

Structural Phase Field Crystal Models as a Lense on Nonequilibrium Kinetic Pathways

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DEDICATION

My dedication....

ACKNOWLEDGEMENTS

Acknowledgments, if included, must be written in complete sentences. Do not use direct address. For example, instead of Thanks, Mom and Dad!, you should say I thank my parents.

ABSTRACT

Abstract in English and French are required. The text of the abstract in English begins here.

ABRÉGÉ

The text of the abstract in French begins here.

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CHAPTER 1

Introduction

CHAPTER 2

Fundamentals

In this chapter we'll describe the fundamental physics behind the phase field crystal theory. Like many physical theories, it is derived using a set of successive approximations. Each approximation yield a new theory that is more narrow in scope, but more tractible to either analytic or numerical analysis.

PFC is ultimately a thermodynamic theory and as such it makes connection to fundamental, microscopic physics by way of statistical mechanics. Statistical mechanics tied the macroscopic observables to microscopic phenomena with a probabilistic approach. The basic assumption at this level is that, if a system is sufficiently complex, there are circumstances under which its statistical behaviour becomes relatively simple. Now for systems with macroscopic ($\mathcal{O}(10^{23})$) amount of particles this is almost always the case and so for this large systems we can often compute the macroscopic or thermodynamic observables using a statistical approach instead of solving the microscopic equations of motion.

At the fundamental level, our systems of interest are governed by quantum mechanics and so we might use the theory of quantum statistical mechanics to attempt to compute the thermodynamic observables of our system. We will see that for our systems of interest that the quantum statistical theory is quite intractible, but with an approximation we can treat our system in the *semi-classical limit*.

In semi-classical limit, we can talk in a robust way about the structure of the density field, using the Classical Density Functional Theory (CDFT) framework. While CDFT supplies the correct setting to discuss the density, it is again rarely feasible to perform exact calculations.

Finally, we'll see that an approximation of the exact CDFT free energy functional will yield the PFC theory that is amenable to both analytic and numerical analysis.

2.1 Statistical Mechanics in the Semi-classical limit

Although the quantum statistical mechanics picture gives us a link between the microscopic and macroscopic reality of thermodynamics systems, it still contains too much detail for many systems of interest. For instance, for many systems of interest, the precise bosonic or fermionic nature of the particles in the system has little consequence on the thermodynamic properties. We can ignore some of these quantum mechanical details by looking at statistical mechanics in the *semi-classical limit*.

For the sake of clarity, we'll look at a system of N identical particles in the canonical ensemble but generalization to multi-component systems and other ensembles is straight forward. We start with the definition of the partition function for a system of many particles,

$$Z = \text{Tr} \left(e^{-\beta \hat{H}} \right), \quad (2.1)$$

where, $\hat{H} = \frac{|\mathbf{p}|^2}{2m} + V(\mathbf{q})$ and $\mathbf{p} = (p_1, p_2, \dots, p_N)$ is the vector of particle momenta. \mathbf{q} is similarly defined for the particle positions. Wigner [12], and, shortly after,

Kirkwood [5] showed that the partition function could be expanded in powers of \hbar , facilitating the calculation of both a classical limit and quantum corrections to the partition function. Their method, the Wigner-Kirkwood expansion, involves evaluating the trace operation over a basis of plain wave solutions,

$$\mathcal{Z}(\beta) = \int \frac{d\mathbf{q}d\mathbf{p}}{(2\pi\hbar)^N} e^{-\frac{i\mathbf{p}\cdot\mathbf{q}}{\hbar}} e^{-\beta\hat{H}} e^{\frac{i\mathbf{p}\cdot\mathbf{q}}{\hbar}} = \int d\Gamma I(p, q), \quad (2.2)$$

Where, $d\Gamma$ is the phase space measure $d\mathbf{p}d\mathbf{q}/(2\pi\hbar)^N$. To compute the integrand, $I(p, q)$, we follow Uhlenbeck and Bethe [11] and first compute its derivative,

$$\frac{\partial I(p, q)}{\partial \beta} = -e^{\frac{i\mathbf{p}\cdot\mathbf{q}}{\hbar}} \hat{H} e^{-\frac{i\mathbf{p}\cdot\mathbf{q}}{\hbar}} I(p, q). \quad (2.3)$$

If we then make a change of variables, $I(q, p) = e^{-\beta\mathcal{H}}W(q, p)$, where \mathcal{H} is the classical Hamiltonian, and use the explicit form of the quantum Hamiltonian we arrive at a partial differential equation for W .

$$\frac{\partial W}{\partial \beta} = \frac{\hbar^2}{2} \left(\nabla_{\mathbf{q}}^2 - \beta(\nabla_{\mathbf{q}}^2 V) + \beta^2(\nabla V)^2 - 2\beta(\nabla_{\mathbf{q}} V) \cdot \nabla_{\mathbf{q}} + 2\frac{i}{\hbar}\mathbf{p} \cdot (\nabla_{\mathbf{q}} - \beta\nabla_{\mathbf{q}}) \right) W(q, p) \quad (2.4)$$

The solution can be written as a power series in \hbar , $W = 1 + \hbar W_1 + \hbar W_2 + \dots$. This creates a power series expansion for the partition function as well,

$$\mathcal{Z} = (1 + \hbar \langle W_1 \rangle + \hbar^2 \langle W_2 \rangle + \dots) \int d\Gamma e^{\beta\mathcal{H}}. \quad (2.5)$$

Where the average, $\langle \cdot \rangle$, denotes the the classical average,

$$\langle A(p, q) \rangle = \frac{1}{\mathcal{Z}} \int d\Gamma A(p, q) e^{-\beta\mathcal{H}}. \quad (2.6)$$

For the sake of brevity we'll simply quote solution to second order, but details can be found in Landau and Lifshitz [6]. Interestingly, the first order term is exactly zero.

$$\langle W_1 \rangle = 0 \quad (2.7)$$

$$\langle W_2 \rangle = -\frac{\beta^3}{24m} \langle |\nabla_{\mathbf{q}} V|^2 \rangle \quad (2.8)$$

In terms of the free energy, for example, the corrections to second order would be,

$$\mathcal{F} = \mathcal{F}_{classical} + \frac{\hbar^2 \beta^2}{24m} \langle |\nabla_{\mathbf{q}} V(\mathbf{q})|^2 \rangle. \quad (2.9)$$

There are a few things to note about this finding, first of all the correction inversely proportional to both the temperature and the particle mass. For copper at room temperature, for instance, the prefactor $\hbar^2 \beta^2 / (24m)$ is $\mathcal{O}(10^{-4})$. The correction is also proportional to the mean of the squared force felt by each particle. So high density materials will have a higher quantum correction because they sample the short-range repulsive region of the pair potential more than their low density counter parts.

