\mathbf{r}d\mathbf{p}}{h^3} \exp\left\{-\mu(\mathbf{r}, \mathbf{p})\right\}\right\}$$

and we have introduced where the ideal grand potential is defined as

$$\Phi^{\text{id}}[\beta, \lambda] \equiv -\ln Z^{\text{id}}[\beta, \lambda]$$

The dimensionless grand potential (22.6) has the form

$$\Phi[\beta, \lambda] = -\ln \sum_{N=0}^{\infty} \frac{1}{N! h^{3N}} \int dz_N \exp\left\{ -\sum_i^N \mu(\mathbf{q}_i, \mathbf{p}_i) - \beta \epsilon \hat{U}(z_N) \right\}$$

$$= \Phi^{\mathrm{id}}[\beta, \lambda] - \ln \left\langle \exp\left\{ -\beta \epsilon \hat{U} \right\} \right\rangle^{\mathrm{id}}$$

where the ideal average is defined as the average with respect to the ideal relevant ensemble (22.6)

$$\langle \cdots \rangle^{\mathrm{id}} = \frac{1}{Z^{\mathrm{id}}[\beta, \lambda]} \sum_{N=0}^{\infty} \frac{1}{N! h^{3N}} \int dz_N \exp\left\{ -\sum_i^N \mu(\mathbf{q}_i, \mathbf{p}_i) \right\} \cdots$$

Therefore, the relevant ensemble (22.6) can be expressed in terms of the ideal relevant ensemble as follows

$$\overline{\rho}(z_N) = \overline{\rho}^{\mathrm{id}}(z_N) \exp\left\{ -\beta \epsilon \Delta \hat{U}(z_N) \right\}$$

where we have introduced

$$\beta \epsilon \Delta \hat{U}(z_N) \equiv \beta \epsilon \hat{U}(z_N) + \ln \left\langle \exp\left\{ -\beta \epsilon \hat{U} \right\} \right\rangle^{\mathrm{id}}$$

The entropy, which is obtained by evaluating the Gibbs-Jaynes entropy (**??**) at the relevant ensemble, can now be expressed as

$$S[f, \overline{E}] = -\mathrm{Tr}\left[\overline{\rho}^{\mathrm{id}} \exp\left\{ -\beta \epsilon \Delta \hat{U} \right\} \ln \overline{\rho}^{\mathrm{id}} \right] - \beta \epsilon \mathrm{Tr}\left[\overline{\rho}^{\mathrm{id}} \exp\left\{ -\beta \epsilon \Delta \hat{U} \right\} \Delta \hat{U} \right]$$

The results (22.6), (22.6) are rigorous and exact. Recall that the relevant ensemble depends on the conjugate variables λ, β that are adjusted to give the averages $f, \overline{E}$. In the present case, the parameter λ is hidden inside $\overline{\rho}^{\mathrm{id}}(z_N)$. **[This argument can be used exactly in the same way for the DFT level of description, in order to find the *excess entropy*.]**

We may now consider the limit in which ϵ is very small, i.e. the interactions are very week. In this case, we may expand to low orders in ϵ. For example, the term (22.6) becomes

$$\Delta \hat{U}(z_N) = \hat{U}(z_N) - \left\langle \hat{U} \right\rangle^{\mathrm{id}} + \mathcal{O}(\epsilon^2)$$

and the entropy, to first order in ϵ is given by

$$S[f, \overline{E}] = -\mathrm{Tr}\left[\overline{\rho}^{\mathrm{id}} \ln \overline{\rho}^{\mathrm{id}} \right] + \beta \epsilon \mathrm{Tr}\left[\Delta \hat{U} \overline{\rho}^{\mathrm{id}} \ln \overline{\rho}^{\mathrm{id}} \right]$$

This expression is still not explicit in $f, \overline{E}$, because the ideal relevant ensemble (**??**) depends on the conjugate variable $\mu(\mathbf{r}, \mathbf{p})$

A first order expansion in ϵ of the grand potential (22.6) gives the grand potential of

the weak interacting gas model

$$\Phi[\beta, \lambda] = \Phi^{\mathrm{id}}[\beta, \lambda] + \beta\epsilon \left\langle \hat{U} \right\rangle^{\mu}$$

Hence, the ideal grand potential is

$$\Phi^{\mathrm{id}}[\beta, \lambda] = - \int \frac{d\mathbf{r}d\mathbf{p}}{h^3} \exp\left\{-\mu(\mathbf{r}, \mathbf{p})\right\}$$

that has the following derivatives

$$\frac{\delta \Phi^{\mathrm{id}}}{\delta \lambda(\mathbf{r}, \mathbf{p})}[\beta, \lambda] = \exp\left\{-\mu(\mathbf{r}, \mathbf{p})\right\}$$

$$\frac{\partial \Phi^{\mathrm{id}}}{\partial \beta}[\beta, \lambda] = \int \frac{d\mathbf{r}d\mathbf{p}}{h^3} \exp\left\{-\mu(\mathbf{r}, \mathbf{p})\right\} \left[\frac{\mathbf{p}^2}{2m} + V^{\mathrm{ext}}(\mathbf{r})\right]$$

Let us now find the connection between the CG variables $f(\mathbf{r}, \mathbf{p}), \overline{E}$ and the conjugate variables $\lambda(\mathbf{r}, \mathbf{p}), \beta$, which are obtained from (22.6), this is

$$f(\mathbf{r}, \mathbf{p}) = \frac{\delta \Phi^{\mathrm{id}}[\beta, \lambda]}{\delta \lambda(\mathbf{r}, \mathbf{p})} + \beta\epsilon \frac{\delta}{\delta \lambda(\mathbf{r}, \mathbf{p})} \left\langle \hat{U} \right\rangle^{\mu}$$

$$\overline{E} = \frac{\partial \Phi^{\mathrm{id}}[\beta, \lambda]}{\partial \beta} + \epsilon \left\langle \hat{U} \right\rangle^{\mu} + \beta\epsilon \frac{\partial}{\partial \beta} \left\langle \hat{U} \right\rangle^{\mu}$$

We will need the derivatives of the ideal average of the potential energy, that are given by

$$\frac{\delta}{\delta \lambda(\mathbf{r}, \mathbf{p})} \left\langle \hat{U} \right\rangle^{\mu} = - \left\langle \hat{U} \delta \hat{f}_{\mathbf{rp}} \right\rangle^{\mu}$$

$$\frac{\partial}{\partial \beta} \left\langle \hat{U} \right\rangle^{\mu} = - \int d\mathbf{r}d\mathbf{p} \left\langle \hat{U} \delta \hat{f}_{\mathbf{rp}} \right\rangle^{\mu} \left[\frac{\mathbf{p}^2}{2m} + V^{\mathrm{ext}}(\mathbf{r})\right]$$

where the fluctuations with respect to the average are defined in the usual way $\delta \hat{f}_{\mathbf{rp}} = \hat{f}_{\mathbf{rp}} - f(\mathbf{r}, \mathbf{p})$. By using (22.6) and (22.6) in (22.6) we have

$$f(\mathbf{r}, \mathbf{p}) = \exp\{-\mu(\mathbf{r}, \mathbf{p})\} + \beta\epsilon \left\langle \hat{U} \delta \hat{f}_{\mathbf{rp}} \right\rangle^{\mu}$$

$$\overline{E} = \int d\mathbf{r}d\mathbf{p} \left[\frac{\mathbf{p}^2}{2m} + V^{\mathrm{ext}}(\mathbf{r})\right] f(\mathbf{r}, \mathbf{p}) + \epsilon \left\langle \hat{U} \right\rangle^{\mu}$$

Note that the last term in the first equation vanishes upon integrating over $\mathbf{r}, \mathbf{p}$. Therefore,

$$\overline{N} = \int d\mathbf{r}d\mathbf{p} f(\mathbf{r}, \mathbf{p}) = \int d\mathbf{r}d\mathbf{p} \exp\{-\mu(\mathbf{r}, \mathbf{p})\} = \Phi^{\mathrm{id}}[\beta, \lambda]$$

Note that the total average energy $\overline{E}$ is given in terms of the one particle energy plus

the ideal average of the interaction part, which seems quite natural in this order of approximation. In principle, for a fixed $f(\mathbf{r}, \mathbf{p})$ this equation can be inverted in order to give the conjugate variable β (hidden in μ) in terms of $\overline{E}$ and $f(\mathbf{r}, \mathbf{p})$. Therefore, (22.6) give the one to one connection between the averages $f(\mathbf{r}, \mathbf{p}), \overline{E}$ and the conjugate variables $\lambda(\mathbf{r}, \mathbf{p}), \beta$.

We can now compute the entropy function from (22.6)

$$
\begin{aligned}
S[f, \overline{E}] &= -\Phi^{\text{id}}[\beta, \lambda] - \beta\epsilon \left\langle \hat{U} \right\rangle^{\mu} + \int d\mathbf{r} d\mathbf{p} \lambda(\mathbf{r}, \mathbf{p}) f(\mathbf{r}, \mathbf{p}) + \beta \left[\int d\mathbf{r} d\mathbf{p} \left[\frac{\mathbf{p}^2}{2m} + V^{\text{ext}}(\mathbf{r}) \right] f(\mathbf{r}, \mathbf{p}) + \epsilon \left\langle \hat{U} \right\rangle^{\mu} \right] \\
&= -\Phi^{\text{id}}[\beta, \lambda] + \int d\mathbf{r} d\mathbf{p} \mu(\mathbf{r}, \mathbf{p}) f(\mathbf{r}, \mathbf{p}) \\
&= \int d\mathbf{r} d\mathbf{p} f(\mathbf{r}, \mathbf{p}) \left[\mu(\mathbf{r}, \mathbf{p}) - 1 \right] \\
&= \int d\mathbf{r} d\mathbf{p} f(\mathbf{r}, \mathbf{p}) \left[\ln \left(h^3 f(\mathbf{r}, \mathbf{p}) - \beta\epsilon \left\langle \hat{U} \delta \hat{f}_{\mathbf{rp}} \right\rangle^{\mu} \right) - 1 \right] \\
&= \int d\mathbf{r} d\mathbf{p} f(\mathbf{r}, \mathbf{p}) \left[\ln h^3 f(\mathbf{r}, \mathbf{p}) - 1 \right] + \int d\mathbf{r} d\mathbf{p} f(\mathbf{r}, \mathbf{p}) \ln \left(1 - \frac{\beta\epsilon \left\langle \hat{U} \delta \hat{f}_{\mathbf{rp}} \right\rangle^{\mu}}{h^3 f(\mathbf{r}, \mathbf{p})} \right)
\end{aligned}
$$

In this expression, β and $\mu(\mathbf{r}, \mathbf{p})$ should be understood as functionals of $f(\mathbf{r}, \mathbf{p})$ and functions of $\overline{E}$ though the inverse of Eqs. (22.6). This entropy is exact, given the model (22.6). However, as the model itself is valid only to first order in ϵ, we may approximate the entropy functional itself to first order in ϵ, with the result

$$
S[f, \overline{E}] = \int d\mathbf{r} d\mathbf{p} f(\mathbf{r}, \mathbf{p}) \left[\ln h^3 f(\mathbf{r}, \mathbf{p}) - 1 \right] + \mathscr{O}(\epsilon^2)
$$

Note that the entropy is given by the ideal entropy *up to second order in* ϵ.

The functional derivative of the entropy is given by (**??**) that now becomes

$$
\ln h^3 f(\mathbf{r}, \mathbf{p}) = \lambda(\mathbf{r}, \mathbf{p}) + \mathscr{O}(\epsilon^2)
$$

[This does not seem to be consistent!]

For pair-wise interactions, we may compute the ideal average of the interaction energy as follows

$$
\left\langle \hat{U} \right\rangle^{\mu} = \left\langle \frac{1}{2} \sum_{ij}' \Phi_{ij} \right\rangle^{\mu} = \int d\mathbf{r} d\mathbf{r}' \Phi(\mathbf{r} - \mathbf{r}') \left\langle \frac{1}{2} \sum_{ij}' \delta(\mathbf{r} - \mathbf{q}_i) \delta(\mathbf{r}' - \mathbf{q}_j) \right\rangle^{\mu} =
$$

where the prime in the sum means that the terms $i = j$ are to be excluded. Therefore,

we have

$$\left\langle \hat{U} \right\rangle^{\mu} = \int d\mathbf{r} d\mathbf{r}' \Phi(\mathbf{r} - \mathbf{r}') \frac{1}{2} \sum_{ij}' \frac{1}{Z^{\text{id}}[\beta, \lambda]} \sum_{N=0}^{\infty} \frac{1}{N! h^{3N}} \int dz_N \exp\left\{-\sum_{k}^{N} \mu(\mathbf{r}_k, \mathbf{p}_k)\right\} \delta(\mathbf{r} - \mathbf{q}_i) \delta(\mathbf{r}' - \mathbf{q}_j)$$

Note that

$$\int dz_N \exp\left\{-\sum_{k}^{N} \mu(\mathbf{r}_k, \mathbf{p}_k)\right\} \delta(\mathbf{r} - \mathbf{q}_i) \delta(\mathbf{r}' - \mathbf{q}_j)$$

$$= \int d\mathbf{p} d\mathbf{p}' \int dz_N \exp\left\{-\sum_{k}^{N} \mu(\mathbf{r}_k, \mathbf{p}_k)\right\} \delta(\mathbf{r} - \mathbf{q}_i) \delta(\mathbf{r}' - \mathbf{q}_j) \delta(\mathbf{p} - \mathbf{p}_i) \delta(\mathbf{p}' - \mathbf{p}_j)$$

$$= \int d\mathbf{p} d\mathbf{p}' \exp\left\{-\mu(\mathbf{r}, \mathbf{p}) - \mu(\mathbf{r}', \mathbf{p}')\right\} \left[\int d\mathbf{r}'' d\mathbf{p}'' \exp\left\{-\mu(\mathbf{r}'', \mathbf{p}'')\right\}\right]^{N-2}$$

Therefore

$$\left\langle \hat{U} \right\rangle^{\mu} = \int d\mathbf{r} d\mathbf{r}' \Phi(\mathbf{r} - \mathbf{r}') \frac{N(N-1)}{2} \frac{\int d\mathbf{p} d\mathbf{p}' \exp\left\{-\mu(\mathbf{r}, \mathbf{p}) - \mu(\mathbf{r}', \mathbf{p}')\right\}}{\left[\int d\mathbf{r}'' d\mathbf{p}'' \exp\left\{-\mu(\mathbf{r}'', \mathbf{p}'')\right\}\right]^2}$$

In summary, we have the following explicit form for the grand potential of a very weakly interacting gas

$$\Phi[\beta, \lambda] = -\int \frac{d\mathbf{r} d\mathbf{p}}{h^3} \exp\left\{-\mu(\mathbf{r}, \mathbf{p})\right\} + \beta\epsilon \frac{N(N-1)}{2} \int d\mathbf{r} d\mathbf{r}' \Phi(\mathbf{r} - \mathbf{r}') \frac{\int d\mathbf{p} d\mathbf{p}' \exp\left\{-\mu(\mathbf{r}, \mathbf{p}) - \mu(\mathbf{r}', \mathbf{p}')\right\}}{\left[\int d\mathbf{r}'' d\mathbf{p}'' \exp\left\{-\mu(\mathbf{r}'', \mathbf{p}'')\right\}\right]^2}$$

where $\mu(\mathbf{r}, \mathbf{p})$ is given in (22.6).

Non-Ideal gas

The ideal gas model is only appropriate when the particles of the gas are so far appart than the interactions can be neglected. For dense gases or fluids, we cannot neglect the interaction potential energy anymore, $\hat{U}(z) \neq 0$. In this case, we will still use the ideal gas model as a reference system and consider contributions to the free energy due to the interactions. This is in complete analogy with the Density Functional Theory level of description. In this way, we write the free energy functional of the system as a sum of ideal and interaction parts

$$F[f, \beta] = F^{\text{id}}[f, \beta] + F^{\text{int}}[f, \beta]$$

The interaction free energy allows us to introduce the direct correlation functions in phase space

$$\mathscr{C}^{(1)}(\mathbf{r}, \mathbf{p}) \equiv -\frac{\delta F^{\text{int}}[f, \beta]}{\delta f(\mathbf{r}, \mathbf{p})}$$

$$\mathscr{C}^{(2)}(\mathbf{r}, \mathbf{p}, \mathbf{r}', \mathbf{p}') \equiv -\frac{\delta^2 F^{\text{int}}[f, \beta]}{\delta f(\mathbf{r}, \mathbf{p}) \delta f(\mathbf{r}', \mathbf{p}')}$$

A most remarkable fact is that the interaction free energy $F^{\text{int}}[f, \beta]$ is given by the interaction free energy of the DFT level of description, this is

$$F^{\text{int}}[f, \beta] = F_{\text{DFT}}^{\text{int}}[n[f], \beta]$$

where $n[f]$ is the number density field corresponding to $f(\mathbf{r}, \mathbf{p})$, i.e.

$$n[f] \to n(\mathbf{r}) = \int d\mathbf{p} f(\mathbf{r}, \mathbf{p})$$

This is quite fortunate because all the knowledge that has been accumulated in the usual DFT can be directly incorporated to the level of Isothermal Kinetic Theory. As we show shortly, all the direct correlation functions in phase space $\mathscr{C}^{(n)}(\mathbf{r}_1, \mathbf{p}_1, \cdots, \mathbf{r}_n, \mathbf{p}_n)$ as defined in Eq. (22.6) are momentum independent and identical to the direct correlation functions in configuration space $c^{(n)}(\mathbf{r}_1, \cdots, \mathbf{r}_n)$.

The proof goes as follows. From Eqs. (22.6)-(22.6) we easily arrive at

$$f(\mathbf{r}, \mathbf{p}) = \frac{1}{h} \exp\left\{-\lambda(\mathbf{r}, \mathbf{p}) - \beta\left(\frac{p^2}{2m} + V^{\text{ext}}(\mathbf{r})\right) + \mathscr{C}^{(1)}(\mathbf{r}, \mathbf{p})\right\}$$

By taking the derivative of (22.6) with respect to the position we obtain the equation

$$\frac{\partial f}{\partial \mathbf{r}} = -f\frac{\partial \lambda}{\partial \mathbf{r}} - f\beta\frac{\partial V^{\text{ext}}}{\partial \mathbf{r}} + f\frac{\partial \mathscr{C}^{(1)}}{\partial \mathbf{r}}$$

However, from $f(\mathbf{r}, \mathbf{p}) = \text{Tr}[\rho \sum_i \delta(\mathbf{r} - \mathbf{r}_i)\delta(\mathbf{p} - \mathbf{p}_i)]$ it is possible to obtain also this derivative directly.

$$\frac{\partial}{\partial \mathbf{r}} f(\mathbf{r}, \mathbf{p}) = \frac{\partial}{\partial \mathbf{r}} \text{Tr}\left[\rho \sum_i \delta(\mathbf{r} - \mathbf{r}_i)\delta(\mathbf{p} - \mathbf{p}_i)\right] = \text{Tr}\left[\sum_i \delta(\mathbf{r} - \mathbf{r}_i)\delta(\mathbf{p} - \mathbf{p}_i)\frac{\partial}{\partial \mathbf{q}_i}\overline{\rho}\right]$$

By using the expression (22.6) for the relevant ensemble, we obtain

$$\frac{\partial}{\partial \mathbf{q}_i}\overline{\rho}(z) = -\overline{\rho}(z)\left[\beta\frac{\partial \hat{H}}{\partial \mathbf{q}_i} + \frac{\partial}{\partial \mathbf{q}_i}\lambda(\mathbf{q}_i, \mathbf{p}_i)\right]$$

By inserting this result into (22.6) we obtain, for pair wise interactions between particles,

the result

$$\frac{\partial f}{\partial \mathbf{r}} + f\frac{\partial \lambda}{\partial \mathbf{r}} + f\beta\frac{\partial V^{\text{ext}}}{\partial \mathbf{r}} = \beta \int d\mathbf{r}' d\mathbf{p}' \mathbf{F}(\mathbf{r} - \mathbf{r}')\langle \hat{f}_{\mathbf{rp}}\hat{f}_{\mathbf{r}',\mathbf{p}'}\rangle^\lambda$$

where $\mathbf{F}(\mathbf{r} - \mathbf{r}')$ is the force between two molecules at positions $\mathbf{r}, \mathbf{r}'$. The comparison of Eqs. (22.6) and (22.6) leads to the important result

$$\beta \int d\mathbf{r}' d\mathbf{p}' \mathbf{F}(\mathbf{r} - \mathbf{r}')\langle \hat{f}_{\mathbf{rp}}\hat{f}_{\mathbf{r}',\mathbf{p}'}\rangle^\lambda = f(\mathbf{r}, \mathbf{p})\frac{\partial \mathscr{C}^{(1)}(\mathbf{r}, \mathbf{p})}{\partial \mathbf{r}}$$

Now, if we take the momentum derivative of $f(\mathbf{r}, \mathbf{p})$ in Eq. (22.6) we get

$$\frac{\partial f}{\partial \mathbf{p}} = f\left[-\beta\frac{\mathbf{p}}{m} - \frac{\partial \lambda}{\partial \mathbf{p}} + \frac{\partial \mathscr{C}^{(1)}}{\partial \mathbf{p}}\right]$$

Again, this partial derivative can be computed directly from the definition (22.6) with the result

$$\frac{\partial f}{\partial \mathbf{p}} = f\left[-\beta\frac{\mathbf{p}}{m} - \frac{\partial \lambda}{\partial \mathbf{p}}\right]$$

Eqs. (22.6) and (22.6) together imply that the direct function $\mathscr{C}^{(1)}(\mathbf{r}, \mathbf{p}) = \mathscr{C}^{(1)}(\mathbf{r})$ is independent of momentum. Now, we want to show that $\mathscr{C}^{(1)}(\mathbf{r})$ is identical to the usual direct correlation function $c^{(1)}(\mathbf{r})$ of the DFT level of description.

To this end, we integrate both sides of Eq. (22.6) with respect to $\mathbf{p}$ to obtain

$$\beta \int d\mathbf{r}' \mathbf{F}(\mathbf{r} - \mathbf{r}')\langle \hat{n}_{\mathbf{r}}\hat{n}_{\mathbf{r}'}\rangle^\lambda = n(\mathbf{r})\frac{\partial \mathscr{C}^{(1)}(\mathbf{r})}{\partial \mathbf{r}}$$

At this point we want to relate the average $\langle \hat{n}_{\mathbf{r}}\hat{n}_{\mathbf{r}'}\rangle^\lambda$ with the average $\langle \hat{n}_{\mathbf{r}}\hat{n}_{\mathbf{r}'}\rangle^\phi$, which is defined as a usual equilibrium average in an external field $\phi(\mathbf{r})$. We introduce an auxiliary potential $\overline{\phi}(\mathbf{r})$ defined through

$$\exp\{-\beta\overline{\phi}(\mathbf{r})\} = \int d\mathbf{p} \exp\left\{-\lambda(\mathbf{r}, \mathbf{p}) - \beta\frac{p^2}{2m}\right\}$$

Clearly, $\overline{\phi}$ is a functional of the conjugate variable λ. We can now integrate the momentum variables that appear in the average $\langle \hat{n}_{\mathbf{r}}\hat{n}_{\mathbf{r}'}\rangle^\lambda$ with the result

$$\langle \hat{n}_{\mathbf{r}}\hat{n}_{\mathbf{r}'}\rangle^\lambda = \langle \hat{n}_{\mathbf{r}}\hat{n}_{\mathbf{r}'}\rangle^{\phi=\overline{\phi}}$$

This result can be inserted in the left hand side of Eq. (22.6)

$$\beta \int d\mathbf{r}' \mathbf{F}(\mathbf{r} - \mathbf{r}')\langle \hat{n}_{\mathbf{r}}\hat{n}_{\mathbf{r}'}\rangle^{\phi=\overline{\phi}} = n(\mathbf{r})\frac{\partial \mathscr{C}^{(1)}(\mathbf{r})}{\partial \mathbf{r}}$$

Eq. (57) of Ref. [?] shows that the left hand side of Eq. (22.6) is actually $n(\mathbf{r})\nabla c^{(1)}(\mathbf{r})$,

where $c^{(1)}(\mathbf{r})$ is the usual direct correlation function. Therefore we arrive at

$$\mathscr{C}^{(1)}(\mathbf{r}, \mathbf{p})[\lambda] = c^{(1)}(\mathbf{r})[\overline{\phi}[\lambda]]$$

Given the one to one connection between λ and f, we can understand this Eq (22.6) as a functional of f

$$\mathscr{C}^{(1)}(\mathbf{r}, \mathbf{p})[f] = c^{(1)}(\mathbf{r})[n[f]]$$

This shows that the direct correlation function in phase space $\mathscr{C}^{(1)}(\mathbf{r}, \mathbf{p})$, which depends functionally on f is identical to the direct correlation function in configuration space $c^{(1)}(\mathbf{r})$ evaluated at $n = \int d\mathbf{p} f(\mathbf{r}, \mathbf{p})$. As a result, all higher order direct correlations in phase space $\mathscr{C}^{(n)}(\mathbf{r}_1, \mathbf{p}_1, \cdots, \mathbf{r}_n, \mathbf{p}_n)$ as defined in Eq. (22.6) coincide with those in configuration space $c^{(n)}(\mathbf{r}_1, \cdots, \mathbf{r}_n)$ and, therefore, the interaction part of the entropy of the Isothermal Kinetic Theory level coincides with the interaction part of the Density Functional Theory level of description.

The following sum rule, which is equivalent to (22.6) will be used below

$$\beta \int d\mathbf{r}' d\mathbf{p}' \mathbf{F}(\mathbf{r} - \mathbf{r}') \langle \hat{f}_{\mathbf{rp}} \hat{f}_{\mathbf{r}',\mathbf{p}'} \rangle^{\lambda} = f(\mathbf{r}, \mathbf{p}) \frac{\partial c^{(1)}(\mathbf{r})}{\partial \mathbf{r}}$$

Note that, consistently, if we integrate Eq. (22.6) with respect to $\mathbf{p}'$ we obtain a well-known sum rule [?]

We may now get back to the form of the relevant ensemble (22.6)

$$\overline{\rho}(z) = \frac{1}{Z[\beta, \lambda]} \rho_0^N \exp \left\{ -\beta \hat{H}(z) - \sum_i^N \lambda(\mathbf{q}_i, \mathbf{p}_i) \right\}$$

By using (22.6), we can express (22.6) in the form

$$\overline{\rho}(z) = \frac{1}{Z[\beta, \lambda] N!} \prod_{i=1}^N f(\mathbf{q}_i, \mathbf{p}_i) \exp \left\{ \sum_i^N c^{(1)}(\mathbf{q}_i) - \beta \hat{U}(z) \right\}$$

This expression is to be compared with the relevant ensemble that is obtained in the ideal gas model given in (22.6). We observe that the interactions appear in the additional contribution $\exp \left\{ \sum_i^N c^{(1)}(\mathbf{q}_i) - \beta \hat{U}(z) \right\}$.

[I am willing to identify, in a "first order expansion" in the interaction strength, or density, the relevant ensemble with the ideal gas form of the relevant ensemble. I would like the following to be true

$$\left\langle \sum_i^N c^{(1)}(\mathbf{q}_i) \right\rangle_{\text{eq}} = \beta \left\langle \hat{U} \right\rangle_{\text{eq}}$$

which probably should be written in the form

$$\int d\mathbf{r} \frac{\delta \mathscr{F}}{\delta n(\mathbf{r})} n(\mathbf{r}) = \beta \overline{E}$$

that looks like an Euler theorem.]

22.7   TKT: Thermal Kinetic Theory $f(\mathbf{r}, \mathbf{p}), e(\mathbf{r})$.

[I think this is a better level of description because we can take advantadge of the entropy functional of the FTD level of description.]

22.8   TKT: Thermal Kinetic Theory $f(\mathbf{r}, \mathbf{p}, \epsilon)$.

This level of description is characterized by the following relevant variable

$$\hat{f}_{\mathbf{rp}\epsilon}(z) = \sum_i^N \delta(\mathbf{r} - \mathbf{q}_i)\delta(\mathbf{p} - \mathbf{p}_i)\delta(\epsilon - \phi_i)$$

where $\phi_i = \frac{1}{2}\sum_j \phi_{ij}$ is the potential energy of particle i, where we assume that the interaction is pair-wise and assign one half of the interaction energy to each element of the pair. The average of this relevant variable is denoted with

$$f(\mathbf{r}, \mathbf{p}, \epsilon) = \sum_{N=0}^{\infty} \frac{1}{N! h^{3N}} \int dz_N \rho(z_N) \hat{f}_{\mathbf{rp}\epsilon}(z)$$

The number of particles $\hat{\mathcal{N}}(z)$, the total momentum $\hat{\mathbf{P}}(z)$ and the total energy $H(z)$ can be expressed entirely as functionals of the relevant variable. Indeed,

$$\hat{N}(z) = \int d\mathbf{r} d\mathbf{p} d\epsilon \, \hat{f}_{\mathbf{rp}\epsilon}(z)$$

$$\hat{\mathbf{P}}(z) = \int d\mathbf{r} d\mathbf{p} d\epsilon \, \mathbf{p} \hat{f}_{\mathbf{rp}\epsilon}(z)$$

$$\hat{H}(z) = \int d\mathbf{r} d\mathbf{p} d\epsilon \left[\frac{\mathbf{p}^2}{2m} + V^{\text{ext}}(\mathbf{r}) + \epsilon \right] \hat{f}_{\mathbf{rp}\epsilon}(z)$$

Therefore, these dynamic invariants will not be considered in the list of CG variables.

The relevant ensemble (1.11.3) is now

$$\overline{\rho}(z) = \frac{1}{Z[\mu]} \rho_0^N \exp\left\{ -\int d\mathbf{r} \mathbf{p} d\epsilon \mu(\mathbf{r}, \mathbf{p}, \epsilon) \hat{f}_{\mathbf{rp}\epsilon}(z) \right\}$$

where the partition function is

$$Z[\mu] = \sum_{N=0}^{\infty} \frac{1}{N!h^{3N}} \int dz_N \exp\left\{-\sum_{i}^{N} \mu(\mathbf{q}_i, \mathbf{p}_i, \phi_i)\right\}$$

Note that due the fact that the potential energy of particle i depends on the coordinates of the rest of particles, the above integral does not decouple in integrals per particle.

The ideal gas

For the ideal gas, we have that the interaction energy is negligible, $\phi_i = 0$. This implies that

$$\hat{f}_{\mathbf{rp}\epsilon}(z) = \delta(\epsilon)\hat{f}_{\mathbf{rp}}(z)$$

The partition function now can be explicitly computed

$$Z[\mu] = \sum_{N=0}^{\infty} \frac{1}{N!h^{3N}} \int dz_N \exp\left\{-\sum_{i}^{N} \mu(\mathbf{q}_i, \mathbf{p}_i, 0)\right\} = \exp\left\{\frac{1}{h^3} \int d\mathbf{r} d\mathbf{p} \exp\left\{-\mu(\mathbf{r}, \mathbf{p}, 0)\right\}\right\}$$

The grand potential is

$$\Phi[\mu] = -\ln Z[\mu] = \frac{1}{h^3} \int d\mathbf{r} d\mathbf{p} \exp\left\{-\mu(\mathbf{r}, \mathbf{p}, 0)\right\}$$

22.9   The Bridge Theorem: How the entropies of two levels of description are related

These levels of description are listed in increased level of detail. Something that is characteristic of these levels is that the CG variables of one level of description are *linear functionals* of the finer levels of description. In particular

$$\overline{N} = \int d\mathbf{r}\, n(\mathbf{r})$$

$$\overline{E} = \int d\mathbf{r}\, e(\mathbf{r})$$

$$n(\mathbf{r}) = \int d\mathbf{p}\, f(\mathbf{r}, \mathbf{p})$$

$$\mathbf{g}(\mathbf{r}) = \int d\mathbf{p}\, f(\mathbf{r}, \mathbf{p})\mathbf{p}$$

We will see in the present section how the entropies of different levels of description are related when the relevant variables of the two levels of description are related through a linear functional. In this section, we show how the entropies (12.2) of two levels of descriptions are related. We consider two levels of description, characterized by the set

of phase functions $\hat{Y}(z), \hat{X}(z)$. We assume that $\hat{X}(z) = \mathscr{X}(\hat{Y}(z))$ and, therefore, the x-level is less detailed than the y-level of description (which, in turn, is less detailed than the microscopic level described by z). We may refer to y as fine grained (FG) variables and x as coarse-grained (CG) variables. The basic question that we want to answer in this subsection is what is the connection between the functional form of the entropy $S_x(x)$ and the entropy $S_y(y)$ of each level of description? Although we may consider a general functional $\mathscr{X}(y)$ form connecting the CG variables of different levels of description, we restrict ourselves to a linear relationship of the form

$$\hat{X}(z) = A\hat{Y}(z)$$

where A is a rectangular constant matrix. It turns out that this connection between levels of descriptions is, in fact, quite common and, in particular, the levels of MT, DFT and FTD have CG variables connected in a linear way.

The maximization of the entropy functional (12.2) subject to give prescribed averages $y = \mathrm{Tr}[\rho Y]$ or $x = \mathrm{Tr}[\rho X]$ give the two relevant ensembles of each level of description

$$\overline{\rho}_y(z) = \rho^0 \frac{\exp\{-\lambda_y \hat{Y}(z)\}}{Z_y(\lambda_y)}$$

$$\overline{\rho}_x(z) = \rho^0 \frac{\exp\{-\lambda_x \hat{X}(z)\}}{Z_x(\lambda_x)}$$

where λ_y and λ_x are the Lagrange multiplier enforcing the constraints

$$y = \mathrm{Tr}[\overline{\rho}_y Y]$$
$$x = \mathrm{Tr}[\overline{\rho}_x X]$$

respectively. In addition, we will enforce that the averages are related according to $x = Ay$. This implies, for example, that the average of the CG variable $\hat{X}(z)$ with respect the relevant ensemble of the FG y-level is precisely x, this is

$$\mathrm{Tr}\left[\overline{\rho}_y X\right] = x$$

This is a condition on the possible values that y may take, given x.