2.1.1 Indistinguishability

There is an important distinction to be made between the quantum theory and the theory in the semi-classical limit. The integral over phase space of the partition function must only take into account the *physically different* states of the system. In the quantum theory this is achieved by tracing over any orthonormal basis of the Hilbert space, but in the classical theory we need to be careful not to double count states when identical particles are in the theory. Exchange of

two identical particles does not result in a physically different state and thus this state should only be considered only once in the sum over states in the partition function. More precisely, we should write the classical partition function as,

$$\mathcal{Z} = \int' d\Gamma e^{-\beta\mathcal{H}}, \quad (2.10)$$

Where the primed integral denotes integration only over the physically distinct states. In the common case of N identical particles, the phase space integral becomes,

$$\int' d\Gamma \rightarrow \frac{1}{N!} \int d\Gamma \quad (2.11)$$

Aggregating our results, we can write the partition function in the semi-classical limit as,

$$\mathcal{Z}(\beta) = \frac{1}{N!} \int d\Gamma e^{-\beta\mathcal{H}}, \quad (2.12)$$

Or, in the grand canonical ensemble,

$$\Xi(\mu, \beta) = \sum_{N=0}^{\infty} \frac{e^{\beta\mu N}}{N!} \int d\Gamma e^{-\beta\mathcal{H}} \quad (2.13)$$

Of course, this is exactly the form taught in introductory courses on statistical mechanics and derived by Gibbs¹ prior to any knowledge of quantum mechanics

¹ The \hbar in Gibbs' formula was justified on dimensional grounds and was simply a scaling factor with units of action ($J \cdot s$)

[2]. The key insight here is to understand in a controlled way when this approximation is accurate and the magnitude of the next quantum correction is as seen in equation 2.9.

2.2 Classical Density Functional Theory

Ostensibly, when we study formation and evolution of microstructure in solids, our observable of interest is the density field. As per usual in theories of statistical thermodynamics we must distinguish between microscopic operators and macroscopic observables (the later being the ensemble average of the former). In classical statistical mechanics, operators are simply functions over the phase space, Γ . We use the term operator to make connection with the quantum mechanical theory. In the case of the density field, the microscopic operator is sum of Dirac delta functions at the position of each particle,

$$\hat{\rho}(x; \mathbf{q}) = \sum_{i=0}^N \delta^{(3)}(x - q_i) \quad (2.14)$$

Whence the thermodynamic observable is,

$$\rho(x) = \langle \hat{\rho}(x; \mathbf{q}) \rangle = \text{Tr}(\hat{\rho}(x; \mathbf{q}) f(\mathbf{q}, \mathbf{p})) \quad (2.15)$$

Where, $\text{Tr}(\cdot)$ denotes the classical trace²,

$$\text{Tr}(A(\mathbf{q}, \mathbf{p})) = \sum_{N=0}^{\infty} \frac{1}{N!} \int d\Gamma A(\mathbf{q}, \mathbf{p}), \quad (2.16)$$

² The classical trace in the grand canonical example in this particular case

And, $f(\mathbf{q}, \mathbf{p})$ is the probability density function,

$$f(\mathbf{q}, \mathbf{p}) = \frac{e^{-\beta(\mathcal{H}-\mu N)}}{\Xi(\mu, \beta)}. \quad (2.17)$$

To construct a theory of the density field we review the usual methodology for statistical thermodynamics. We will do so in the frame of entropy maximization in which the entropy is maximized subject to the macroscopically available information. Taking the existence of a average of the density field, particle number and energy as the macroscopically available information, we can maximize the entropy functional,

$$S[f(\mathbf{q}, \mathbf{p})] = -k_b \text{Tr} (f(\mathbf{q}, \mathbf{p}) \ln (f(\mathbf{q}, \mathbf{p}))), \quad (2.18)$$

With a probability density function of the form,

$$f(\mathbf{q}, \mathbf{p}) \propto \exp \left(-\beta(\mathcal{H} - \mu N + \int dx \phi(x) \hat{\rho}(x)) \right). \quad (2.19)$$

Where, β , μ and $\phi(x)$ are the Lagrange multipliers associated with constraints of average energy, number of particles and density respectively. As you might imagine the constraints of average particle number and density are not independent and we with the insight that,

$$N = \int dx \hat{\rho}(x), \quad (2.20)$$

We can combine their Lagrange multipliers into one,

$$f(\mathbf{q}, \mathbf{p}) \propto \exp \left(-\beta(\mathcal{H} - \int dx \psi(x) \hat{\rho}(x)) \right), \quad (2.21)$$

Where, $\psi(x) = \mu - \phi(x)$, is the combined Langrange multiplier named the *intrinsic chemical potential*. Recalling that chemical potential is the change Helmholtz free energy made by virtue of adding particles to the system,

$$\frac{\partial F}{\partial N} = \mu, \quad (2.22)$$

The interpretation of the intrinsic chemical potential follows as the Helmholtz free energy change due to particles being added to a specific location. We'll see this in more detail briefly. Now, as with all statistical mechanics theories, the challenge to is to compute the moment generating function (partition function) or equivalently the cumulant generating function (free energy) so as to compute the statistics of our observable of choice. In case of observables of the density field, this is made somewhat more technical by the fact that the density is an entire function instead of a scalar variable. As such the partition function is more precisely called the partition *functional* and the free energy function is more precisely called the free energy *functional*. Specifically, the grand canonical partition functional is,

$$\Xi[\psi(x)] = \text{Tr} \left(\exp \left(-\beta \mathcal{H} + \beta \int dx \psi(x) \hat{\rho}(x) \right) \right). \quad (2.23)$$