The entropies of each level of description are given by (12.2) which now take the form

$$S_y(y) = \ln Z_y(y) + \lambda_y(y)y$$
$$S_x(x) = \ln Z_x(x) + \lambda_x(x)x$$

Consider now the maximum y^* of $S_y(y)$ subject to the restriction (22.9). The state y^* is obviously a function of x appearing in the restriction (22.9). It is easily shown that by evaluating $S_y(y)$ at y^* we obtain precisely $S_x(x)$, this is

$$S_y(y^*(x)) = S_x(x)$$

In order to prove this, let us maximize without constraints the function

$$S_y(y) - \mu \mathrm{Tr}\left[\overline{\rho}_y X\right] = S_y(y) - \mu \mathrm{Tr}\left[\overline{\rho}_y AY\right]$$
$$= S_y(y) - \mu Ay$$

where μ is the set of Lagrange multipliers enforcing (22.9). The derivative of this function equated to zero is

$$\lambda_y(y^*) - \mu A = 0$$

This is an implicit equation for y^* that will depend parametrically on μ. The actual value of μ is obtained by requiring the fulfilment of the constraint (22.9) that now becomes

$$\mathrm{Tr}\left[\overline{\rho}_{y^*} AY\right] = x \quad \rightarrow \quad Ay^* = x$$

In this way, for every particular x, we have a given $\mu(x)$. Finally, the entropy of the y-level, evaluated at this particular maximum becomes

$$\begin{aligned}
S_y(y^*) &= \ln Z_y(\lambda_y(y^*)) + \lambda_y(y^*)y^* \\
&= \ln \mathrm{Tr}\left[\exp\{-\lambda_y(y^*)Y\}\right] + \lambda_y(y^*)y^* \\
&= \ln \mathrm{Tr}\left[\exp\{-\mu(x)AY\}\right] + \mu(x)Ay^* \\
&= \ln \mathrm{Tr}\left[\exp\{-\mu(x)X\}\right] + \mu(x)x \\
&= \phi(x)
\end{aligned}$$

We have to prove still that $\phi(x) = S_x(x)$. Consider again (22.9) now with the relevant ensemble $\overline{\rho}_{y^*}$ (22.9) corresponding to y^*, this is

$$\frac{\mathrm{Tr}\left[\rho_0 \exp\{-\lambda_y(y^*)Y\}X\right]}{\mathrm{Tr}\left[\rho_0 \exp\{-\lambda_y(y^*)Y\}\right]} = x$$

Use Eq. (22.9) in this last equation to obtain

$$\frac{\mathrm{Tr}\left[\rho_0 \exp\{-\mu(x)X\}X\right]}{\mathrm{Tr}\left[\rho_0 \exp\{-\mu(x)X\}\right]} = x$$

This is to be compared with the second equation in (22.9) that takes the form

$$\frac{\mathrm{Tr}\left[\rho_0 \exp\{-\lambda_x(x)X\}X\right]}{\mathrm{Tr}\left[\rho_0 \exp\{-\lambda_x(x)X\}\right]} = x$$

Because the connection between the averages x and the conjugate variables $\lambda_x(x)$ is unique, it follows that $\mu(x) = \lambda_x(x)$ and therefore, $\phi(x) = S_x(x)$, this is

$$S_y(y^*) = S_x(x)$$

The Bridge Theorem can be expressed in very compact form as follows

$$\max_{\text{Tr}[\rho Ay]=x} \mathscr{S}[\rho] = \max_{x=Ay}\left[\max_{\text{Tr}[\rho Y]=y} \mathscr{S}[\rho]\right]$$

In words, the left hand side finds the maximum of the Gibbs entropy functional $\mathscr{S}[\rho]$ for those ensembles in the subset satisfying $\text{Tr}[\rho Y] = y$ and then the maximum in the smaller, but fully contained subset of ensembles fulfilling $x = Ay$, while the right hand side finds the maximum in the set $\text{Tr}[\rho Ay] = x$ directly. Dwandaru and Schmidt [?] have recently considered this double maximization process when relating the DFT and MT levels of description. In the entropy language, their Eqs. (43)-(44) in Ref. [?] become

$$\max_{\substack{\text{Tr}[\rho H]=E \\ \text{Tr}[\rho H]=N}} \mathscr{S}[\rho] = \max_{\int d\mathbf{r}n(\mathbf{r})=N}\left[\max_{\substack{\text{Tr}[\rho H]=E \\ \text{Tr}[\rho \hat{n}_{\mathbf{r}}]=n(\mathbf{r})}} \mathscr{S}[\rho]\right]$$

The left hand side is just the usual macroscopic thermodynamic entropy while the term inside brackets of the right hand side is the entropy functional at the DFT level of description. Eq. (22.9) is just a particular realization of the general Bridge Theorem (22.9).

In conclusion, if we know the entropy of a FG level of description, we automatically know the entropy of any CG level of description whose CG variables are linear combinations of the FG variables. The recipe is simple: maximize the entropy of the FG level subject to the constraint that the average of the FG variables gives the CG variables, and substitute back this maximum value into the entropy of the FG level. The result is the entropy at the CG level.

The Bridge Theorem (22.9) is a generalization of the second part of Mermin's theorem that allows one to connect the entropies of different levels of descriptions provided that the CG variables of each level are connected in a linear functional form. When the level of description is DFT the above theorem is just the original Mermin theorem [?]. The Bridge Theorem (22.9) can be of great importance as a guiding tool for the construction of the entropy functional of detailed levels of description if we know the corresponding entropy at CG levels of description (like Macroscopic Thermodynamics or Density Functional Theory). In a similar way, it allows to compute the entropy of MT from molecular models that we may construct for the entropy at the DFT or FTD levels of description.

Connection of the DFT level with the level of Thermostatics

Note that if one gives $n(\mathbf{r})$ one is, in fact, providing the average number of particles in the system, because

$$\langle N \rangle = \int d\mathbf{r}n(\mathbf{r})$$

In this way, the MT level of description is obtained from the DFT level of description through a linear relationship between the coarse-grained variables $\hat{\mathcal{N}}(z), \hat{\mathscr{E}}(z)$ and the fine-grained variables $n_{\mathbf{r}}(z), \hat{H}(z)$. Therefore, the Theorem (22.9) applies and the MT entropy is completely determined from the DFT entropy. The entropy functional of the

DFT level allows one to obtaining the equilibrium profile $n^{\text{eq}}(\mathbf{r})$ by maximization of the functional (**??**) subject to have an average number of particles $\overline{N}$ and average energy $\overline{E}$. In fact, we have to maximize with respect to $n(\mathbf{r})$ without constraints the following functional

$$S[n, \overline{E}] + \mu \int d\mathbf{r} n(\mathbf{r})$$

Here μ is the Lagrange multipliers that enforces that the average number of particles is N. Note that this maximization is equivalent to obtaining the extremum of $F[n, (\beta)] - \mu \int d\mathbf{r} n(\mathbf{r})$, which is the usual recipe in DFT.

By taking the functional derivative with respect to $n(\mathbf{r})$ we have that the equilibrium solution is characterized by

$$\lambda(\mathbf{r})[n^{\text{eq}}, \overline{E}] = \mu_0$$

By solving this functional equation, we obtain the equilibrium profile $n^{\text{eq}}(\mathbf{r})$ when the system has an average number of particles N and an energy E. This solution depends parametrically on μ_0 and can be denoted as $n^{\text{eq}}(\mathbf{r})(\mu_0)$. The value of μ_0 is obtained from the request that $n^{\text{eq}}(\mathbf{r})$ corresponds, in fact, to having an average N of particles, this is,

$$\int d\mathbf{r} n^{\text{eq}}(\mathbf{r})(\mu_0) = N$$

This is an implicit equation for μ_0. Once obtained, the equilibrium average is a function of N, E, this is $n^{\text{eq}}(\mathbf{r})(N, E)$.

Finally, the MT entropy $S(N, E)$ and the entropy at the DFT level are related according to theorem (22.9), this is

$$S(N, E) = S[n^{\text{eq}}(N, E), \overline{E}]$$

This is, by evaluating the equilibrium profile into the DFT entropy functional we recover the macroscopic thermodynamic entropy function.

Connection of FTD with MT and DFT

The MT level of description and the DFT level of description can be *both* obtained from the Functional Thermodynamics level of description because the CG variables of the former can be obtained as linear combinations of the fine grained variables $n_{\mathbf{r}}(z), e_{\mathbf{r}}(z)$. Therefore, the theorem (22.9) applies and, consequently, if we know the entropy at the FTD level of description, we know both the entropy at the MT level of description and at the DFT level of description. Let us discuss the connection with each level separately.

Connection with MT

Note that the averages $n(\mathbf{r}), e(\mathbf{r})$ which are computed with the relevant ensemble (22.4) do not correspond to the *equilibrium* averages of the number density and energy density, *except* when the Lagrange multipliers are constant functions λ_0, β_0. In this case, the relevant ensemble (22.4) becomes an equilibrium ensemble with parameters λ_0, β_0. Because

of Eq. (22.4), the conditions

$$\lambda(\mathbf{r}) = \lambda_0$$
$$\beta(\mathbf{r}) = \beta_0$$

can be understood, in fact, as two functional equations to be satisfied by the equilibrium averages $n^{\mathrm{eq}}(\mathbf{r}), e^{\mathrm{eq}}(\mathbf{r})$, this is

$$\frac{\delta S_{\mathrm{FTD}}[n^{\mathrm{eq}}, e^{\mathrm{eq}}]}{\delta n(\mathbf{r})} = \lambda_0$$
$$\frac{\delta S_{\mathrm{FTD}}[n^{\mathrm{eq}}, e^{\mathrm{eq}}]}{\delta e(\mathbf{r})} = \beta_0$$

In turn, these equations can be obtained also from the maximization of the following functional

$$S_{\mathrm{FTD}}[n, e] - \beta_0 \int d\mathbf{r}\, n(\mathbf{r}) - \lambda_0 \int d\mathbf{r}\, e(\mathbf{r})$$

In this way, the equilibrium averages $n^{\mathrm{eq}}(\mathbf{r}), e^{\mathrm{eq}}(\mathbf{r})$ are the ones that maximize the functional (22.9). This is equivalent to maximizing the FTD entropy functional subject to the constraint that the average number of particles and energy are N, E. The solution of (22.9) gives $n^{\mathrm{eq}}(\mathbf{r}), e^{\mathrm{eq}}(\mathbf{r})$ that will depend parametrically on λ_0, β_0. By requesting that the constraints

$$\int d\mathbf{r}\, n^{\mathrm{eq}}(\mathbf{r}) = N$$

$$\int d\mathbf{r}\, e^{\mathrm{eq}}(\mathbf{r}) = E$$

are fullfilled, we get the implicit connection between the Lagrange multipliers λ_0, β_0 and N, E. The equilibrium profiles $n^{\mathrm{eq}}(\mathbf{r}), e^{\mathrm{eq}}(\mathbf{r})$ depend, therefore, parametrically on N, E.

Note that the recipe just obtained (maximizing (22.9)) to compute the equilibrium profiles coincides exactly with the recipe given by Theorem (22.9) that we would need to follow in order to obtain the MT entropy out of the FTD entropy. Because of that theorem, the MT entropy $S(N, E)$ is obtained from the substitution of the equilibrium profiles into the FTD entropy, this

$$S_{\mathrm{MT}}(N, E) = S_{\mathrm{FTD}}[n^{\mathrm{eq}}(N, E), e^{\mathrm{eq}}(N, E)]$$

Connection with DFT

DFT is a CG level of description with respect to FTD characterized by relevant variables that are linear combinations of the FTD relevant variables. Therefore, the entropy of the DFT level of description can be obtained, according to the Theorem (22.9) from the

entropy of the FTD level by maximizing the last one subject to give the restrictions

$$n(\mathbf{r}) = n_0(\mathbf{r})$$

$$\int d\mathbf{r} e(\mathbf{r}) = E$$

The unconstrained functional to maximize is now

$$S_{\mathrm{FTD}}[n, e] - \int d\mathbf{r} \lambda(\mathbf{r}) n(\mathbf{r}) - \beta_0 \int d\mathbf{r} e(\mathbf{r})$$

The maximum occurs at $n^*(\mathbf{r}), e^*(\mathbf{r})$ which are the solution of

$$\frac{\delta S_{\mathrm{FTD}}[n^*(\mathbf{r}), e^*(\mathbf{r})]}{\delta n(\mathbf{r})} = \lambda(\mathbf{r})$$

$$\frac{\delta S_{\mathrm{FTD}}[n^*(\mathbf{r}), e^*(\mathbf{r})]}{\delta e(\mathbf{r})} = \beta_0$$

The profiles $n^*(\mathbf{r}), e^*(\mathbf{r})$ depend on $\lambda(\mathbf{r}), \beta_0$ and, after substitution into the constraints (I), we obtain the dependence of $\lambda(\mathbf{r}), \beta_0$ on $n_0(\mathbf{r}), E$. Therefore, we have the profiles $n^*(\mathbf{r}), e^*(\mathbf{r})$ as functions of $n_0(\mathbf{r}), E$, this is

$$n^*(\mathbf{r}) = n_0(\mathbf{r})$$

$$e^*(\mathbf{r}) = e^*(\mathbf{r})[n_0(\mathbf{r}), \overline{E}]$$

According to the Theorem (22.9), substitution of (I) into the FTD entropy leads to the DFT entropy, this is

$$S_{\mathrm{FTD}}(n_0(\mathbf{r}), e^*(\mathbf{r})[n_0(\mathbf{r}), \overline{E}]) = S_{\mathrm{DFT}}[n_0(\mathbf{r}), \overline{E}]$$

Note that by comparing (**??**) and (22.4) we arrive at the following relationship between the dimensionles grand potentials (**??**) and (22.4),

$$\Phi_{\mathrm{DFT}}[\lambda(\mathbf{r}), (\beta_0)] = \Phi_{\mathrm{FTD}}[\lambda(\mathbf{r}), \beta_0]$$

This is, the grand dimensionless potential at the DFT level is obtained from the grand dimensionless potential at the FTD level by simply setting the Lagrange multiplier to a constant $\beta(\mathbf{r}) = \beta_0$.

23

Microcanonical averages

23.0.1   Appendix: Microcanonical averages

Let us consider the vector space R^M whose elements are vectors $\mathbf{x}$. The integral of an arbitrary function $F(\mathbf{x}) = f(|\mathbf{x}|)$ that depends on $\mathbf{x}$ only through its modulus can be computed by changing to polar coordinates

$$\int F(\mathbf{x})d^N\mathbf{x} = \omega_N \int_0^\infty f(r)r^{N-1}dr$$

The numerical factor ω_N, which cames from the integration of the angles, can be computed by considering the special case when $f(r)$ is a Gaussian. The result is

$$\omega_N = 2\frac{\pi^{N/2}}{\Gamma(N/2)}$$

By using Eqn. (24.5.1) we can compute the following integral

$$\int \delta(|\mathbf{x}|^2 - E)d^N\mathbf{x} = \omega_N \int_0^\infty \delta(r^2 - E)r^{N-1}dr$$

We need now the property

$$\delta(f(x)) = \sum_i \frac{\delta(x - x_i)}{|f'(x_i)|}$$

where x_i are the zeros of $f(x_i) = 0$. For the case of Eqn. (24.5.3) we have $f(x) = x^2 - E$, $x_i = \pm E^{1/2}$ and $f'(x) = 2x$. Therefore,

$$\int \delta(|\mathbf{x}|^2 - E)d^N\mathbf{x} = \omega_N \int_0^\infty \frac{\delta(r - E^{1/2})}{2r}r^{N-1}dr$$

$$= \frac{1}{2}\omega_N E^{\frac{N-2}{2}}$$

Now we want to consider the following integral

$$\Omega_0 = \int d^{DN}\mathbf{p}\,\delta^D\delta\left(\sum_i^N \frac{p_i^2}{2m_i} - E\right) = \prod_i^N (2m_i)^{D/2} \int d^{DN}\mathbf{p}\,\delta\left(\sum_i^N p_i^2 - E\right)$$

$$= (2m)^{DN/2}\frac{1}{2}\omega_{DN}E^{\frac{DN}{2}}$$

24

Gaussian integrals

24.1 Gaussian integrals with non-singular Hessian

24.1.1 Generating function

We first recall how to compute the following Gaussian integral

$$\Omega_0(J) = \int dx \exp\left\{-\frac{1}{2}x^T A x + J^T x\right\}$$

where $x \in \mathbb{R}^N$, $J \in \mathbb{R}^N$, and the Hessian matrix $A \in \mathbb{R}^{N \times N}$ is invertible. Introduce the rotated variables $x' = Rx$, $J' = RJ$ where the rotation matrix R ($R^T R = RR^T = 1$) is the one that diagonalizes the symmetric matrix $RAR^T = D$. Then

$$
\begin{aligned}
\Omega_0(J) &= \int dx' \exp\left\{-\frac{1}{2}x'^T D x + J'x'\right\} \\
&= \int dx'_1 \cdots dx'_N \exp\left\{-\sum_{i=1}^N \left[\frac{d_i}{2}x_i'^2 - J_i'x_i'\right]\right\} \\
&= \int dx'_1 \cdots dx'_N \exp\left\{-\sum_{i=1}^N \left[\frac{d_i}{2}\left(x_i' - \frac{J_i'}{d_i}\right)^2 - \frac{J_i'^2}{2d_i}\right]\right\} \\
&= \exp\left\{\sum_{i=1}^N \frac{J_i'^2}{2d_i}\right\} \prod_{i=1}^N \int dx_i \exp\left\{-\frac{d_i}{2}x_i^2\right\} = \exp\left\{\sum_{i=1}^N \frac{J_i'^2}{2d_i}\right\} \prod_{i=1}^N \frac{(2\pi)^{1/2}}{d_i^{1/2}} = \frac{(2\pi)^{N/2}}{\det A^{1/2}} \exp\left\{\frac{1}{2}J^T A^{-1} J\right\}
\end{aligned}
$$

24.1.2   Gaussian moments

Then

$$\langle x_i \cdots x_j \rangle \equiv \frac{\det[A]^{1/2}}{(2\pi)^{N/2}} \int d^N x (x_i \cdots x_j) \exp\left\{-\frac{1}{2}x^T A x + J^T x\right\} = \lim_{J \to 0} \frac{\partial}{\partial J_i} \cdots \frac{\partial}{\partial J_j} \exp\left\{\frac{1}{2}J^T A^{-1} J\right\}$$

We define the following shortcuts

$$G = \exp\left\{\frac{1}{2}J^T A^{-1} J\right\}$$

$$\partial_i G = \frac{\partial}{\partial J_i}G = GP_i$$

$$P_i = A_{ij'}^{-1} J_{j'}$$

$$\partial_j P_i = A_{ij}^{-1}$$

Example

$$\langle x_i x_j \rangle = \partial_i \partial_j G = \partial_i G P_j = G(P_i P_j + A_{ij}^{-1})$$

$$\langle x_i x_j x_k \rangle = \partial_k G(P_i P_j + A_{ij}^{-1}) = GP_k(P_i P_j + A_{ij}^{-1}) + G(A_{ik}^{-1} P_j + A_{jk}^{-1} P_i)$$
$$= G(P_k P_i P_j + A_{ij}^{-1} P_k + A_{ik}^{-1} P_j + A_{jk}^{-1} P_i)$$

$$\langle x_i x_j x_k x_l \rangle = \partial_l G(P_k P_i P_j + A_{ij}^{-1} P_k + A_{ik}^{-1} P_j + A_{jk}^{-1} P_i)$$
$$= GP_l(P_k P_i P_j + A_{ij}^{-1} P_k + A_{ik}^{-1} P_j + A_{jk}^{-1} P_i) + G(\partial_l(P_k P_i P_j) + A_{ij}^{-1} A_{kl}^{-1} + A_{ik}^{-1} A_{jl}^{-1} + A_{jk}^{-1} A_{il}^{-1})$$
$$= G(P_l P_k P_i P_j + A_{ij}^{-1} P_l P_k + A_{ik}^{-1} P_l P_j + A_{jk}^{-1} P_l P_i + + P_i P_j A_{kl}^{-1} + P_k P_j A_{il}^{-1} + P_k P_i A_{jl}^{-1}$$
$$+ G(A_{ij}^{-1} A_{kl}^{-1} + A_{ik}^{-1} A_{jl}^{-1} + A_{jk}^{-1} A_{il}^{-1})$$

$$\langle x_1 x_2 x_3 x_4 x_5 \rangle = \partial_5 \langle x_1 x_2 x_3 x_4 \rangle$$
$$= GP_5(P_1 P_2 P_3 P_4 + A_{12}^{-1} P_3 P_4 + A_{13}^{-1} P_2 P_4 + A_{14}^{-1} P_2 P_3 + A_{23}^{-1} P_1 P_4 + A_{24}^{-1} P_1 P_3 + A_{34}^{-1} P_1 P_2)$$
$$+ GP_5(A_{12}^{-1} A_{34}^{-1} + A_{13}^{-1} A_{24}^{-1} + A_{14}^{-1} A_{23}^{-1})$$
$$+ G(\partial_5 P_1 P_2 P_3 P_4 + A_{12}^{-1} A_{35}^{-1} P_4 + A_{12}^{-1} A_{45}^{-1} P_4 + A_{13}^{-1} A_{25}^{-1} P_4 + A_{13}^{-1} A_{45}^{-1} P_2 + A_{14}^{-1} A_{25}^{-1} P_3 + A_{14}^{-1} A_{35}^{-1} P_2$$
$$+ A_{23}^{-1} A_{15}^{-1} P_4 + A_{23}^{-1} A_{45}^{-1} P_1 + A_{24}^{-1} A_{15}^{-1} P_3 + A_{24}^{-1} A_{35}^{-1} P_1 + A_{34}^{-1} A_{15}^{-1} P_2 + A_{34}^{-1} A_{25}^{-1} P_1$$

$$\langle x_1 x_2 x_3 x_4 x_5 x_6 \rangle = \partial_6 \langle x_1 x_2 x_3 x_4 x_6 \rangle$$
$$= A_{12}^{-1} A_{34}^{-1} A_{56}^{-1} + A_{13}^{-1} A_{24}^{-1} A_{56}^{-1} + A_{14}^{-1} A_{23}^{-1} A_{56}^{-1}$$
$$+ A_{12}^{-1} A_{35}^{-1} A_{46}^{-1} + A_{12}^{-1} A_{45}^{-1} A_{46}^{-1} + A_{13}^{-1} A_{25}^{-1} A_{46}^{-1}$$
$$+ A_{14}^{-1} A_{25}^{-1} A_{36}^{-1} + A_{24}^{-1} A_{15}^{-1} A_{36}^{-1} + A_{21}^{-1} A_{45}^{-1} A_{36}^{-1}$$
$$+ A_{13}^{-1} A_{45}^{-1} A_{26}^{-1} + A_{14}^{-1} A_{35}^{-1} A_{26}^{-1} + A_{34}^{-1} A_{15}^{-1} A_{26}^{-1}$$
$$+ A_{23}^{-1} A_{45}^{-1} A_{16}^{-1} + A_{24}^{-1} A_{35}^{-1} A_{16}^{-1} + A_{34}^{-1} A_{25}^{-1} A_{16}^{-1}$$

$$\langle x_1 x_2 x_3 x_4 \rangle = A_{12}^{-1} A_{34}^{-1} + A_{13}^{-1} A_{24}^{-1} + A_{14}^{-1} A_{23}^{-1}$$

In our case the matrix A_{ij} is diagonal

$$\langle \cdots \rangle = \frac{1}{Z} \int d^N Q d^N P \exp \left\{ -\beta \sum_{k=0}^{N-1} \left[\frac{m\omega_k^2}{2} Q_k^2 + \frac{1}{2m} P_k^2 \right] \right\} \cdots$$

This is for positions

$$A_{12} = \frac{m\omega_1^2}{k_B T} \delta_{12}$$
$$A_{12}^{-1} = \frac{k_B T}{m\omega_1^2} \delta_{12}$$

and for momenta

$$A_{12} = \frac{1}{m k_B T} \delta_{12}$$
$$A_{12}^{-1} = m k_B T \delta_{12}$$

For example

$$\langle Q_k Q_{k'} \rangle = \frac{1}{Z} \int d^N Q Q_k Q_{k'} \exp \left\{ -\beta \sum_{k=0}^{N-1} \frac{m\omega_k^2}{2} Q_k^2 \right\} = \frac{k_B T}{m\omega_k^2} \delta_{kk'}$$

$$\langle Q_{k_1} Q_{k_2} Q_{k_3} Q_{k_4} \rangle = \left(\frac{k_B T}{m} \right)^2 \left[\frac{1}{\omega_2^2 \omega_3^2} \delta_{12} \delta_{34} + \frac{1}{\omega_1^2 \omega_2^2} \delta_{13} \delta_{24} + \frac{1}{\omega_1^2 \omega_3^2} \delta_{14} \delta_{23} \right]$$

$$\langle Q_{k_1} Q_{k_2} Q_{k_3} Q_{k_4} Q_{k_5} Q_{k_6} \rangle = (k_B T/m)^3 \times$$

$$\frac{1}{\omega_1^2 \omega_3^2 \omega_6^2} \delta_{12} \delta_{34} \delta_{56} + \frac{1}{\omega_1^2 \omega_4^2 \omega_6^2} \delta_{13} \delta_{24} \delta_{56} + \frac{1}{\omega_1^2 \omega_2^2 \omega_6^2} \delta_{14} \delta_{23} \delta_{56}$$

$$+ \frac{1}{\omega_1^2 \omega_5^2 \omega_6^2} \delta_{12} \delta_{35} \delta_{46} + \frac{1}{\omega_3^2 \omega_5^2 \omega_6^2} \delta_{13} \delta_{25} \delta_{46} + \frac{1}{\omega_3^2 \omega_5^2 \omega_6^2} \delta_{15} \delta_{32} \delta_{46}$$

$$+ \frac{1}{\omega_1^2 \omega_5^2 \omega_6^2} \delta_{14} \delta_{25} \delta_{36} + \frac{1}{\omega_4^2 \omega_5^2 \omega_6^2} \delta_{24} \delta_{15} \delta_{36} + \frac{1}{\omega_2^2 \omega_5^2 \omega_6^2} \delta_{21} \delta_{45} \delta_{36}$$

$$+ \frac{1}{\omega_1^2 \omega_5^2 \omega_6^2} \delta_{13} \delta_{45} \delta_{26} + \frac{1}{\omega_4^2 \omega_5^2 \omega_6^2} \delta_{14} \delta_{35} \delta_{26} + \frac{1}{\omega_3^2 \omega_5^2 \omega_6^2} \delta_{34} \delta_{15} \delta_{26}$$

$$+ \frac{1}{\omega_3^2 \omega_5^2 \omega_6^2} \delta_{23} \delta_{45} \delta_{16} + \frac{1}{\omega_2^2 \omega_5^2 \omega_6^2} \delta_{24} \delta_{35} \delta_{16} + \frac{1}{\omega_4^2 \omega_5^2 \omega_6^2} \delta_{34} \delta_{25} \delta_{16}$$

and

$$\langle P_k P_{k_1} P_{k_2} P_{k_3} \rangle = \frac{1}{Z} \int d^N P P_k P_{k_1} P_{k_2} P_{k_3} \exp \left\{ -\beta \sum_{k=0}^{N-1} \frac{1}{2m} P_k^2 \right\} = (k_B T m)^2 \left(\delta_{k k_1} \delta_{k_2 k_3} + \delta_{k k_2} \delta_{k_1 k_3} + \delta_{k k_3} \delta_{k_1 k_2} \right)$$

Averages of arbitrary functions

A general result for multidimensional integrals of Gaussian functions

$$\int d^M \mathbf{k} f(\mathbf{k}) \exp \left\{ -\frac{1}{2} \mathbf{k}^T \mathbf{A} \mathbf{k} \right\} = \frac{(2\pi)^{M/2}}{\det \mathbf{A}} \exp \left\{ \mathcal{L} \right\} f(\mathbf{k}) \Big|_{\mathbf{k}=0}$$

where the differential operator $\mathcal{L}$ is defined by

$$\mathcal{L} \equiv -\frac{1}{2} \mathbf{A}_{\mu\nu} \frac{\partial}{\partial \mathbf{k}_\mu} \frac{\partial}{\partial \mathbf{k}_\nu}$$

and the operator $\exp\{\mathcal{L}\}$ is defined through the Taylor series of the exponential. For example, take $f(\mathbf{k}) = \cos(\mathbf{a}\cdot\mathbf{k})$, then we have that $\mathscr{L} \cos(\mathbf{a}\cdot\mathbf{k}) = \alpha \cos(\mathbf{a}\cdot\mathbf{k})$ with $\alpha = -\frac{1}{2} \mathbf{A}_{\mu\nu} a_\mu a_\nu$. Therefore, the action of the exponential operator is simply $\exp\{\mathscr{L}\} \cos(\mathbf{a}\cdot\mathbf{k}) = \exp\{\alpha\} \cos(\mathbf{a}\cdot\mathbf{k})$.

24.1.3   CG probability

Consider a probability distributions of the form

$$\Omega(y, J) = \frac{1}{\Omega_0(J)} \int dx \exp\left\{-\frac{1}{2}x^T A x + J^T x\right\} \delta(\Pi x - y)$$

where $x \in \mathbb{R}^N$, $y \in \mathbb{R}^M$, $A \in \mathbb{R}^{N \times N}$ is invertible, $\Pi \in \mathbb{R}^{M \times N}$ is rectangular matrix, and $J \in \mathbb{R}^N$. The normalization factor is given by Eq. (24.1.1). We start first with the numerator integral and we introduce the Fourier transform of the Dirac delta function in order to compute

$$\int dx \exp\left\{-\frac{1}{2}x^T A x + J^T x\right\} \delta(\Pi x - y)$$

$$= \int \frac{d\lambda}{(2\pi)^M} \exp\{-i\lambda^T y\} \int dx \exp\left\{-\frac{1}{2}x^T A x + J^T x\right\} \exp\{i\lambda^T \Pi x\}$$

$$= \int \frac{d\lambda}{(2\pi)^M} \exp\{-i\lambda y\} \int dx \exp\left\{-\frac{1}{2}x^T A x + (J + i\Pi^T \lambda)^T x\right\}$$

$$= \int \frac{d\lambda}{(2\pi)^M} \exp\{-i\lambda y\} \frac{(2\pi)^{N/2}}{\det A^{1/2}} \exp\left\{\frac{1}{2}(J + i\Pi^T \lambda)^T A^{-1}(J + i\Pi^T \lambda)\right\}$$

$$= \frac{(2\pi)^{N/2}}{\det A^{1/2}} \int \frac{d\lambda}{(2\pi)^M} \exp\{-i\lambda y\} \exp\left\{\frac{1}{2}(J + i\Pi^T \lambda)^T A^{-1}(J + i\Pi^T \lambda)\right\}$$

$$= \frac{(2\pi)^{N/2}}{\det A^{1/2}} \int \frac{d\lambda}{(2\pi)^M} \exp\{-i\lambda(y + \Pi A^{-1}J)\} \exp\left\{-\frac{1}{2}\lambda^T \Pi A^{-1}\Pi^T \lambda + \frac{1}{2}J^T A^{-1}J\right\}$$

$$= \frac{(2\pi)^{N/2}}{\det A^{1/2}} \frac{\det \overline{A}^{1/2}}{(2\pi)^{M/2}} \exp\left\{-\frac{1}{2}(y + \Pi A^{-1}J)^T \overline{A}(y + \Pi A^{-1}J) + \frac{1}{2}J^T A^{-1}J\right\}$$

where we have introduced the *coarse-grained inverse matrix* $\overline{A} \in \mathbb{R}^{M \times M}$ as

$$\overline{A} \equiv \left[\Pi A^{-1}\Pi^T\right]^{-1}$$

provided that the inverse exists. For future reference, consider the eigenvectors $\overline{v}_\mu$ of the matrix $\overline{A}^{-1} = \Pi A^{-1}\Pi^T$, this is $\overline{A}^{-1}\overline{v}_\mu = \overline{d}_\mu \overline{v}_\mu$. We may write the matrix $\overline{A}$ as

$$\overline{A} = \sum_{\mu=1}^{M} \overline{v}_\mu \frac{1}{\overline{d}_\mu} \overline{v}_\mu^T$$

Finally, the probability (24.1.3) is given by

$$\Omega(y, J) = \frac{\det \overline{A}^{1/2}}{(2\pi)^{M/2}} \exp\left\{-\frac{1}{2}(y + \Pi A^{-1}J)^T \overline{A}(y + \Pi A^{-1}J)\right\}$$

24.1.4   Gaussian conditional moments

We may be interested in computing the following moments

$$\langle x_i \cdots x_j \rangle^y \equiv \frac{1}{\Omega_0(J)} \int dx\, x_i \cdots x_j \exp\left\{ -\frac{1}{2} x^T A x + J^T x \right\} \delta(\Pi x - y)$$

24.1.5 Probability in anharmonic perturbation theory

Consider probability distributions of the form

$$\Omega(y, \epsilon) = \frac{1}{\Omega_1} \int dx \exp\left\{-\frac{1}{2}x^T A x - \epsilon V(x)\right\} \delta(\Pi x - y)$$

Here, $x \in \mathbb{R}^N$, $y \in \mathbb{R}^M$, $A \in \mathbb{R}^{N \times N}$ is an invertible matrix, $\Pi \in \mathbb{R}^{M \times N}$ is a rectangular matrix, $V(x) : \mathbb{R}^N \to \mathbb{R}$ is an arbitrary potential function such that the above integral exists. The normalization factor is

$$\Omega_1 \equiv \int dx \exp\left\{-\frac{1}{2}x^T A x - \epsilon V(x)\right\}$$

We introduce the Gaussian average as

$$\langle \cdots \rangle^G \equiv \frac{1}{\Omega_0} \int dx \exp\left\{-\frac{1}{2}x^T A x\right\} \cdots$$

with

$$\Omega_0 = \int dx \exp\left\{-\frac{1}{2}x^T A x\right\} = \frac{(2\pi)^{N/2}}{(\det A)^{1/2}}$$

We can write compactly Eq. (24.1.5) as

$$\Omega(y, \epsilon) = \frac{\langle \exp\{-\epsilon V\} \delta(Y - y) \rangle^G}{\langle \exp\{-\epsilon V\} \rangle^G}$$

where $Y = \Pi x$. We are looking for a perturbative calculation of the effective potential. Therefore, we expand the logarithm of the probability (24.3.3)

$$\ln \Omega(y, \epsilon) = \ln \Omega(y, 0) + \epsilon \frac{\partial}{\partial \epsilon} \ln \Omega(y, 0) + \frac{1}{2}\epsilon^2 \frac{\partial^2}{\partial \epsilon \partial \epsilon} \ln \Omega(y, 0) + \cdots$$

Note that

$$\ln \Omega(y, \epsilon) = \ln \langle \exp\{-\epsilon V\} \delta(Y - y) \rangle^G - \ln \langle \exp\{-\epsilon V\} \rangle^G$$

$$\frac{\partial}{\partial \epsilon} \ln \Omega(y, \epsilon) = -\frac{\langle \exp\{-\epsilon V\} V \delta(Y - y) \rangle^G}{\langle \exp\{-\epsilon V\} \delta(Y - y) \rangle^G} + \frac{\langle \exp\{-\epsilon V\} V \rangle^G}{\langle \exp\{-\epsilon V\} \rangle^G}$$

$$\frac{\partial^2}{\partial \epsilon \partial \epsilon} \ln \Omega(y, \epsilon) = \frac{\langle \exp\{-\epsilon V\} V^2 \delta(Y - y) \rangle^G}{\langle \exp\{-\epsilon V\} \delta(Y - y) \rangle^G} - \left(\frac{\langle \exp\{-\epsilon V\} V \delta(Y - y) \rangle^G}{\langle \exp\{-\epsilon V\} \delta(Y - y) \rangle^G} \right)^2$$

$$- \frac{\langle \exp\{-\epsilon V\} V^2 \rangle^G}{\langle \exp\{-\epsilon V\} \rangle^G} + \left(\frac{\langle \exp\{-\epsilon V\} V \rangle^G}{\langle \exp\{-\epsilon V\} \rangle^G} \right)^2$$