As eluded to above, the partition function is a type of moment generating functional in that repeated functional differentiation yields moments of the density field:

$$\frac{\beta^{-n}}{\Xi} \frac{\delta^n \Xi[\psi]}{\delta \psi(x_1) \dots \delta \psi(x_n)} = \langle \hat{\rho}(x_1) \dots \hat{\rho}(x_n) \rangle. \quad (2.24)$$

Similarly, we can construct a free energy functional by taking the logarithm of the partition function. This free energy functional in particular is called the *grand*

potential functional.

$$\Omega[\psi(x)] = -k_b T \ln (\Xi[\psi(r)]) \quad (2.25)$$

The grand potential functional is a type of cumulant generating functional in the sense that repeated functional differentiation yields cumulants of the density field:

$$-\beta^{-n} \frac{\delta^n \beta \Omega[\psi]}{\delta \psi(x_1) \dots \delta \psi(x_n)} = \langle \hat{\rho}(x_1) \dots \hat{\rho}(x_n) \rangle_c \quad (2.26)$$

Where, $\langle A^1 \dots A^n \rangle_c$, denotes the n-variable joint cumulant.

If we examine, the first two cumulants we discover something remarkable about average the average density, $\rho(x)$. The mean is,

$$\frac{\delta \Omega[\psi]}{\delta \psi(x)} = -\langle \hat{\rho}(x) \rangle \equiv \rho(x), \quad (2.27)$$

And the pair correlation function can be expressed as,

$$\frac{\delta^2 \Omega[\psi]}{\delta \psi(x) \delta \psi(x')} = -\beta \langle (\hat{\rho}(x) - \rho(x))(\hat{\rho}(x') - \rho(x')) \rangle. \quad (2.28)$$

As noted by Espanol et al [cite], the real underpinning of classical density functional theory is in the combination of these two equations. The first, implies that the average density field is a function of only its conjugate field, the intrinsic chemical potential, and the second implies that that relationship is invertible³. To

³ The inverse function theorem only implies local invertibility, there is no guarantee of global invertibility. Indeed phase coexistence is a manifestation of this fact where a single intrinsic chemical potential is shared by two phases

see this note that the Jacobian,

$$\frac{\delta\rho(x)}{\delta\psi(x')} = \beta \langle (\hat{\rho}(x) - \rho(x))(\hat{\rho}(x') - \rho(x')) \rangle, \quad (2.29)$$

must be positive semi-definite because of the correlation function on the right hand side. Furthermore, we can make a new thermodynamic potential called the *intrinsic free energy functional* by applying a Legendre transform to the grand potential,

$$\mathcal{F}[\rho(x)] = \Omega[\psi[\rho]] + \int dx \rho(x) \psi(x). \quad (2.30)$$

It can be shown [3] that $\rho(x)$ must be the global minimum of the grand potential, which sets the stage for the methodology of classical density functional theory: if we have a defined intrinsic free energy functional, \mathcal{F} , we can find the equilibrium density field by solving the associated Euler-Lagrange equation,

$$\frac{\delta\Omega[\rho]}{\delta\rho(r)} = 0. \quad (2.31)$$

2.2.1 Techniques in Density Functional Theory

The difficulty in formulating a density functional theory is the construction of an appropriate free energy functional. While exact calculations are rarely feasible, there are a variety of techniques that help in building approximate functionals. Its important to note first what we *can* compute exactly. In the case of the ideal gas,

we can compute the grand potential and free energy functional exactly,

$$\Omega_{id}[\psi] = -\frac{k_b T}{\Lambda^3} \int dx e^{\beta\psi(x)} \quad (2.32)$$

$$\mathcal{F}_{id}[\rho] = k_b T \int dx \left\{ \rho(x) \ln (\Lambda^3 \rho(x)) - \rho(x) \right\}, \quad (2.33)$$

Where Λ is the thermal de Broglie wavelength,

$$\Lambda = \sqrt{\frac{h^2}{2\pi m k_b T}}. \quad (2.34)$$

We may then express a deviations from ideality by factoring the ideal contribution out of the partition function,

$$\Xi[\psi] = \Xi_{id}[\psi] \Xi_{ex}[\psi], \quad (2.35)$$

leading to grand potential and free energy functionals split into ideal and *excess* components,

$$\Omega = \Omega_{id} + \Omega_{ex} \quad (2.36)$$

$$\mathcal{F} = \mathcal{F}_{id} + \mathcal{F}_{ex}. \quad (2.37)$$

The interaction potential, $V(\mathbf{q})$, in the excess partition function typically makes a direct approach to calculating the excess free energy intractable. Though perturbative methods, including the cluster expansion technique (cite Mayer and Montrell '41), have been developed to treat the interaction potential systematically, other approximation schemes for the excess free energy are typically more pragmatic. In particular, we can approximate the excess free energy by expanding

around a reference homogeneous fluid with chemical potential μ_0 and density ρ_0 ,

$$\mathcal{F}_{ex}[\rho] = \mathcal{F}_{ex}[\rho_0] + \left. \frac{\delta \mathcal{F}_{ex}}{\delta \rho(x)} \right|_{\rho_0} * \Delta \rho(x) + \frac{1}{2} \Delta \rho(x') * \left. \frac{\delta^2 \mathcal{F}_{ex}}{\delta \rho(x) \delta \rho(x')} \right|_{\rho_0} * \Delta \rho(x) + \dots, \quad (2.38)$$

Where $\Delta \rho(x) = \rho(x) - \rho_0$ and we have introduced the notation, $*$ to mean integration over repeated co-ordinates,

$$f(x') * g(x') \equiv \int dx' f(x') g(x'). \quad (2.39)$$

The excess free energy is the generating functional of family of correlation functions called *direct correlation functions*,

$$\frac{\delta^n \mathcal{F}_{ex}[\rho]}{\delta \rho(x_1) \dots \delta \rho(x_n)} = -\beta C^n(x_1, \dots, x_n). \quad (2.40)$$