Therefore, (24.1.5) becomes

$$\ln \Omega(y, \epsilon) = \ln \Omega(y, 0) - \epsilon \left[\frac{\langle V \delta(Y - y) \rangle^G}{\langle \delta(Y - y) \rangle^G} - \langle V \rangle^G \right]$$

$$+ \frac{1}{2} \epsilon^2 \left[\frac{\langle V^2 \delta(Y - y) \rangle^G}{\langle \delta(Y - y) \rangle^G} - \left(\frac{\langle V \delta(Y - y) \rangle^G}{\langle \delta(Y - y) \rangle^G} \right)^2 - \langle V^2 \rangle^G + \left(\langle V \rangle^G \right)^2 \right] + \cdots$$

and, therefore,

$$\Omega(y, \epsilon) = \Omega(y, 0) \exp \left\{ -\epsilon \left[\frac{\langle V \delta(Y - y) \rangle^G}{\langle \delta(Y - y) \rangle^G} - \langle V \rangle^G \right] \right\}$$

$$\times \exp \left\{ \frac{1}{2} \epsilon^2 \left[\frac{\langle V^2 \delta(Y - y) \rangle^G}{\langle \delta(Y - y) \rangle^G} - \left(\frac{\langle V \delta(Y - y) \rangle^G}{\langle \delta(Y - y) \rangle^G} \right)^2 - \langle V^2 \rangle^G + \left(\langle V \rangle^G \right)^2 \right] + \cdots \right\}$$

The factor $\Omega(y, 0)$ can be explicitly computed, because it is a Gaussian integral, with the result

$$\Omega(y, 0) \equiv \frac{1}{\Omega_0} \int dx \exp \left\{ -\frac{1}{2} x^T A x \right\} \delta(\Pi x - y) = \frac{1}{(2\pi)^{M/2} \det \overline{A}^{1/2}} \exp \left\{ -\frac{1}{2} y^T \overline{A} y \right\}$$

The normalization Ω_0 ensures that $\Omega(y, 0)$ is normalized to unity. The coarse-grained matrix $\overline{A} \in \mathbb{R}^{M \times M}$ in Eq. (24.3.3) is

$$\overline{A}^{-1} \equiv \Pi^T A^{-1} \Pi$$

The probability (24.3.3) is no longer normalized after the perturbative calculation. Note that if we consider the first order result and expand the exponential, then we have

$$\Omega(y,\epsilon) = \Omega(y,0)\left[1 - \epsilon\left[\frac{\langle V\delta(Y-y)\rangle^G}{\langle\delta(Y-y)\rangle^G} - \langle V\rangle^G\right]\right]$$

$$= \langle\delta(Y-y)\rangle^G - \epsilon\left[\langle V\delta(Y-y)\rangle^G - \langle V\rangle^G\langle\delta(Y-y)\rangle^G\right]$$

which is, indeed, normalized. We may simply brute force normalize Eq. (24.3.3) at each level of perturbation, and this will not affect the functional form of the effective potential, appart from irrelevant constant terms.

In summary, we have

$$\Omega(y,\epsilon) = \frac{1}{\Omega_1}\int dx \exp\left\{-\frac{1}{2}x^T Ax - \epsilon V(x)\right\}\delta(\Pi x - y) = \frac{1}{\Omega(\epsilon)}\exp\left\{-\frac{1}{2}y^T\overline{A}y - \epsilon\overline{V}(y,\epsilon)\right\}$$

$$\Omega(\epsilon) \equiv \int dy \exp\left\{-\frac{1}{2}y^T\overline{A}y - \epsilon\overline{V}(y,\epsilon)\right\}$$

$$\overline{A}^{-1} \equiv \Pi^T A^{-1}\Pi$$

$$\overline{V}(y,\epsilon) \equiv \frac{\langle V\delta(Y-y)\rangle^G}{\langle\delta(Y-y)\rangle^G} + \frac{1}{2}\epsilon\left[\frac{\langle V^2\delta(Y-y)\rangle^G}{\langle\delta(Y-y)\rangle^G} - \left(\frac{\langle V\delta(Y-y)\rangle^G}{\langle\delta(Y-y)\rangle^G}\right)^2\right] + \mathcal{O}(\epsilon^2)$$

where $\Omega(\epsilon)$ is the normalization constant, and we have introduced the anharmonic effective potential $\overline{V}(y,\epsilon)$. To first order of perturbation in ϵ, the CG potential is given by

$$\overline{V}(y,0) = \frac{\int dx V(x)\exp\left\{-\frac{1}{2}x^T Ax\right\}\delta(\Pi x - y)}{\int dx \exp\left\{-\frac{1}{2}x^T Ax\right\}\delta(\Pi x - y)}$$

24.2   Sectioned Gaussian integrals with non-singular Hessian

In this appendix, we consider Gaussian integrals with non-singular Hessian but with a conservation Dirac delta function.

24.2.1   Generating function

The integral that we now compute is

$$\int dx \exp\left\{\frac{1}{2}x^T A x + J^T x\right\} \delta(v^T x) = \int \frac{d\omega}{2\pi} \int dx \exp\left\{\frac{1}{2}x^T A x + (J^T + i\omega v^T)x\right\} \delta(v^T x)$$

$$= \frac{(2\pi)^{N/2}}{(\det A)^{1/2}} \int \frac{d\omega}{2\pi} \exp\left\{\frac{1}{2}(J + i\omega v)^T A^{-1}(J + i\omega v)\right\}$$

$$= \frac{(2\pi)^{(N-1)/2}}{(\det A)^{1/2}(v^T A^{-1} v)^{1/2}} \exp\left\{\frac{1}{2}J^T A^+ J\right\}$$

where we have introduced

$$A^+ = A^{-1} - \frac{A^{-1} v v^T A^{-1}}{v^T A^{-1} v}$$

that satisfies $A^+ v = 0$.

24.2.2   The probability

The next integral that we consider is **check**

$$\int dx \exp\left\{\frac{1}{2}x^T A x + J^T x\right\} \delta(v^T x)\delta(\Pi x - y)$$

$$= \int \frac{d\lambda}{(2\pi)^M} \exp\{-i\lambda^T y\} \int dx \exp\left\{\frac{1}{2}x^T A x + (J + i\lambda^T \Pi v)^T x\right\} \delta(v^T x)$$

$$= \frac{(2\pi)^{(N-1)/2}}{(\det A)^{1/2}(v^T A^{-1} v)^{1/2}} \exp\left\{\frac{1}{2}J^T A^+ J\right\} \int \frac{d\lambda}{(2\pi)^M} \int dx \exp\left\{-\frac{1}{2}\lambda^T \Pi^T A^+ \Pi \lambda - i\lambda^T (\Pi^T A^+ J + y)\right\}$$

$$= \frac{(2\pi)^{(N-1)/2}}{(\det A)^{1/2}(v^T A^{-1} v)^{1/2}} \frac{1}{(2\pi)^{M/2}(\det \Pi^T A^+ \Pi)^{1/2}} \exp\left\{\frac{1}{2}J^T A^+ J - \frac{1}{2}(y + \Pi A^+ J)^T (\Pi^T A^+ \Pi)^{-1}(y + \Pi A^+ J)\right\}$$

If we normalize, we obtain a probability

$$\Omega(y, J) = \frac{\int dx \exp\left\{\frac{1}{2}x^T A x + J^T x\right\} \delta(v^T x)\delta(\Pi x - y)}{\int dx \exp\left\{\frac{1}{2}x^T A x + J^T x\right\} \delta(v^T x)}$$

By using the two previous results we obtain

$$\Omega(y, J) = \frac{1}{(2\pi)^{M/2}(\det \Pi^T A^+ \Pi)^{1/2}} \exp\left\{-\frac{1}{2}(y + \Pi A^+ J)^T \overline{A}(y + \Pi A^+ J)\right\}$$

where we have introduced the coarse-grained matrix $\overline{A} \in \mathbb{R}^{M \times M}$ as

$$\overline{A} \equiv \left[\Pi^T A^+ \Pi\right]^{-1}$$

provided that the inverse exists.

Singular case when $v = \Pi^T v'$

The result (24.2.2) is valid in general, provided that the inverse of the matrix $\Pi^T A^+ \Pi$ exists. One case in which this does not happen is when the vector $v = \Pi^T v'$ for some $v' \in \mathbb{R}^M$. Note that $v \in \mathbb{R}^M$ and $v' \in \mathbb{R}^{M'}$ with $M > M'$ and, therefore, the system $v = \Pi^T v'$ is overdetermined in general. However, the system may have solution for some v'. In that case, the matrix is of the form

$$\Pi^T A^+ \Pi = \Pi^T A^{-1} \Pi - \frac{\Pi^T A^{-1} \Pi v' v'^T \Pi^T A^{-1} \Pi}{v'^T \Pi^T A^{-1} \Pi v}$$

that satisfies $\Pi^T A^+ \Pi v' = 0$ and does not have inverse. In this case, we need to proceed in a different way by noting that

$$\Omega(y, J) = \frac{\int dx \exp\left\{-\frac{1}{2}x^T Ax + J^T x\right\} \delta(v'^T \Pi x)\delta(\Pi x - y)}{\int dx \exp\left\{-\frac{1}{2}x^T Ax + J^T x\right\} \delta(v^T x)} = \delta\left(v'^T y\right) \frac{\int dx \exp\left\{-\frac{1}{2}x^T Ax + J^T x\right\} \delta(\Pi x - y)}{\int dx \exp\left\{-\frac{1}{2}x^T Ax + J^T x\right\} \delta(v^T x)}$$

and an overall Dirac delta function is expelled from inside the integral. We now use the results (24.1.3) and (24.2.1)

$$\int dx \exp\left\{-\frac{1}{2}x^T Ax + J^T x\right\} \delta(\Pi x - y) = \frac{(2\pi)^{N/2}}{\det A^{1/2}} \frac{\det \overline{A}^{1/2}}{(2\pi)^{M/2}} \exp\left\{-\frac{1}{2}(y + \Pi A^{-1} J)^T [\Pi^T A^{-1} \Pi]^{-1}(y + \Pi A^{-1} J) - \frac{1}{2}J^T A^{-1} J\right\}$$

$$\int dx \exp\left\{-\frac{1}{2}x^T Ax + J^T x\right\} \delta(v^T x) = \frac{(2\pi)^{(N-1)/2}}{(\det A)^{1/2}(v^T A^{-1} v)^{1/2}} \exp\left\{\frac{1}{2}J^T A^+ J\right\}$$

in order to get

$$\Omega(y, J) = \delta\left(v'^T y\right) \frac{\det \overline{A}^{1/2}(v'^T \overline{A}^{-1} v')^{1/2}}{(2\pi)^{(M-1)/2}} \exp\left\{-\frac{1}{2}(y + \Pi A^{-1} J)^T \overline{A}(y + \Pi A^{-1} J) + \frac{1}{2}\frac{J^T A^{-1} v v^T A^{-1} J}{v^T A^{-1} v}\right\}$$

where here

$$\overline{A} = [\Pi^T A^{-1} \Pi]^{-1}$$

24.2.3   Probability in perturbation theory

Consider probability distributions with non-singular Hessian matrices of the form

$$\Omega(y, \epsilon) = \frac{1}{\Omega_1} \int dx \exp\left\{-\frac{1}{2}x^T Ax - \epsilon V(x)\right\} \delta(\Pi x - y)\delta(v^T x)$$

Here, $x \in \mathbb{R}^N$, $y \in \mathbb{R}^M$, $A \in \mathbb{R}^{N \times N}$ is an invertible matrix, $\Pi \in \mathbb{R}^{M \times N}$ is a rectangular matrix, $V(x) : \mathbb{R}^N \to \mathbb{R}$ is an arbitrary potential function such that the above integral exists. The normalization factor is

$$\Omega_1 \equiv \int dx \exp\left\{-\frac{1}{2}x^T Ax - \epsilon V(x)\right\} \delta(v^T x)$$

We introduce the sectioned Gaussian average as

$$\langle \cdots \rangle^{G'} \equiv \frac{1}{\Omega_0} \int dx \exp\left\{-\frac{1}{2}x^T Ax\right\} \delta(v^T x) \cdots$$

The normalization Ω_0 is given in Eq. (24.2.1)

$$\Omega_0 = \int dx \exp\left\{-\frac{1}{2}x^T Ax\right\} \delta(v^T x) = \frac{(2\pi)^{(N-1)/2}}{(\det A)^{1/2}(v^T A^{-1} v)^{1/2}}$$

We can write compactly Eq. (24.2.3) as

$$\Omega(y, \epsilon) = \frac{\langle \exp\{-\epsilon V\}\delta(Y - y)\rangle^{G'}}{\langle \exp\{-\epsilon V\}\rangle^{G'}}$$

where $Y = \Pi x$. We may proceed exactly in the same way as in Sec. 24.1.5 and, therefore,

$$\Omega(y, \epsilon) = \Omega(y, 0) \exp\left\{-\epsilon \left[\frac{\langle V\delta(Y - y)\rangle^{G'}}{\langle \delta(Y - y)\rangle^{G'}} - \langle V\rangle^{G'}\right]\right\}$$

$$\times \exp\left\{\frac{1}{2}\epsilon^2 \left[\frac{\langle V^2\delta(Y - y)\rangle^{G'}}{\langle \delta(Y - y)\rangle^{G'}} - \left(\frac{\langle V\delta(Y - y)\rangle^{G'}}{\langle \delta(Y - y)\rangle^{G'}}\right)^2 - \langle V^2\rangle^{G'} + \left(\langle V\rangle^{G'}\right)^2\right] + \cdots\right\}$$

The factor $\Omega(y, 0)$ has been explicitly computed in Eq. (24.2.2)

$$\Omega(y, 0) = \frac{\det \overline{A}^{1/2}}{(2\pi)^{M/2}} \exp\left\{-\frac{1}{2}y^T \overline{A} y\right\}$$

The normalization Ω_0 ensures that $\Omega(y, 0)$ is normalized to unity. Note though that if we truncate the expansion, the resulting probability is no longer normalized. Nevertheless, we can enforce the normalization at every order of the perturbation theory.

In summary, we have

$$\Omega(y,\epsilon) = \frac{1}{\Omega_1}\int dx \exp\left\{-\frac{1}{2}x^T Ax - \epsilon V(x)\right\}\delta(\Pi x - y)\delta(v^T x) = \frac{1}{\Omega(\epsilon)}\exp\left\{-\frac{1}{2}y^T\overline{A}y - \epsilon\overline{V}(y,\epsilon)\right\}\delta(\overline{n}^T y)$$

$$\Omega(\epsilon) \equiv \int dy \exp\left\{-\frac{1}{2}y^T\overline{A}y - \epsilon\overline{V}(y,\epsilon)\right\}\delta(\overline{n}^T y)$$

$$\overline{A} \equiv \left[\Pi^T A^+ \Pi\right]^{-1}$$

$$\overline{V}(y,\epsilon) \equiv \frac{\langle V\delta(Y-y)\rangle^{G'}}{\langle\delta(Y-y)\rangle^{G'}} + \frac{1}{2}\epsilon\left[\frac{\langle V^2\delta(Y-y)\rangle^{G'}}{\langle\delta(Y-y)\rangle^{G'}} - \left(\frac{\langle V\delta(Y-y)\rangle^{G'}}{\langle\delta(Y-y)\rangle^{G'}}\right)^2\right] + \mathcal{O}(\epsilon^2)$$

where $\Omega(\epsilon)$ is the normalization constant, and we have introduced the anharmonic effective potential $\overline{V}(y,\epsilon)$. To first order of perturbation in ϵ, the CG potential is given by

$$\overline{V}(y,0) = \frac{\int dx V(x)\exp\left\{-\frac{1}{2}x^T Ax\right\}\delta(\Pi x - y)\delta(n^T x)}{\int dx \exp\left\{-\frac{1}{2}x^T Ax\right\}\delta(\Pi x - y)\delta(n^T x)}$$

Singular case when $v = \Pi^T v'$

As before, the above calculation is valid except when $v = \Pi v'$. In this case, there are some inverses that do not exist and we have to proceed in a different way. In particular, we have to reformulate the calculations of Sec 24.1.5 because now the logarithm of the probability is not well-defined due to the presence of the conservation Dirac delta function. We have

$$\Omega(y,\epsilon) = \delta\left(v'^T y\right)\frac{\int dx \exp\left\{-\frac{1}{2}x^T Ax - \epsilon V(x)\right\}\delta(\Pi x - y)}{\int dy\delta(v'^T y)\int dx \exp\left\{-\frac{1}{2}x^T Ax - \epsilon V(x)\right\}\delta(\Pi x - y)} \equiv \delta\left(v'^T y\right)\Omega'(y,\epsilon)$$

On the newly defined non-singular part of the probability we can perform a Taylor series of its logarithm, i.e.

$$\ln\Omega'(y,\epsilon) = \ln\Omega'(y,0) + \epsilon\frac{\partial}{\partial\epsilon}\ln\Omega'(y,0) + \frac{1}{2}\epsilon^2\frac{\partial^2}{\partial\epsilon\partial\epsilon}\ln\Omega'(y,0) + \cdots$$

We have

$$\ln\Omega'(y,\epsilon) = \ln\int dx \exp\left\{-\frac{1}{2}x^T Ax - \epsilon V(x)\right\}\delta(\Pi x - y) - \ln\int dy\delta(v'^T y)\int dx \exp\left\{-\frac{1}{2}x^T Ax - \epsilon V(x)\right\}\delta(\Pi x - y)$$

$$\frac{\partial}{\partial \epsilon} \ln \Omega'(y, \epsilon) = -\frac{\int dx \exp\left\{-\frac{1}{2}x^T A x - \epsilon V(x)\right\} \delta(\Pi x - y) V(x)}{\int dx \exp\left\{-\frac{1}{2}x^T A x - \epsilon V(x)\right\} \delta(\Pi x - y)}$$

$$+ \frac{\int dy \delta(v'^T y) \int dx \exp\left\{-\frac{1}{2}x^T A x - \epsilon V(x)\right\} \delta(\Pi x - y) V(x)}{\int dy \delta(v'^T y) \int dx \exp\left\{-\frac{1}{2}x^T A x - \epsilon V(x)\right\} \delta(\Pi x - y)}$$

$$= -\frac{\langle \exp\{-\epsilon V\} V \delta(Y - y)\rangle^G}{\langle \exp\{-\epsilon V\} \delta(Y - y)\rangle^G} + \frac{\int dy \delta(v'^T y) \langle \exp\{-\epsilon V\} V \delta(Y - y)\rangle^G}{\int dy \delta(v'^T y) \langle \exp\{-\epsilon V\} \delta(Y - y)\rangle^G}$$

$$\frac{\partial^2}{\partial \epsilon^2} \ln \Omega'(y, \epsilon) = -\frac{\partial}{\partial \epsilon} \frac{\langle \exp\{-\epsilon V\} V \delta(Y - y)\rangle^G}{\langle \exp\{-\epsilon V\} \delta(Y - y)\rangle^G} + \frac{\partial}{\partial \epsilon} \frac{\int dy \delta(v'^T y) \langle \exp\{-\epsilon V\} V \delta(Y - y)\rangle^G}{\int dy \delta(v'^T y) \langle \exp\{-\epsilon V\} \delta(Y - y)\rangle^G}$$

$$= \frac{\langle \exp\{-\epsilon V\} V^2 \delta(Y - y)\rangle^G}{\langle \exp\{-\epsilon V\} \delta(Y - y)\rangle^G} - \left[\frac{\langle \exp\{-\epsilon V\} V \delta(Y - y)\rangle^G}{\langle \exp\{-\epsilon V\} \delta(Y - y)\rangle^G}\right]^2$$

$$- \frac{\int dy \delta(v'^T y) \langle \exp\{-\epsilon V\} V^2 \delta(Y - y)\rangle^G}{\int dy \delta(v'^T y) \langle \exp\{-\epsilon V\} \delta(Y - y)\rangle^G} + \left[\frac{\int dy \delta(v'^T y) \langle \exp\{-\epsilon V\} V \delta(Y - y)\rangle^G}{\int dy \delta(v'^T y) \langle \exp\{-\epsilon V\} \delta(Y - y)\rangle^G}\right]^2$$

Then

$$\ln \Omega'(y, \epsilon) = \ln \frac{\langle \delta(Y - y)\rangle^G}{\int dy \delta(v'^T y) \langle \delta(Y - y)\rangle^G}$$

$$+ \epsilon \left[-\frac{\langle V \delta(Y - y)\rangle^G}{\langle \delta(Y - y)\rangle^G} + \frac{\int dy \delta(v'^T y) \langle V \delta(Y - y)\rangle^G}{\int dy \delta(v'^T y) \langle \delta(Y - y)\rangle^G}\right]$$

$$+ \epsilon^2 \left[\frac{\langle V^2 \delta(Y - y)\rangle^G}{\langle \delta(Y - y)\rangle^G} - \left[\frac{\langle V \delta(Y - y)\rangle^G}{\langle \delta(Y - y)\rangle^G}\right]^2 - \frac{\int dy \delta(v'^T y) \langle V^2 \delta(Y - y)\rangle^G}{\int dy \delta(v'^T y) \langle \delta(Y - y)\rangle^G} + \left[\frac{\int dy \delta(v'^T y) \langle V \delta(Y - y)\rangle^G}{\int dy \delta(v'^T y) \langle \delta(Y - y)\rangle^G}\right]^2\right]$$

$$+ \mathcal{O}(\epsilon^3)$$

Returning back to Eq. (24.2.3) we have

$$\Omega(y, \epsilon) = \frac{\delta\left(v'^T y\right) \langle \delta(Y - y)\rangle^G \exp\{-\epsilon \overline{V}(y)\}}{\int dy \delta\left(v'^T y\right) \langle \delta(Y - y)\rangle^G \exp\{-\epsilon \overline{V}(y)\}}$$

The coarse-grained potential $\overline{V}(y)$ is the same as in Eq. (24.1.5) and $\langle \delta(Y - y) \rangle^G$ is computed in Eq. (24.1.3). The final result is

$$\Omega(y, \epsilon) = \frac{\delta\left(v'^T y\right) \exp\left\{-\frac{1}{2} y^T \overline{A} y - \epsilon \overline{V}(y)\right\}}{\int dy \, \delta\left(v'^T y\right) \exp\left\{-\frac{1}{2} y^T \overline{A} y - \epsilon \overline{V}(y)\right\}}$$

where we have made use of the fact that $\Omega(y, \epsilon)$ is properly normalized.

24.3   Sectioned Gaussian Integrals with Semi-definite Hessian

24.3.1   Generating function

Consider now the case that the matrix $A \in \mathbb{R}^{N \times N}$ has a unit eigenvector n of null non-degenerate eigenvalue, this is $An = 0$. This is the case for translationally invariant Hamiltonians. The matrix A in this case is not invertible and the integral (24.1.1) does not exists. However, for translationally invariant systems, the proper ensemble will lead in a natural way to the following integral, instead of (24.1.1)

$$\Omega_0(J) = \int dx \exp\left\{ -\frac{1}{2} x^T A x + J^T x \right\} \delta\left(v^T x \right)$$

which exists and can be computed. Geometrically, what we have is that when the matrix A is singular because of translational invariance, the Gaussian becomes not a "hump" but an infinitely long "tunnel" in the direction of n and is, therefore, not normalizable. The delta function sections that tunnel transversally, rendering the integral over the resulting $N - 1$ dimensional Gaussian finite.

We compute (24.3.1) by introducing the rotated variables $x' = Rx$, $J' = RJ$ where the rotation matrix R $(R^T R = R R^T = 1)$ is the one that diagonalizes the symmetric matrix $R A R^T = D$. The diagonal matrix of eigenvalues $D = \text{Diag}[0, a_2, \cdots, a_N]$ has a zero entry. The rotated vector $n' = Rn$ has the components $(1, 0, \cdots, 0)$ because n itself is an eigenvector and n' is the components of the eigenvector in the eigenbasis. Then

$$\Omega_0(J) = \int dx' \exp\left\{ -\frac{1}{2} x'^T D x + J' x' \right\} \delta(x'_1)$$

$$= \int dx'_2 \cdots dx'_N \exp\left\{ -\sum_{i=2}^{N} \left[\frac{a_i}{2} x_i'^2 - J'_i x'_i \right] \right\}$$

$$= \int dx'_2 \cdots dx'_N \exp\left\{ -\sum_{i=2}^{N} \left[\frac{a_i}{2} \left(x'_i - \frac{J'_i}{a_i} \right)^2 - \frac{J'^2_i}{2a_i} \right] \right\}$$

$$= \exp\left\{ \sum_{i=2}^{N} \frac{J'^2_i}{2a_i} \right\} \prod_{i=2}^{N} \int dx_i \exp\left\{ -\frac{a_i}{2} x_i^2 \right\}$$

$$= \exp\left\{ \sum_{i=2}^{N} \frac{J'^2_i}{2a_i} \right\} \prod_{i=2}^{N} \frac{(2\pi)^{1/2}}{a_i^{1/2}}$$

$$= \exp\left\{ J'^T D^+ J \right\} \prod_{i=2}^{N} \frac{(2\pi)^{1/2}}{a_i^{1/2}}$$

where we have introduced the diagonal matrix $D^+ = \text{Diag}[0, a_2^{-1}, \cdots, a_N^{-1}]$ and construct the matrix $A^+ = R^T D^+ R$. This matrix is the so called Moore–Penrose pseudoinverse of A and satisfies $A A^+ A = A$. This matrix satisfies that $A^+ n = 0$ and the eigenvector n

has also zero eigenvalue. Then we have

$$\Omega_0(J) = \exp\left\{\frac{1}{2}J^T A^+ J\right\} \prod_{i=2}^{N} \frac{(2\pi)^{1/2}}{a_i^{1/2}}$$

and this satisfies the translation invariance $\Omega(J + \alpha n) = \Omega(J) \quad \forall \alpha$.

24.3.2   CG probability

Let us now consider the CG probability when the microscopic probability is a Gaussian with a singular Hessian. Instead of Eq. (24.1.3) (which does not exists) we have to compute now

$$\Omega(y, J) = \frac{1}{\Omega_0(J)} \int dx \delta\left(v^T x\right) \exp\left\{-\frac{1}{2} x^T A x + J^T x\right\} \delta(\Pi x - y)$$

where $\Omega_0(J)$ is the normalization factor. The first steps are similar to what we have done in (24.1.3) by considering the Fourier representation of Dirac's delta function

$$\Omega(y, J) = \frac{1}{\Omega_0(J)} \int \frac{d\lambda}{(2\pi)^M} \exp\left\{-i\lambda^T y\right\} \int dx \delta\left(v^T x\right) \exp\left\{-\frac{1}{2} x^T A x + J^T x\right\} \exp\{i\lambda^T \Pi x\}$$

$$= \frac{1}{\Omega_0(J)} \int \frac{d\lambda}{(2\pi)^M} \exp\left\{-i\lambda^T y\right\} \int dx \delta(v^T x) \exp\left\{-\frac{1}{2} x^T A x + (J + i\Pi^T \lambda)^T x\right\}$$

We rotate $x' = Rx$, $J' = R(J + i\Pi^T \lambda)$ with $RAR^T = D = \text{Diag}[0, a_2, \cdots, a_N]$

$$\Omega(y, J) = \frac{1}{\Omega_0(J)} \int \frac{d\lambda}{(2\pi)^M} \exp\left\{-i\lambda^T y\right\} \int dx'_1 \cdots dx'_N \delta(x'_1) \exp\left\{-\sum_{i=1}^N \frac{1}{2} a_i x'^2_i - J'_i x'_i\right\}$$

$$= \frac{1}{\Omega_0(J)} \int \frac{d\lambda}{(2\pi)^M} \exp\left\{-i\lambda^T y\right\} \int dx'_2 \cdots dx'_N \exp\left\{-\sum_{i=2}^N \left[\frac{1}{2} a_i \left(x'_i - \frac{J'_i}{a_i}\right)^2 - \frac{J'^2_i}{2a_i}\right]\right\}$$

$$= \frac{1}{\Omega_0(J)} \int \frac{d\lambda}{(2\pi)^M} \exp\left\{-i\lambda^T y\right\} \exp\left\{-\sum_{i=2}^N \frac{J'^2_i}{2a_i}\right\} \prod_{i=2}^N \int dx'_i \exp\left\{-\frac{1}{2a_i} x'^2_i\right\}$$

$$= \frac{1}{\Omega_0(J)} \int \frac{d\lambda}{(2\pi)^M} \exp\left\{-i\lambda^T y\right\} \exp\left\{(J + i\Pi^T \lambda)^T \frac{A^+}{2}(J + i\Pi^T \lambda)\right\} \prod_{i=2}^N \frac{(2\pi)^{1/2}}{a_i^{1/2}}$$

where we have defined

$$A^+ \equiv R D^+ R^T$$

$$D^+ = \text{Diag}[0, a_2^{-1}, \cdots, a_N^{-1}]$$

By using the result (24.3.1) for the denominator we have

$$\Omega(y, J) = \exp\left\{-\frac{1}{2} J^T A^+ J\right\} \int \frac{d\lambda}{(2\pi)^M} \exp\left\{-i\lambda^T y\right\} \exp\left\{(J + i\Pi^T \lambda)^T \frac{A^+}{2}(J + i\Pi^T \lambda)\right\}$$

$$= \int \frac{d\lambda}{(2\pi)^M} \exp\{-i\lambda^T(y - \Pi A^+ J)\} \exp\left\{-\lambda^T \frac{\overline{A}^+}{2}\lambda\right\}$$

where we have introduced the $\mathbb{R}^{M \times M}$ matrix

$$\overline{A}^+ \equiv \Pi A^+ \Pi^T$$

This matrix $\overline{A}^+$ is singular because the vector $\overline{n} = (1, \cdots, 1) \in \mathbb{R}^M$ is eigenvector of null eigenvalue, this is

$$\overline{A}^+ \overline{n} = \Pi A^+ \Pi^T \overline{n} = 0$$

because, due to (**??**) we have that $\Pi^T \overline{n} \propto n$ and $A^+ n = 0$. We now consider the rotation $O \in \mathbb{R}^{M \times M}$ that diagonalizes $\overline{A}^+$, i.e. $\overline{D}^+ = O \overline{A}^+ O^T = \text{Diag}[0, \overline{a}_2^+, \cdots, \overline{a}_M^+]$ where $\overline{a}_\mu^+$ are the eigenvalues of $\overline{A}^+$. The matrix O^T has as columns the normalized eigenvectors $\overline{v}_\mu$, i.e. $\overline{A}^+ \overline{v}_\mu = \overline{a}_\mu \overline{v}_\mu$. Note that, due to (24.3.2) we have

$$\overline{v}_1 = \overline{n} = \frac{1}{M^{1/2}} (1, \cdots, 1) \in \mathbb{R}^M$$

By performing the change of variables $\lambda' = O\lambda$ in Eq. (24.3.2) we have

$$\Omega(y, J) = \int \frac{d\lambda}{(2\pi)^M} \exp\left\{-i\lambda'^T O(y - \Pi A^+ J)\right\} \exp\left\{-\lambda'^T \frac{\overline{D}^+}{2} \lambda'\right\}$$

$$= \int \frac{d\lambda}{(2\pi)^M} \exp\left\{-i \sum_{\mu=1}^M \lambda'_\mu \overline{v}_\mu^T (y - \Pi A^+ J)\right\} \exp\left\{-\sum_{\mu=2}^M -\overline{a}_\mu^+ \frac{\lambda'^2_\mu}{2}\right\}$$

$$= \delta\left(\overline{v}_1^T (y - \Pi A^+ J)\right) \int \frac{d\lambda_2 \cdots d\lambda_2}{(2\pi)^{(M-1)}} \exp\left\{-\sum_{\mu=2}^M \left[i\lambda'_\mu \overline{v}_\mu^T (y - \Pi A^+ J) - \overline{a}_\mu^+ \frac{\lambda'^2_\mu}{2}\right]\right\}$$

$$= \delta\left(\overline{v}_1^T (y - \Pi A^+ J)\right) \prod_{\mu=2}^M \int \frac{d\lambda_\mu}{2\pi} \exp\left\{-i\lambda'_\mu \overline{v}_\mu^T (y - \Pi A^+ J) - \overline{a}_\mu^+ \frac{\lambda'^2_\mu}{2}\right\}$$

If we rename for notation simplicity $c_\mu = i\overline{v}_\mu^T(y - \Pi A^+ J)$ we have

$$\Omega(y, J) = \delta\left(\overline{v}_1^T(y - \Pi A^+ J)\right) \prod_{\mu=2}^{M} \int \frac{d\lambda_\mu}{2\pi} \exp\left\{-\lambda'_\mu c_\mu - \overline{a}_\mu^+ \frac{\lambda_\mu'^2}{2}\right\}$$

$$= \delta\left(\overline{v}_1^T(y - \Pi A^+ J)\right) \prod_{\mu=2}^{M} \int \frac{d\lambda_\mu}{2\pi} \exp\left\{-\frac{\overline{a}_\mu^+}{2}\left(\lambda_\mu + \frac{c_\mu}{\overline{a}_\mu^+}\right)^2 + \frac{c_\mu^2}{2\overline{a}_\mu^+}\right\}$$

$$= \delta\left(\overline{v}_1^T(y - \Pi A^+ J)\right) \exp\left\{\sum_{\mu=2}^{M} \frac{c_\mu^2}{2\overline{a}_\mu^+}\right\} \prod_{\mu=2}^{M} \int \frac{d\lambda_\mu}{2\pi} \exp\left\{-\frac{\overline{a}_\mu^+}{2}\lambda_\mu^2\right\}$$

$$= \delta\left(\overline{v}_1^T(y - \Pi A^+ J)\right) \exp\left\{-(y - \Pi A^+ J)^T \sum_{\mu=2}^{M} \overline{v}_\mu \left[\frac{1}{2\overline{a}_\mu^+}\overline{v}_\mu^T\right](y - \Pi A^+ J)\right\} \prod_{\mu=2}^{M} \frac{1}{(2\pi\overline{a}_\mu^+)^{1/2}}$$

Because of (24.3.2) and $\Pi^T \overline{n} = n$, we have that $\overline{v}_1^T \Pi A^+ J = 0$. The overall delta function simplifies and (24.3.2) becomes

$$\Omega(y, J) = \delta\left(\overline{n}^T y\right) \exp\left\{-\frac{1}{2}(y - \Pi A^+ J)^T \overline{A}(y - \Pi A^+ J)\right\} \prod_{\mu=2}^{M} \frac{1}{(2\pi\overline{a}_\mu^+)^{1/2}}$$

where we have introduced the matrix

$$\overline{A} = \sum_{\mu=2}^{M} \overline{v}_\mu \frac{1}{\overline{a}_\mu^+} \overline{v}_\mu^T$$

It should be remarked that if A in Eq. (24.3.2) is not singular, the whole calculation remains intact.