The first of which, for a uniform fluid, is the excess contribution to the chemical potential which we may express as the total chemical potential less the ideal contribution,

$$\left. \frac{\delta F_{ex}}{\delta \rho} \right|_{\rho_0} = \mu_0^{ex} = \mu_0 - \mu_{id} = \mu_0 - k_b T \ln(\Lambda^3 \rho_0). \quad (2.41)$$

Combining ideal and excess contributions and subtracting off the constant reference free energy we arrive at an approximation for the deviation in free energy from the reference.

$$\beta \Delta \mathcal{F}[\rho] = \int dx \left\{ \rho(x) \ln \left(\frac{\rho(x)}{\rho_0} \right) - (1 - \beta \mu_0) \Delta \rho(x) \right\} - \frac{1}{2} \Delta \rho(r) * C_0^{(2)}(r, r') * \Delta \rho(r') \quad (2.42)$$

Its reasonable to ask at this point whether or not we have really gained anything with this approximation scheme. Although we have arrived at a relatively

simple form for the free energy functional, we've added a lot of parameters to the functional based on the reference fluid. In fact, finding the direct pair correlation function, $C_0^{(2)}(x, x')$, for the reference fluid involves solving a difficult integral in its own right. There are potential resolutions to this problem: the first is that something about HNC blargh

CHAPTER 3
Classical Density Functional Theory of Freezing

Classical density function theory

CHAPTER 4

Fake

4.1 Introduction

To describe the process of solidification we will be using the phase field crystal theory. Phase field crystal theory is a type of classical density functional theory. Work by Youssof and Ramakrishnan[9] and Evans[cite] extended the classical density functional theory of inhomogeneous fluids to the phenomena of solidification in pure materials. While the phase field crystal theory was first produced through purely phenomenological means as a variation on the Swift-Hohenberg model[cite], later work showed that the model can be seen as simplification of the Youssof and Ramakrishnan work on the density functional theory of freezing [cite].

The connection between phase field crystal theory and density functional theory is important in that it supplies a microscopic motivation of the parameters in the phase field crystal. CDFT is an important ground for motivating any modifications to the PFC theory. To establish both the language of the phase field crystal model as well as its underlying microscopic origins we'll proceed by deriving the classical density functional theory for a pure material. Later we'll see that this generalizes readily to the case of a binary material and how we can construct equations of motion for the density using the so-called Dynamic Density Functional Theory (DDFT).

The following derivation will follow the work of Hansan [cite theory of simple liquids / or pep espanol].

4.2 Deriving the Intrinsic Free Energy Functional

The central object of classical density functional theory is the density field of the system, $\rho(x)$, defined as,

$$\rho(x) = \sum_{i=1}^N \delta^{(3)}(x - x_i). \quad (4.1)$$

To construct a statistical theory for the density field we begin by finding the equilibrium probability by maximizing the entropy subject to the macroscopically available information. Should we take the macroscopically available information to be the existence of an average energy, average particle number and average density field, we arrive at a modification of the grand canonical ensemble,

$$f(\mathbf{r}^N, \mathbf{p}^N, N) = \frac{1}{\Xi[\psi(r)]} \frac{\exp \left\{ -\beta \mathcal{H}(\mathbf{r}^N, \mathbf{p}^N) + \beta \int dr \psi(r) \rho(r) \right\}}{h^{3N} N!}. \quad (4.2)$$

β , the Lagrange multiplier associated with the constraint of average energy, we immediately associate with the temperature via $\beta = (k_b T)^{-1}$. Interesting, the constraints of average particle number and density are not independent and their separate Lagrange multipliers, traditionally associated with the chemical potential μ and external potential $\phi(x)$, can be combined into a single multiplier, $\psi(r)$, called the *intrinsic chemical potential*.

The partition function, Ξ , is a normalization constant and can be seen as a modification to the grand partition function,

$$\Xi[\psi(r)] = \sum_{N=0}^{\infty} \frac{1}{h^{3N} N!} \int d\mathbf{r}^N d\mathbf{p}^N \exp \left\{ -\beta \mathcal{H}(\mathbf{r}^N, \mathbf{p}^N) + \beta \int dr \psi(r) \rho(r) \right\}. \quad (4.3)$$

We can also establish an associated thermodynamic potential in the traditional manner which we will call the grand potential for convenience.

$$\Omega[\psi(r)] = -k_b T \ln \Xi[\psi(r)] \quad (4.4)$$

The grand potential produces cumulants of the density field under functional differentiation as we might expect. Specifically, the average density field is,

$$\frac{\delta \Omega[\psi]}{\delta \psi(r)} = -\langle \rho(r) \rangle \equiv \rho_1(r), \quad (4.5)$$

And the pair correlation function can be expressed as,

$$\frac{\delta^2 \Omega[\psi]}{\delta \psi(r) \delta \psi(r')} = -\beta \langle (\rho(r) - \rho_1(r)) (\rho(r') - \rho_1(r')) \rangle. \quad (4.6)$$

As noted by Espanol et al [cite], the real underpinning of classical density functional theory is in the combination of these two equations. The first, implies that the average density field is a function of only its conjugate field, the intrinsic chemical potential, and the second implies that that relationship is invertible. To see this note that the Jacobian,

$$\frac{\delta \rho_1(r)}{\delta \psi(r')} = \beta \langle (\rho(r) - \rho_1(r)) (\rho(r') - \rho_1(r')) \rangle, \quad (4.7)$$

must be positive semi-definite because of the correlation function on the right hand side. Furthermore, we can make a new thermodynamic potential called the *intrinsic free energy functional* by applying a Legendre transform to the grand potential,

$$\mathcal{F}[\rho_1(x)] = \Omega[\psi[\rho]] + \int dr \rho_1(r) \psi(r). \quad (4.8)$$

It can be shown [cite Hansen appendix] that $\rho_1(x)$ must be the global minimum of the grand potential, which sets the stage for the methodology of classical density functional theory: if we have a defined intrinsic free energy functional, \mathcal{F} , we can find the equilibrium density field by solving the associated Euler-Lagrange equation,

$$\frac{\delta \Omega[\rho]}{\delta \rho(r)} = 0. \quad (4.9)$$

4.3 Approximating $\mathcal{F}[\rho]$

To build a theory a freezing using the classical density functional theory we must first construct an appropriate intrinsic free energy functional. We can split the contribution to the free energy functional into two terms: the ideal and excess.

$$\mathcal{F}[\rho] = \mathcal{F}_{id}[\rho] + \mathcal{F}_{ex}[\rho] \quad (4.10)$$

The ideal term is generated from the kinetic energy term in the Hamiltonian. Assuming that there are not momentum dependent interactions in the Hamiltonian this contribution can be computed exactly as,

$$\mathcal{F}_{id}[\rho] = k_b T \int dr \rho(r) \ln (\Lambda^3 \rho(r)) - \rho(r). \quad (4.11)$$

Where, Λ , is the thermal deBroglie wavelength,

$$\Lambda = \sqrt{\frac{h^2}{2\pi m k_b T}}. \quad (4.12)$$

The excess term, on the other hand, typically needs to be approximated in some way because it is generated from the interaction potential term in the Hamiltonian which, for most systems, leads to a completely intractable integral. While some perturbation theories exist to approach this problem, including the cluster expansion [Mayer & Montrell 1941], it is typically more successful to resort to a judicious choice of closure for the Ornstein-Zernike equation. It can be shown that closures of the Ornstein-Zernike equation are equivalent to summing a subset of terms in the cluster expansion to all orders in the perturbation theory.

Youssof and Ramakrishnan argued that the HNC or hyper-netted chain approximation was just such a choice of closure for the problem of solidification. The HNC closure is known to give accurate solutions in the case of weak long range potentials such as those seen in plasmas. Though the pair potential of a solidifying system may be short-range, in a solid the short-ranged potentials combine to make an effectively long-ranged periodic potential of the lattice and thus the HNC closure is a good choice.

The HNC closure can be seen as a simple Taylor expansion of the excess free energy functional about a uniform reference fluid of density ρ_0 ,

$$\mathcal{F}_{ex}[\rho] \approx \mathcal{F}_{ex}[\rho_0] + \int dr \left. \frac{\delta \mathcal{F}_{ex}}{\delta \rho(r)} \right|_{\rho_0} \Delta \rho(r) + \frac{1}{2} \int dr dr' \Delta \rho(r) \left. \frac{\delta^2 \mathcal{F}_{ex}}{\delta \rho(r) \delta \rho(r')} \right|_{\rho_0} \Delta \rho(r') + \dots \quad (4.13)$$

The excess free energy is the generating functional of direct correlation functions,

$$\frac{\delta^n \mathcal{F}_{ex}[\rho]}{\delta \rho(r_1) \dots \delta \rho(r_n)} = -\beta C^n(r_1, \dots, r_n). \quad (4.14)$$

The first of which, for a uniform fluid, is the excess contribution to the chemical potential which we may express as the total chemical potential less the ideal contribution,

$$\left. \frac{\delta F_{ex}}{\delta \rho} \right|_{\rho_0} = \mu_0^{ex} = \mu_0 - k_b T \ln(\Lambda^3 \rho_0). \quad (4.15)$$

Combining ideal and excess contributions and subtracting off the constant reference free energy we arrive at an approximation for the deviation in free energy from the reference.

$$\Delta \mathcal{F}[\rho] = k_b T \int dr \rho(r) \ln \left(\frac{\rho(r)}{\rho_0} \right) - (1 - \beta \mu_0) \Delta \rho(r) - \frac{1}{2} \Delta \rho(r) \int dr' C^{(2)}(r, r') \Delta \rho(r') \quad (4.16)$$

At this stage we carry out the methodology of classical density functional theory as previously mentioned by Legendre transforming to the grand potential and minimizing with respect to the density. Doing so reveals a self-consistent form for the equilibrium density field,

$$\rho_1(x) = \rho_0 \exp \left\{ -\beta \phi(r) + \int dr' \Delta \rho_1(r') C^{(2)}(r, r') \right\} \quad (4.17)$$

Further manipulations of this solutions would show that it is equivalent to the HNC closure, but the important result due to Youssof and Ramakrishnan is to note that, in the absense of an external field there are two solutions: the trivial reference solutions ρ_0 and a period *solid* solution at higher densities. The take home story as it contributes to the phase field crystal theory is that the free energy functional in equation [free energy reference] contains a enough information to describe solidification. The free energy functional used in phase field crystal theories is a further simplification of HNC version involving a variety of models and simplifications of the pair correlation function and modification or expansions of the logarithm term.

CHAPTER 5

Dynamics

5.1 Introduction

CHAPTER 6

Applications

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Noise in Nonlinear Langevin Equations

When using Langevin equations to study non-equilibrium statistical mechanics the noise strength can be linked to the transport coefficients through a generalization of the Einstein relation. The generalization was first developed by Onsager and Machlup [8]. The typical strategy for deriving such a relationship is to evaluate the equilibrium pair correlation function by two separate methods: the equilibrium partition functional and the equation of motion¹.

While the equilibrium partition functional gives pair correlation through the typical statistical mechanical calculation, the equation of motion can be used to derive a dynamic pair correlation function that must be equal to the equilibrium pair correlation function in the long time limit.

In what follows we'll look at how to formulate a generalized Einstein relation from a generic Langevin equation and then calculate two specific examples using Model A dynamics and a ϕ^4 theory and Time Dependent Density Functional Theory (TDDFT) and a general Helmholtz free energy.