24.3.3 Probability in anharmonic perturbation theory

Now, consider probability distributions with singular Hessian matrices of the form

$$\Omega(y,\epsilon) = \frac{1}{\Omega_1}\int dx \exp\left\{-\frac{1}{2}x^T A x - \epsilon V(x)\right\}\delta(\Pi x - y)\delta(v^T x)$$

Here, $x \in \mathbb{R}^N$, $y \in \mathbb{R}^M$, $A \in \mathbb{R}^{N\times N}$ is an invertible matrix, $\Pi \in \mathbb{R}^{M\times N}$ is a rectangular matrix, $V(x) : \mathbb{R}^N \to \mathbb{R}$ is an arbitrary potential function such that the above integral exists. The normalization factor is

$$\Omega_1 \equiv \int dx \exp\left\{-\frac{1}{2}x^T A x - \epsilon V(x)\right\}\delta(v^T x)$$

We introduce the Gaussian average as

$$\langle\cdots\rangle^{G'} \equiv \frac{1}{\Omega_0}\int dx \exp\left\{-\frac{1}{2}x^T A x\right\}\delta(v^T x)\cdots$$

with, from Eq. (**??**)

$$\Omega_0 = \int dx \exp\left\{-\frac{1}{2}x^T A x\right\}\delta(v^T x) = \prod_{i=2}^{N}\frac{(2\pi)^{1/2}}{a_i^{1/2}}$$

We can write compactly Eq. (24.3.3) as

$$\Omega(y,\epsilon) = \frac{\langle\exp\{-\epsilon V\}\delta(Y - y)\rangle^{G'}}{\langle\exp\{-\epsilon V\}\rangle^{G'}}$$

where $Y = \Pi x$. We may proceed exactly in the same way as in Eqs. (24.1.5)-(24.3.3) and, therefore,

$$\Omega(y,\epsilon) = \Omega(y,0)\exp\left\{-\epsilon\left[\frac{\langle V\delta(Y - y)\rangle^{G'}}{\langle\delta(Y - y)\rangle^{G'}} - \langle V\rangle^{G'}\right]\right\}$$

$$\times\exp\left\{\frac{1}{2}\epsilon^2\left[\frac{\langle V^2\delta(Y - y)\rangle^{G'}}{\langle\delta(Y - y)\rangle^{G'}} - \left(\frac{\langle V\delta(Y - y)\rangle^{G'}}{\langle\delta(Y - y)\rangle^{G'}}\right)^2 - \langle V^2\rangle^{G'} + \left(\langle V\rangle^{G'}\right)^2\right] + \cdots\right\}$$

The factor $\Omega(y,0)$ has been explicitly computed in Eq. (24.3.2)-(24.3.2)

$$\Omega(y,0) \equiv \frac{1}{\Omega_0}\int dx \exp\left\{-\frac{1}{2}x^T A x\right\}\delta(\Pi x - y)\delta(v^T x) = \frac{1}{(2\pi)^{M/2}\det\overline{A}^{1/2}}\exp\left\{-\frac{1}{2}y^T\overline{A}y\right\}\delta(\overline{n}^T y)$$

The normalization Ω_0 ensures that $\Omega(y, 0)$ is normalized to unity. The coarse-grained matrix $\overline{A} \in \mathbb{R}^{M \times M}$ in Eq. (24.3.3) is

$$\overline{A}^+ \equiv \Pi^T A^+ \Pi$$

In summary, we have

$$\Omega(y, \epsilon) = \frac{1}{\Omega_1} \int dx \exp\left\{-\frac{1}{2}x^T A x - \epsilon V(x)\right\} \delta(\Pi x - y)\delta(v^T x) = \frac{1}{\Omega(\epsilon)} \exp\left\{-\frac{1}{2}y^T \overline{A} y - \epsilon \overline{V}(y, \epsilon)\right\} \delta(\overline{n}^T y)$$

$$\Omega(\epsilon) \equiv \int dy \exp\left\{-\frac{1}{2}y^T \overline{A} y - \epsilon \overline{V}(y, \epsilon)\right\} \delta(\overline{n}^T y)$$

$$\overline{A}^+ \equiv \Pi^T A^+ \Pi$$

$$\overline{V}(y, \epsilon) \equiv \frac{\langle V\delta(Y-y)\rangle^{G'}}{\langle \delta(Y-y)\rangle^{G'}} + \frac{1}{2}\epsilon\left[\frac{\langle V^2\delta(Y-y)\rangle^{G'}}{\langle \delta(Y-y)\rangle^{G'}} - \left(\frac{\langle V\delta(Y-y)\rangle^{G'}}{\langle \delta(Y-y)\rangle^{G'}}\right)^2\right] + \mathcal{O}(\epsilon^2)$$

where $\Omega(\epsilon)$ is the normalization constant, and we have introduced the anharmonic effective potential $\overline{V}(y, \epsilon)$. To first order of perturbation in ϵ, the CG potential is given by

$$\overline{V}(y, 0) = \frac{\int dx V(x) \exp\left\{-\frac{1}{2}x^T A x\right\} \delta(\Pi x - y)\delta(n^T x)}{\int dx \exp\left\{-\frac{1}{2}x^T A x\right\} \delta(\Pi x - y)\delta(n^T x)}$$

24.4 Microcanonical averages

24.5 Integral over a hypersphere

Let us consider the vector space R^M whose elements are vectors $\mathbf{x}$. The integral of an arbitrary function $F(\mathbf{x}) = f(|\mathbf{x}|)$ that depends on $\mathbf{x}$ only through its modulus can be computed by changing to polar coordinates

$$\int F(\mathbf{x})d^N\mathbf{x} = \omega_N \int_0^\infty f(r)r^{N-1}dr \tag{24.5.1}$$

The numerical factor ω_N, which cames from the integration of the angles, can be computed by considering the special case when $f(r)$ is a Gaussian. The result is

$$\omega_N = 2\frac{\pi^{N/2}}{\Gamma(N/2)} \tag{24.5.2}$$

By using Eqn. (24.5.1) we can compute the following integral

$$\int \delta(|\mathbf{x}|^2 - E)d^N\mathbf{x} = \omega_N \int_0^\infty \delta(r^2 - E)r^{N-1}dr \qquad (24.5.3)$$

We need now the property

$$\delta(f(x)) = \sum_i \frac{\delta(x - x_i)}{|f'(x_i)|} \qquad (24.5.4)$$

where x_i are the zeros of $f(x_i) = 0$. For the case of Eqn. (24.5.3) we have $f(x) = x^2 - E$, $x_i = \pm E^{1/2}$ and $f'(x) = 2x$. Therefore,

$$\begin{aligned}
\int \delta(|\mathbf{x}|^2 - E)d^N\mathbf{x} &= \omega_N \int_0^\infty \frac{\delta(r - E^{1/2})}{2r}r^{N-1}dr \\
&= \frac{1}{2}\omega_N E^{\frac{N-2}{2}}
\end{aligned} \qquad (24.5.4)$$

24.6   Integral over momenta

Now we want to consider the following integral

$$\Omega_0 = \int d^{DN}\mathbf{p}\,\delta^D\left(\sum_i^N \mathbf{p}_i - \mathbf{P}\right)\delta\left(\sum_i^N \frac{p_i^2}{2m_i} - E\right) \qquad (24.6.1)$$

which appears repeatedly when computing molecular averages. In order to simplify the calculations and without losing generality, we can always select a reference frame in which the total momentum $\mathbf{P} = 0$.

$$\begin{aligned}
\Omega_0 &= \int d^{DN}\mathbf{p}\,\delta^D\left(\sum_i^N \mathbf{p}_i\right)\delta\left(\sum_i^N \frac{p_i^2}{2m_i} - E\right) \\
&= \prod_i^N (2m_i)^{D/2} \\
&\times \int d^{DN}\mathbf{p}\,\delta^D\left(\sum_i^N (2m_i)^{1/2}\mathbf{p}_i\right)\delta\left(\sum_i^N p_i^2 - E\right)
\end{aligned} \qquad (24.6.0)$$

The equation $\sum_i^N (2m_i)^{1/2}\mathbf{p}_i = 0$ are actually D equations (one for each component of the momentum) which define three planes in R^{DN} that pass through the origin. The integral in (24.6.1) is actually over a submanifold which is the intersection of the D planes with the surface of a DN dimensional sphere of radius $E^{1/2}$. This intersection will be also a sphere of dimension $D(N-1)$ and radius equal to $E^{1/2}$, because the planes pass

through the origin.

We claim, therefore, that

$$\Omega_0 \;\; = \;\; \prod_i^N (2m_i)^{D/2} \int d^{D(N-1)} \mathbf{p}\, \delta \left(\sum_i^{N-1} p_i^2 - E \right) \tag{24.6.1}$$

and, by using Eq. (??) we obtain

$$\Omega_0 \;\; = \;\; \prod_i^N (2m_i)^{DN/2} \frac{1}{2} \omega_{D(N-1)} E^{\frac{D(N-1)-2}{2}} \tag{24.6.2}$$

Next we want to compute the following integral

$$\boldsymbol{\Omega}_{ij} \;\; = \;\; \int d^{DN} \mathbf{p}\, \mathbf{p}_i \mathbf{p}_j \delta^D \left(\sum_i^N \mathbf{p}_i \right) \delta \left(\sum_i^N \frac{p_i^2}{2m_i} - E \right) \tag{24.6.3}$$

Again with a scaling of momenta we obtain

$$\boldsymbol{\Omega}_{ij} \;\; = \;\; \prod_i^N (2m_i)^{DN/2} (2m_i)^{1/2} (2m_j)^{1/2} \int d^{DN} \mathbf{p}\, \mathbf{p}_i \mathbf{p}_j$$

$$\times \;\; \delta^D \left(\sum_i^N (2m_i)^{1/2} \mathbf{p}_i \right) \delta \left(\sum_i^N p_i^2 - E \right) \tag{24.6.3}$$

Consider first the case $D = 1$ where the integral becomes

$$\mathbf{I}_1 \;\; = \;\; \int d^N \mathbf{y}\, \mathbf{y}\mathbf{y}\, \delta \left(\boldsymbol{\beta} \cdot \mathbf{y} \right) \delta \left(y^2 - E \right) \tag{24.6.4}$$

where the vector $\boldsymbol{\beta} = \left((2m_1)^{1/2}, \ldots, (2m_N)^{1/2} \right)$.

We make the following ansatz for the value of the integral

$$\mathbf{I}_1 \;\; = \;\; a \mathbf{1}_N + b \frac{\boldsymbol{\beta}\boldsymbol{\beta}}{\beta^2} \tag{24.6.5}$$

where $\mathbf{1}_N$ is the identity tensor in N dimensions. The coefficients a, b are obtained by knowing that

$$\mathrm{Tr}\mathbf{I}_1 \;\; = \;\; E I_0$$
$$\boldsymbol{\beta}\boldsymbol{\beta} : \mathbf{I}_1 \;\; = \;\; 0 \tag{24.6.5}$$

where

$$I_0 = \int d^N \mathbf{y} \delta \left(\boldsymbol{\beta} \cdot \mathbf{y} \right) \delta \left(y^2 - E \right) \tag{24.6.6}$$

Note, from Eq. (24.6.3) that $(D = 1)$

$$\Omega_0 = \prod_i^N (2m_i)^{N/2} I_0 \tag{24.6.7}$$

By using Eq. (24.6.5) into Eq. (24.6.5) we obtain

$$
\begin{aligned}
aN + b &= EI_0 \\
a + b &= 0
\end{aligned}
\tag{24.6.7}
$$

with solution

$$
\begin{aligned}
a &= \frac{EI_0}{N-1} \\
b &= -a
\end{aligned}
\tag{24.6.7}
$$

Therefore,

$$\mathbf{I}_1 = \frac{EI_0}{N-1} \left(\mathbf{1}_N - \frac{\boldsymbol{\beta}\boldsymbol{\beta}}{\beta^2} \right) \tag{24.6.8}$$

In summary, we will have

$$
\begin{aligned}
\boldsymbol{\Omega}_{ij} &= \int d^N \mathbf{p} \mathbf{p}_i \mathbf{p}_j \delta \left(\sum_i^N \mathbf{p}_i \right) \delta \left(\sum_i^N \frac{p_i^2}{2m_i} - E \right) \\
&= (2m_i)^{1/2} (2m_j)^{1/2} \frac{E}{N-1} \left(\delta_{ij} - \frac{(2m_i)^{1/2}(2m_j)^{1/2}}{2M} \right) \Omega_0
\end{aligned}
\tag{24.6.8}
$$

It is easy to generalize the above result to D dimensions. In this case, the integral in Eq. (24.6.4)

$$\mathbf{I}_1 = \int d^{DN} \mathbf{y} \mathbf{y} \mathbf{y} \delta \left(\boldsymbol{\beta}_x \cdot \mathbf{y} \right) \delta \left(\boldsymbol{\beta}_y \cdot \mathbf{y} \right) \delta \left(y^2 - E \right) \tag{24.6.9}$$

where $\boldsymbol{\beta}_x = \left((2m_1)^{1/2}, 0, 0, \dots, (2m_N)^{1/2}, 0, 0 \right)$. $\boldsymbol{\beta}_y = \left(0, (2m_1)^{1/2}, 0, \dots, 0, (2m_N)^{1/2} 0, \right)$. The ansatz in Eq. (24.6.5)

$$\mathbf{I}_1 = a\mathbf{1}_N + b_x \frac{\boldsymbol{\beta}_x \boldsymbol{\beta}_x}{\beta_x^2} + b_y \frac{\boldsymbol{\beta}_y \boldsymbol{\beta}_y}{\beta_y^2} \tag{24.6.10}$$

and the conditions in Eq. (??) are just $b_x = b_y = b_z = -a$. The final result is

$$\mathbf{\Omega}_{ij} = \int d^{DN}\mathbf{p}\,\mathbf{p}_i\mathbf{p}_j\delta^D\left(\sum_i^N \mathbf{p}_i\right)\delta\left(\sum_i^N \frac{p_i^2}{2m_i} - E\right)$$

$$= (2m_i)^{1/2}(2m_j)^{1/2}\frac{E}{D(N-1)}\left(\delta_{ij} - \frac{(2m_i)^{1/2}(2m_j)^{1/2}}{2M}\right)\Omega_0\mathbf{1}_D \quad (24.6.10)$$

24.7   The entropy

The entropy of a system is defined as

$$S(N, E, V) \equiv k_B \ln \Omega(N, E, V)$$

$$\equiv k_B \ln \left(\frac{1}{h^{3N} N!} \int_{\mathscr{V}} d\mathbf{q}_1 \dots d\mathbf{q}_N \int d\mathbf{p}_1 \dots d\mathbf{p}_N \delta \left(\sum_i \mathbf{p}_i \right) \delta \left(\sum_i \frac{\mathbf{p}_i^2}{2m} + \phi - E \right) \right) \quad (24.7.0)$$

where k_B is the Boltzmann constant, and h is the Planck constant, and ϕ is the potential energy that depends only on the positions. We integrate over the momenta by using Eq. (??) with the result

$$S(N, E, V) \equiv k_B \ln \Omega(N, E, V)$$

$$= k_B \ln \left(\frac{\pi^{\frac{D(N-1)}{2}}}{\Gamma\left(\frac{D(N-1)}{2}\right)} (2m)^{\frac{D(N-1)}{2}} \frac{1}{h^{3N} N!} \int_{\mathscr{V}} d\mathbf{q}_1 \dots d\mathbf{q}_N \theta(E - \phi) \, (E - \phi)^{\frac{D(N-1)-2}{2}} \right)$$

$$= k_B \ln \left(\frac{(2m\pi\mathscr{E})^{\frac{D(N-1)}{2}}}{\Gamma\left(\frac{D(N-1)}{2}\right)} \frac{\mathscr{V}^N}{h^{3N} N!} \right)$$

$$+ k_B \ln \left(\frac{1}{\mathscr{V}^N} \int_{\mathscr{V}} d\mathbf{q}_1 \dots d\mathbf{q}_N \theta(E - \phi) \left(1 - \frac{1}{E}\phi \right)^{\frac{D(N-1)-2}{2}} \right) \quad (24.7.-2)$$

where $\theta(x)$ is the step function. In this way, we have separated the effects of the interactions from the ideal part. By using Stirlings approximation, we can express the ideal gas part as the Sakur-Tetrode entropy

$$S(N, E, V) = S^{\text{id}}(N, E, V) + S^{\text{int}}(N, E, V)$$

$$S^{\text{id}}(N, E, V) = N k_B \left[\ln \frac{\mathscr{V}}{N} \left(\frac{4\pi m_0 \mathscr{E}}{h^2 N} \right)^{3/2} + \frac{5}{2} \right]$$

$$S^{\text{int}}(N, E, V) = k_B \ln \left(\frac{1}{\mathscr{V}^N} \int_{\mathscr{V}} d\mathbf{q}_1 \dots d\mathbf{q}_N \left(1 - \frac{1}{E}\phi \right)^{\frac{DN}{2}} \right) \quad (24.7.-3)$$

We hipothesize that the assymptotic value of the interaction entropy is given by

$$S^{\text{int}}(N, E, V) = k_B \ln \left(\frac{1}{\mathscr{V}^N} \int_{\mathscr{V}} d\mathbf{q}_1 \dots d\mathbf{q}_N \exp \left\{ -\frac{D}{2e}\phi \right\} \right) \quad (24.7.-2)$$

where $e = E/N$ and we have used the assymptotic result

$$\left(1 + \frac{x}{N} \right)^N \to \exp\{x\} \quad (24.7.-1)$$

Can we compute the interaction entropy numerically? Perform the change $\mathbf{q}_i \to \mathbf{x}_i = \mathbf{q}/L$ where $L^D = \mathscr{V}$ and assume that the potential is pair wise with $\phi = \frac{1}{2} \sum_{ij} \phi\left(\mathbf{q}_{ij}/\sigma\right)$ to obtain

$$S^{\text{int}}(N, E, V) \quad = \quad k_B \ln \left(\int_{1^D} d\mathbf{x}_1 \dots d\mathbf{x}_N \exp\left\{ -\frac{D}{4e} \sum_{ij}^{N} \phi\left(\frac{L\mathbf{x}_{ij}}{\sigma}\right) \right\} \right) \quad (24.7.0)$$

It is more convenient to study the integral

$$\int_{1^D} d\mathbf{x}^N \chi(x) \equiv \int_{1^D} d\mathbf{x}_1 \dots d\mathbf{x}_N \left[1 - \exp\left\{ -\frac{D}{4e} \sum_{ij}^{N} \phi\left(\frac{L\mathbf{x}_{ij}}{\sigma}\right) \right\} \right] \quad (24.7.1)$$

The function $\chi(x)$ takes the value 1 if $x_{ij} = 0$ for some pair i, j and zero if $x_{ij} > \frac{\sigma}{L}$ for all pairs i, j. It is apparent that for N fixed, as we increase the size L of the system the integral tends to zero. Of course, what has a non-trivial value is the limit $L \to \infty, N \to \infty$ with $n = N/L^D$ fixed. Therefore, what has to be explored is the assymptotic behaviour as a function of N of the following integral

$$\left[\int_{1^D} d\mathbf{x}_1 \dots d\mathbf{x}_N \left[1 - \exp\left\{ -\frac{D}{4e} \sum_{ij}^{N} \phi\left(\frac{N^{1/D}\mathbf{x}_{ij}}{n^{1/D}\sigma}\right) \right\} \right] \right]^{1/N} \quad (24.7.2)$$

If the thermodynamic limit exists, this integral must be a well-defined function of e, n, independent of N. I think this is the bare-bone formulation of the problem of equilibrium statistical mechanics. As it is presented, it suggest a way to compute with Monte-Carlo sampling, which can be biased to have contributions only for $x_{ij} \sim 0$. The hope is that the thermodynamic limit is reached very rapidly with N but, of course, this has to be checked.