6.1 Generalized Einstein Relations in an Arbitrary Model

We start by considering a set of microscopic observables, $a_i(r, t)$, that are governed by a nonlinear Langevin equation,

¹ For considerations far from equilibrium see [7, 10, 1]

$$\frac{\partial \mathbf{a}(r, t)}{\partial t} = F[\mathbf{a}(r, t)] + \boldsymbol{\xi}(r, t). \quad (6.1)$$

Where, \mathbf{a} , denotes a vector of our fields of interest. These microscopic equation of motion may have been derived from linear response, projection operators or some other non-equilibrium formalism. We assume that the random driving force, $\boldsymbol{\xi}(r, t)$ is unbiased, Gaussian noise that is uncorrelated in time.

$$\langle \boldsymbol{\xi}(r, t) \rangle = 0 \quad (6.2)$$

$$\langle \boldsymbol{\xi}(r, t) \boldsymbol{\xi}^\dagger(r', t') \rangle = \mathbf{L}(r, r') \delta(t - t') \quad (6.3)$$

We wish to constrain the form of the covariance matrix, \mathbf{L} , by demanding that the solution to the Langevin equation eventually decays to equilibrium and that correlations in equilibrium are given by Boltzmann statistics.

We begin by linearizing the equation of motion about an equilibrium solution, $\mathbf{a}(r, t) = \mathbf{a}_{eq}(r) + \hat{\mathbf{a}}(r, t)$.

$$\frac{\partial \hat{\mathbf{a}}(r, t)}{\partial t} = \mathbf{M}(r, r') * \hat{\mathbf{a}}(r', t) + \boldsymbol{\xi}(r, t) \quad (6.4)$$

Where, $*$ denotes an inner product and integration over the repeated variable.
eg:

$$\mathbf{M}(r, r') * \hat{\mathbf{a}}(r') = \sum_j \int dr' M_{ij}(r, r') \hat{a}_j(r'). \quad (6.5)$$

We can formally solve our linearized equation of motion,

$$\hat{\mathbf{a}}(r, t) = e^{\mathbf{M}(r, r')t} * \hat{\mathbf{a}}(r', 0) + \int_0^t d\tau e^{\mathbf{M}(r, r')(t-\tau)} * \boldsymbol{\xi}(r', \tau), \quad (6.6)$$

And use this formal solution to evaluate the dynamic pair correlation function.

$$\begin{aligned} \langle \hat{\mathbf{a}}(r, t) \hat{\mathbf{a}}^\dagger(r', t') \rangle &= e^{\mathbf{M}(r, r_1)t} * \langle \hat{\mathbf{a}}(r_1, 0) \hat{\mathbf{a}}^\dagger(r_2, 0) \rangle * e^{\mathbf{M}^\dagger(r', r_2)t'} \\ &+ \int_0^t \int_0^{t'} d\tau d\tau' e^{\mathbf{M}(r, r_1)(t-\tau)} * \langle \boldsymbol{\xi}(r_1, 0) \boldsymbol{\xi}^\dagger(r_2, 0) \rangle * e^{\mathbf{M}^\dagger(r', r_2)(t'-\tau')} \end{aligned} \quad (6.7)$$

To evaluate the equilibrium correlation function we take the limit as each time goes to infinity together ($t = t' \rightarrow \infty$). It is important to note that every eigenvalue of \mathbf{M} must be negative for our solution to decay to equilibrium in the long time limit (eg. $\lim_{t \rightarrow \infty} \hat{\mathbf{a}}(r, t) = 0$) and as such the first term in our dynamic correlation function won't contribute to the equilibrium pair correlation. This is as we might expect as the first term holds the contributions to the dynamic correlation function from the initial conditions. The second term can be evaluated by substituting the noise correlation and evaluating the delta function.

$$\Gamma(r, r') = \lim_{t \rightarrow \infty} \langle \hat{\mathbf{a}}(r, t) \hat{\mathbf{a}}^\dagger(r', t) \rangle = \int_0^\infty dz e^{\mathbf{M}(r, r_1)z} * \mathbf{L}(r_1, r_2) * e^{\mathbf{M}^\dagger(r', r_2)z} \quad (6.8)$$

Considering the product $\mathbf{M}(r, r_1) * \Gamma(r_1, r')$ and performing an integration by parts gives the final generalized Einstein relation.

$$\mathbf{M}(r, r_1) * \mathbf{\Gamma}(r_1, r') + \mathbf{\Gamma}(r, r_1) * \mathbf{M}^\dagger(r_1, r') = -\mathbf{L}(r, r') \quad (6.9)$$

6.2 Example 1 - Model A

As a first example of calculating an Einstein relation consider the following free energy functional under non-conservative, dissipative dynamics.

$$\beta\mathcal{F}[\phi] = \int dr \left\{ \frac{1}{2} |\nabla\phi(x)|^2 + \frac{r}{2} \phi^2(x) + \frac{u}{4!} \phi^4(x) + h(x)\phi(x) \right\} \quad (6.10)$$

$$\frac{\partial\phi(x, t)}{\partial t} = -\Gamma \left(\frac{\delta\beta\mathcal{F}[\phi]}{\delta\phi(x)} \right) + \xi(x, t) \quad (6.11)$$

The random driving force, ξ , is Gaussian noise, uncorrelated in time.

$$\langle \xi(x, t) \rangle = 0 \quad (6.12)$$

$$\langle \xi(x, t) \xi(x', t') \rangle = L(x - x') \delta(t - t') \quad (6.13)$$

To compute the Einstein relation for this theory we start by calculating the pair correlation function using the equilibrium partition function and Boltzmann statistics.

6.2.1 The partition function route

In equilibrium the probability of particular field configuration is given by the Boltzmann distribution.

$$\mathcal{P}_{eq}[\phi] = \frac{e^{-\beta\mathcal{F}[\phi]}}{\mathcal{Z}[h(x)]} \quad (6.14)$$

Where, $\mathcal{Z}[h(x)]$ is the partition functional and is given by a path integral over all field configurations.

$$\mathcal{Z}[h(x)] = \int \mathcal{D}[\phi] e^{-\beta \mathcal{F}[\phi]} \quad (6.15)$$

Evaluation of the partition function is of some importance because it plays the role of a moment generating function.

$$\frac{1}{\mathcal{Z}[h]} \frac{\delta^n \mathcal{Z}[h]}{\delta h(x_1) \dots \delta h(x_n)} = \langle \phi(x_1) \dots \phi(x_n) \rangle \quad (6.16)$$

In general the partition function cannot be computed directly, but in the special case of Gaussian free energies it can. To that end we consider expanding ϕ around an equilibrium solution, $\phi(x) = \phi_0 + \Delta\phi(x)$, and keeping terms to quadratic order in the free energy.

$$\beta \mathcal{F}[\Delta\phi] = \int dr \left\{ \frac{1}{2} \Delta\phi(x) \left(r - \nabla^2 + \frac{u}{2} \phi_0^2 \right) \Delta\phi(x) - h(x) \Delta\phi(x) \right\} \quad (6.17)$$

Here the partition function is written in a suggestive form. As stated previously, functional integrals are difficult to compute in general, but Gaussian functional integrals do have a solution.

Computing the Pair correlation function in the Gaussian approximation

To compute the pair correlation function we use the Fourier space variant of the partition function,

$$\mathcal{Z}[\tilde{h}(k)] \propto \exp \left\{ \frac{1}{2} \int dk \frac{h(k)h^*(k)}{r + \frac{u}{2}\phi_0^2 + |k|^2} \right\}. \quad (6.18)$$

The pair correlation function, $\langle \Delta\tilde{\phi}(k)\Delta\tilde{\phi}^*(k) \rangle$, is then computed using equation 6.16.

$$\langle \Delta\tilde{\phi}(k)\Delta\tilde{\phi}^*(k') \rangle = \frac{2\pi\delta(k+k')}{r + \frac{u}{2}\phi_0^2 + |k|^2} \quad (6.19)$$

6.2.2 The Equation of Motion Route

The equation of motion supplies a second method for evaluating the pair correlation function in equilibrium.

$$\frac{\partial\phi}{\partial t} = -\Gamma \left((r - \nabla^2)\phi(x, t) + \frac{u}{3!}\phi^3(x, t) \right) + \xi(x, t), \quad (6.20)$$

Our equation of motion, can be linearized around an equilibrium solution, ϕ_0 , just as we did in the partition function route to the pair correlation function. In a similar vain, we will Fourier transform the equation of motion as well.

$$\frac{\partial\Delta\tilde{\phi}(k, t)}{\partial t} = -\Gamma \left(\left(r + \frac{u}{2}\phi_0 + |k|^2 \right) \Delta\tilde{\phi}(k, t) \right) + \xi(x, t) \quad (6.21)$$

Comparing with our generalized approach we can read of $M(k, k')$ from the lineared equation of motion:

$$M(k, k') = -\Gamma \left(\left(r + \frac{u}{2}\phi_0 + |k|^2 \right) \right) \delta(k + k') \quad (6.22)$$

Finally, once we compute the generalized Einstein relation with our specific pair correlation and $M(k, k')$ we find,

$$L(k, k') = 2\Gamma\delta(k + k'), \quad (6.23)$$

Or equivalently,

$$L(x, x') = 2\Gamma\delta(x - x'). \quad (6.24)$$

6.3 Example 2 - Time Dependent Density Functional Theory

In time dependent density functional theory (TDDFT) we have an equation of motion of the following form,

$$\frac{\partial \rho(r, t)}{\partial t} = D_0 \nabla \cdot \left[\rho(r, t) \nabla \left(\frac{\delta \mathcal{F}[\rho]}{\delta \rho} \right) \right] + \xi(r, t) \quad (6.25)$$

Where, D_0 is the equilibrium diffusion constant and ξ is the stochastic driving force. We assume once again that the driving force has no bias, but we now allow the noise strength to be a generic kernel $L(r, r')$.

$$\langle \xi(r, t) \rangle = 0 \quad (6.26)$$

$$\langle \xi(r, t) \xi(r', t') \rangle = L(r, r') \delta(t - t') \quad (6.27)$$

6.3.1 Pair Correlation from the Partition Functional

Just like with the ϕ^4 model we want to expand our free energy functional around an equilibrium solution. In this case our free energy functional is generic so this expansion is purely formal.

$$\mathcal{F}[\rho] = \mathcal{F}_{eq} + \beta \int dr \left(\frac{\delta \mathcal{F}[\rho]}{\delta \rho(r)} \right) \Big|_{\rho_{eq}} \Delta \rho(r) + \frac{1}{2} \int dr \int dr' \Delta \rho(r) \left(\frac{\delta^2 \mathcal{F}[\rho]}{\delta \rho(r) \delta \rho(r')} \right) \Big|_{\rho_{eq}} \Delta \rho(r') \quad (6.28)$$

The first term we can neglect as it adds an overall scale to the partition function that will not affect any of moments. Second moment only shifts the average so we can ignore it as well and so we're left with a simple quadratic free energy once again.

$$\mathcal{F}[\rho] = \frac{1}{2} \int dr \int dr' \Delta \rho(r) \Gamma^{-1}(r, r') \Delta \rho(r') \quad (6.29)$$

Where, $\Gamma^{-1}(r, r')$ is the second functional derivative of the free energy functional in equilibrium. Computing the pair correlation function from the partition function yields, as might be expected,

$$\langle \Delta \rho(r) \Delta \rho(r') \rangle = \Gamma(r, r') \quad (6.30)$$

6.3.2 Linearizing the equation of motion

Linearizing the equation of motion about an equilibrium solution we find the following form,

$$\frac{\partial \Delta \rho(r, t)}{\partial t} = D_0 \nabla \cdot [\rho_{eq}(r) \nabla (\Gamma^{-1}(r, r') * \Delta \rho(r', t))] + \xi(r, t) \quad (6.31)$$

Once again we can read off the kernel $M(r, r')$ from the linearized equation.

$$M(r, r') = D_0 \nabla \cdot [\rho_{eq}(r) \nabla (\Gamma^{-1}(r, r'))] \quad (6.32)$$

Plugging into the generalized Einstein relation, we find a the factors of the pair correlation cancel giving a simple form for the kernel $L(r, r')$.

$$L(r, r') = -2D_0 \nabla \cdot (\rho_{eq}(r) \nabla) \delta(r - r') \quad (6.33)$$

Gaussian Functional Integrals

Gaussian Functional Integrals

In the study of the statistical physics of fields we often encounter functional integrals of the form,

$$\mathcal{Z}[h(x)] = \int \mathcal{D}[\phi] \exp \left\{ - \int dx \int dx' \left[\frac{1}{2} \phi(x) \mathbf{K}(x, x') \phi(x') \right] + \int dx [h(x) \phi(x)] \right\}. \quad (6.34)$$

Solutions to this integral are not only important in there own right but are also the basis perturbative techniques. The detail of how to solve this integral can be found in [4] and are repeated here for the convenience of the reader.