24.8   Momentum distribution of a single particle

The momentum distribution of a single particle (let's say, the i-th particle) is given in the molecular ensemble by

$$\rho(\mathbf{p}) = \int dx d^{DN} \mathbf{p} \delta^D(\mathbf{p} - \mathbf{p}_i) \rho^{\text{mic}}(x, p) \quad (24.8.1)$$

where the molecular ensemble is given by

$$
\rho^{\text{mic}}(x, p) = \frac{1}{\Omega(\mathbf{P}, E, N)} \delta^D \left(\sum_j^N \mathbf{p}_j - \mathbf{P} \right) \delta \left(\sum_j^N \frac{p_j^2}{2m} - (E - \Phi(x)) \right)
$$

$$
\Omega(\mathbf{P}, E, N) = \int dx d^{DN} \mathbf{p} \delta^D \left(\sum_j^N \mathbf{p}_j - \mathbf{P} \right) \delta \left(\sum_j^N \frac{p_j^2}{2m} - (E - \Phi(x)) \right) \quad (24.8.1)
$$

The term $\Phi(x)$ depends in general on the state variables different from momenta.

Performing the integral over $\mathbf{p}_i$ in Eqn. (??) we obtain

$$
\rho(\mathbf{p}) = \frac{1}{\Omega(\mathbf{P}, E, N)} \int dx d^{D(N-1)} \mathbf{p} \delta^D \left(\sum_j^{N-1} \mathbf{p}_j - (\mathbf{P} - \mathbf{p}) \right) \delta \left(\sum_j^{N-1} \frac{p_j^2}{2m} - (E - \Phi(x) - \frac{\mathbf{p}^2}{2m}) \right) (24.8.2)
$$

Using Eqn. (6.8) we obtain

$$
\rho(\mathbf{p}) = \frac{1}{\Omega(\mathbf{P}, E, N)} \int dx \frac{1}{2} \omega_{N-2} \left(E - \Phi(x) - \frac{\mathbf{p}^2}{2m} - \frac{(\mathbf{P}-\mathbf{p})^2}{2M} \right)^{\frac{D(N-1)-2}{2}}
$$

$$
= \frac{\omega_{N-2}}{\omega_{N-1}} \frac{\int dx \frac{1}{2} \left(E - \Phi(x) - \frac{\mathbf{p}^2}{2m} - \frac{(\mathbf{P}-\mathbf{p})^2}{2M} \right)^{\frac{D(N-1)-2}{2}}}{\int dx \frac{1}{2} \left(E - \Phi(x) - \frac{\mathbf{P}^2}{2M} \right)^{\frac{D(N-1)-2}{2}}} \quad (24.8.2)
$$

Assume for simplicity $\mathbf{P} = 0$

$$
\rho(\mathbf{p}) = \frac{1}{\Omega(E, N)} \int dx \frac{1}{2} \omega_{N-2} \left(E - \Phi(x) - \frac{\mathbf{p}^2}{2m} - \frac{\mathbf{p}^2}{2M} \right)^{\frac{D(N-2)-2}{2}}
$$

$$
= \frac{\omega_{N-2}}{\omega_{N-1}} \frac{\int dx \left(E - \Phi(x) - \frac{\mathbf{p}^2}{2m} - \frac{\mathbf{p}^2}{2M} \right)^{\frac{D(N-2)-2}{2}}}{\int dx \left(E - \Phi(x) \right)^{\frac{D(N-1)-2}{2}}}
$$

$$
= \frac{\omega_{N-2}}{\omega_{N-1}} E^{-D/2} \frac{\int dx \left(1 - \frac{\Phi(x) - \frac{\mathbf{p}^2}{2m} - \frac{\mathbf{p}^2}{2M}}{E} \right)^{\frac{D(N-2)-2}{2}}}{\int dx \left(1 - \frac{\Phi(x)}{E} \right)^{\frac{D(N-1)-2}{2}}} \quad (24.8.1)
$$

Now assume that $E = eN$ with e finite and let $N \to \infty$ to obtain

$$
\rho(\mathbf{p}) = E^{-D/2} \frac{\int dx \exp \left\{ - \frac{\Phi(x) - \frac{\mathbf{p}^2}{2m}}{e} \right\}}{\int dx \exp \left\{ - \frac{\Phi(x)}{e} \right\}}
$$

$$
= \frac{1}{Z} \exp \left\{ - \frac{\mathbf{p}^2}{2me} \right\} \quad (24.8.1)
$$

24.9   Sectioned Gaussian

We compute here the following integral

$$\int \exp\left\{-\frac{1}{2}\mathbf{x}^T A\mathbf{x} + \mathbf{b}\mathbf{x}\right\} \delta(\mathbf{c}^T\mathbf{x} - d)d^M x \qquad (24.9.0)$$

where $\mathbf{c}$ is a given constant vector (in our case $\mathbf{c} = (1,\dots,1)$), $\mathbf{x}^T$ is the transpose of $\mathbf{x}$ and the matrix A is symmetric and definite positive at least on the subspace $\mathbf{c}^t\mathbf{x} = 0$. It will also be assumed that A has inverse A^{-1}

$$= \int \exp\left\{-\frac{1}{2}\mathbf{x}^T A\mathbf{x} + \mathbf{b}^T\mathbf{x}\right\} \int \frac{d\omega}{2\pi} \exp\left\{i\omega(\mathbf{c}^T\mathbf{x} - d)\right\} d^M x$$

$$= \int \frac{d\omega}{2\pi} \exp\left\{-i\omega d\right\} \int d^M x \exp\left\{-\frac{1}{2}\mathbf{x}^T A\mathbf{x} + (\mathbf{b} + i\omega\mathbf{c})^T\mathbf{x}\right\}$$

$$= \int \frac{d\omega}{2\pi} \exp\left\{-i\omega d\right\} \frac{(2\pi)^{M/2}}{(\det \mathbf{A})^{1/2}} \exp\left\{\frac{1}{2}(\mathbf{b} + i\omega\mathbf{c})^T \mathbf{A}^{-1}(\mathbf{b} + i\omega\mathbf{c})\right\}$$

$$= \frac{(2\pi)^{M/2}}{(\det \mathbf{A})^{1/2}} \int \frac{d\omega}{2\pi} \exp\left\{-i\omega d\right\} \exp\left\{\frac{1}{2}\mathbf{b}^T\mathbf{A}^{-1}\mathbf{b}\right\} \exp\left\{\frac{1}{2}i\omega\mathbf{c}^T\mathbf{A}^{-1}\mathbf{b}\right\} \exp\left\{-\frac{1}{2}\omega^2\mathbf{c}^T\mathbf{A}^{-1}\mathbf{c}\right\}$$

$$= \frac{(2\pi)^{M/2}}{(\det \mathbf{A})^{1/2}} \exp\left\{\frac{1}{2}\mathbf{b}^T\mathbf{A}^{-1}\mathbf{b}\right\} \int \frac{d\omega}{2\pi} \exp\left\{-\frac{1}{2}\omega^2\mathbf{c}^T\mathbf{A}^{-1}\mathbf{c} - i\omega\left(d - \frac{1}{2}\mathbf{c}^T\mathbf{A}^{-1}\mathbf{b}\right)\right\}$$

$$= \frac{(2\pi)^{M/2}}{(\det \mathbf{A})^{1/2}} \exp\left\{\frac{1}{2}\mathbf{b}^T\mathbf{A}^{-1}\mathbf{b}\right\} \frac{1}{(4\pi\mathbf{c}^T\mathbf{A}^{-1}\mathbf{c})^{1/2}} \exp\left\{-\frac{1}{2}\frac{\left(d - \frac{1}{2}\mathbf{c}^T\mathbf{A}^{-1}\mathbf{b}\right)^2}{\mathbf{c}^T\mathbf{A}^{-1}\mathbf{c}}\right\}$$

where we have used

$$\int_{-\infty}^{\infty} dx e^{-\frac{x^2}{2} + bx} = \sqrt{\pi}e^{\frac{b^2}{2}}$$

We will need to compute the following integral

$$\int d^N\mathbf{p}\exp\left\{-\beta\sum_i^N\frac{\mathbf{p}_i^2}{2m_i}\right\}\delta^3\left(\sum_i^N\mathbf{p}_i-\mathbf{P}\right)$$

$$=\int\frac{d\boldsymbol{\omega}}{(2\pi)^3}\exp\left\{-i\boldsymbol{\omega}{\cdot}\mathbf{P}\right\}\int d^N\mathbf{p}\exp\left\{-\beta\sum_i^N\frac{\mathbf{p}_i^2}{2m_i}+i\boldsymbol{\omega}{\cdot}\sum_i^N\mathbf{p}_i\right\}$$

$$=\int\frac{d\boldsymbol{\omega}}{(2\pi)^3}\exp\left\{-i\boldsymbol{\omega}{\cdot}\mathbf{P}\right\}\int d^N\mathbf{p}\exp\left\{-\beta\sum_i^N\frac{\mathbf{p}_i^2}{2m_i}+i\boldsymbol{\omega}{\cdot}\sum_i^N\mathbf{p}_i\right\}$$

$$=\int\frac{d\boldsymbol{\omega}}{(2\pi)^3}\exp\left\{-i\boldsymbol{\omega}{\cdot}\mathbf{P}\right\}\int d^N\mathbf{p}\exp\left\{-\beta\sum_i^N\frac{(\mathbf{p}_i-i\boldsymbol{\omega}\frac{m}{\beta})^2}{2m_i}-\frac{mN}{2\beta}\omega^2\right\}$$

$$=\int\frac{d\boldsymbol{\omega}}{(2\pi)^3}\exp\left\{-\frac{mN}{2\beta}\omega^2-i\boldsymbol{\omega}{\cdot}\mathbf{P}\right\}\int d^N\mathbf{p}\exp\left\{-\beta\sum_i^N\frac{\mathbf{p}_i^2}{2m_i}\right\}$$

$$=\exp\left\{-\beta\frac{\mathbf{P}^2}{2Nm}\right\}\left(\frac{2\pi m}{\beta}\right)^{3N/2}$$

25

Operators in phase space

Proofs of the properties of the Kawasaki-Gunton projector

- **Proof of (1.3.19)**

$$\mathcal{P}_{t'}\eta = \overline{\rho}_{t'}(z)\mathrm{Tr}[\eta] + \frac{\partial \overline{\rho}_{t'}}{\partial a(t')}(z)\mathrm{Tr}\left[(A - a(t'))\eta\right]$$

$$\mathcal{P}_t\mathcal{P}_{t'}\eta(z) = \overline{\rho}_t(z)\mathrm{Tr}[\mathcal{P}_{t'}\eta] + \frac{\partial \overline{\rho}_t}{\partial a(t)}(z)\mathrm{Tr}\left[(A - a(t))\mathcal{P}_{t'}\eta\right]$$

$$\mathrm{Tr}[\mathcal{P}_{t'}\eta] = \underbrace{\mathrm{Tr}[\overline{\rho}_{t'}(z)]}_{=1}\mathrm{Tr}[\eta] + \underbrace{\mathrm{Tr}\left[\frac{\partial \overline{\rho}_{t'}}{\partial a(t')}(z)\right]}_{=0}\mathrm{Tr}\left[(A - a(t'))\eta\right] = \mathrm{Tr}[\eta]$$

$$
\begin{aligned}
\mathrm{Tr}\left[(A - a(t))\mathcal{P}_{t'}\eta\right] &= \mathrm{Tr}\left[(A - a(t))\left[\overline{\rho}_{t'}(z)\mathrm{Tr}[\eta] + \frac{\partial \overline{\rho}_{t'}}{\partial a(t')}(z)\mathrm{Tr}\left[(A - a(t'))\eta\right]\right]\right] \\
&= \mathrm{Tr}\left[(A - a(t))\overline{\rho}_{t'}(z)\mathrm{Tr}[\eta]\right] \\
&\quad + \mathrm{Tr}\left[(A - a(t))\frac{\partial \overline{\rho}_{t'}}{\partial a(t')}(z)\mathrm{Tr}\left[(A - a(t'))\eta\right]\right] \\
&= (a(t') - a(t))\mathrm{Tr}[\eta] + \mathrm{Tr}\left[(A - a(t))\frac{\partial \overline{\rho}_{t'}}{\partial a(t')}\right]\mathrm{Tr}\left[(A - a(t'))\eta\right] \\
&= (a(t') - a(t))\mathrm{Tr}[\eta] + \mathrm{Tr}\left[A\frac{\partial \overline{\rho}_{t'}}{\partial a(t')}\right]\mathrm{Tr}\left[(A - a(t'))\eta\right] \\
&= (a(t') - a(t))\mathrm{Tr}[\eta] + \mathrm{Tr}\left[(A - a(t'))\eta\right] \\
&= \mathrm{Tr}\left[(A - a(t))\eta\right]
\end{aligned}
$$

Therefore,

$$\mathcal{P}_t \mathcal{P}_{t'} \eta(z) = \overline{\rho}_t(z) \text{Tr}[\eta] + \frac{\partial \overline{\rho}_t}{\partial a(t)}(z) \text{Tr}\left[(A - a(t))\eta\right] = \mathcal{P}_t \eta(z)$$

- **Proof of (1.3.22)** To prove it, just use the definitions (1.3.8), (1.3.11)

$$\mathcal{P}_t(\overline{\rho}_t F)(z) = \overline{\rho}_t(z) \text{Tr}[\overline{\rho}_t F] + \frac{\partial \overline{\rho}_t}{\partial a(t)}(z) \text{Tr}\left[(A - a(t))\overline{\rho}_t F\right]$$

$$\overline{\rho}_t(z) \mathcal{P}_t^\dagger \hat{F}(z) = \overline{\rho}_t(z) \text{Tr}[\overline{\rho}_t F] + \overline{\rho}_t(z)(\hat{A}(z) - a(t)) \text{Tr}\left[\frac{\partial \overline{\rho}_t}{\partial a(t)} F\right]$$

Then, we have to show that

$$\frac{\partial \overline{\rho}_t}{\partial a_\nu(t)}(z) \text{Tr}\left[(A_\nu - a_\nu(t))\overline{\rho}_t F\right] = \overline{\rho}_t(z)(A_\nu(z) - a_\nu(t)) \text{Tr}\left[\frac{\partial \overline{\rho}_t}{\partial a_\nu(t)} F\right]$$

Let us compute the derivative of the relevant ensemble with respect to the average

$$\frac{\partial \overline{\rho}_t}{\partial a_\nu(t)} = \overline{\rho}_t \frac{\partial \lambda_\mu}{\partial a_\nu(t)}(a_\mu(t) - A_\mu(z))$$

Insert back

$$\overline{\rho}_t \frac{\partial \lambda_\mu}{\partial a_\nu(t)}(a_\mu(t) - A_\mu(z)) \text{Tr}\left[(A_\nu - a_\nu(t))\overline{\rho}_t F\right]$$

$$= \overline{\rho}_t(z)(A_\nu(z) - a_\nu(t)) \text{Tr}\left[\overline{\rho}_t \frac{\partial \lambda_\mu}{\partial a_\nu(t)}(a_\mu(t) - A_\mu(z))F\right]$$

which is seen to be equal.

- $\mathcal{P}_t^\dagger$ is self-adjoint with respect to the relevant ensemble

$$\text{Tr}\left[\overline{\rho}_t F \mathcal{P}_t^\dagger G\right] = \text{Tr}\left[\overline{\rho}_t G \mathcal{P}_t^\dagger F\right]$$

26

Bibliography

These are the books on which this work is based

- Grabert
- HCO
- Berendsen
- Tuckermann
- Andersen