This integral is simply the continuum limit of a multivariable Gaussian integral,

$$\mathcal{Z}[\mathbf{h}] = \int \prod_i dx_i \exp \left\{ - \frac{1}{2} \sum_i \sum_j x_i \mathbf{K}_{ij} x_j + \sum_i h_i x_i \right\}, \quad (6.35)$$

For which the solution is,

$$\mathcal{Z}[\mathbf{h}] = \sqrt{\frac{2\pi}{\det(\mathbf{K})}} \exp \left\{ \frac{1}{2} \sum_i \sum_j h_i \mathbf{K}_{ij}^{-1} h_j \right\}. \quad (6.36)$$

In the continuum limit, the solution has an analogous form.

$$\mathcal{Z}[h(x)] \propto \exp \left\{ \int dx \int dx' \left[\frac{1}{2} h(x) \mathbf{K}^{-1}(x, x') h(x') \right] \right\} \quad (6.37)$$

Where \mathbf{K}^{-1} is defined by,

$$\int dx' \mathbf{K}(x, x') \mathbf{K}^{-1}(x', x'') = \delta(x - x''). \quad (6.38)$$

Ultimately, we don't need to worry about the constant of proportionality in equation 6.37 because we'll be dividing this contribution when calculating correlation functions.

Binary Correlation Functions

When developing the binary PFC model there is a change of variables that must occur from ρ_A and ρ_B to n and c . Computing the bulk terms is a matter of substitution and simplifying as much as possible but the pair correlation terms can be more subtle. When computing the pair correlation terms, careful application of our assumption that c varies over a much longer length scale than n must be applied to get the correct solution. The goal, ultimately, is to find C_{nn} , C_{nc} , C_{cn} and C_{cc} in the following expression,

$$\begin{aligned} \delta\rho_A C_{AA} * \delta\rho_A + \delta\rho_A C_{AB} * \delta\rho_B + \delta\rho_B C_{BA} * \delta\rho_A + \delta\rho_B C_{BB} * \delta\rho_B = \quad (6.39) \\ \rho_0 (n C_{nn} * n + n C_{nc} * \delta c + \delta c C_{cn} * n + \delta c C_{cc} * \delta c). \end{aligned}$$

We begin by rewriting $\delta\rho_B$,

$$\begin{aligned} \delta\rho_B &= \rho c - \rho_0 c_0 \\ &= \rho c - \rho c_0 + \rho c_0 - \rho_0 c_0 \\ &= \delta\rho c + \rho_0 \delta c, \end{aligned}$$

Followed by rewriting $\delta\rho_A$,

$$\begin{aligned}
\delta\rho_A &= \rho(1-c) - \rho_0(1-c_0) \\
&= \delta\rho(1-c) - \rho_0\delta c.
\end{aligned}$$

With those forms established, we can expand $\delta\rho_B C_{BB} * \delta\rho_B$:

$$\begin{aligned}
\delta\rho_B C_{BB} * \delta\rho_B &= (\delta\rho c + \rho_0\delta c) C_{BB} * (\delta\rho c + \rho_0\delta c) \\
&= \delta\rho c C_{BB} * (\delta\rho c) \\
&\quad + \rho_0\delta c C_{BB} * (\delta\rho c) \\
&\quad + \rho_0 (\delta\rho c) C_{BB} * \delta c \\
&\quad + \rho_0^2\delta c C_{BB} * \delta c.
\end{aligned} \tag{6.40}$$

If we examine one term in this expansion in detail, we note that we can simplify by using the long wavelength approximation for the concentration field,

$$\begin{aligned}
\delta\rho c C_{BB} * \delta\rho c &= \delta\rho(r)c(r) \int dr' C_{BB}(r-r')\delta\rho(r')c(r') \\
&\approx \delta\rho(r)c^2(r) \int dr' C_{BB}(r-r')\delta\rho(r').
\end{aligned} \tag{6.41}$$

This is because the concentration field can be considered ostensibly constant over the length scale in which $C_{BB}(r)$ varies. Recall that the pair correlation function typically decays to zero on the order of several particle radii. Using this approximation we can rewrite equation 6.40 as,

$$\begin{aligned}
\delta\rho_B C_{BB} * \delta\rho_B &= \delta\rho (c^2 C_{BB}) * \delta\rho \\
&+ \rho_0 \delta c (c C_{BB}) * \delta\rho c \\
&+ \rho_0 \delta\rho (c C_{BB}) * \delta c \\
&+ \rho_0^2 \delta c C_{BB} * \delta c.
\end{aligned} \tag{6.42}$$

Repeating this procedure with the remaining three terms and then regrouping we can easily identify the required pair correlations.²

$$C_{nn} = \rho_0 (c^2 C_{BB} + (1-c)^2 C_{AA} + 2c(1-c) C_{AB}) \tag{6.43}$$

$$C_{nc} = C_{cn} = \rho_0 (c C_{BB} - (1-c) C_{AA} + (1-2c) C_{AB}) \tag{6.44}$$

$$C_{cc} = \rho_0 (C_{BB} + C_{AA} - 2C_{AB}) \tag{6.45}$$

² Note that we may also take advantage of the fact that $C_{AB} = C_{BA}$.

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KEY TO ABBREVIATIONS