

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

Thesis Subtitle

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A thesis presented for the degree of
Master's of Science



Department of Physics
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??-??-2017

Dedication

Dedication here...

Acknowledgements

Acknowledgements here...

Abstract

English abstract...

Abrégé

French abstract...

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Chapter 1

Introduction

Chapter 2

Fundamentals

In this chapter we will describe the fundamental physics behind the phase field crystal theory. Like many physical theories, it is derived using successive approximations. Each approximation yields a new theory that is more narrow in scope, yet more tractable 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 ties macroscopic observables to microscopic phenomena with a probabilistic approach. The premise is that, if a system is sufficiently complex, there are circumstances under which its statistical behaviour becomes relatively simple. In fact, using statistical inference instead of solving any microscopic equations of motion can lead to highly accurate calculations of many thermodynamic observables in these special cases.¹

At the level of fundamental physics, 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 completely intractable, but with an approximation we can treat our system in the *semi-classical limit*.

¹Further details of statistical mechanics as a form of statistical inference can be seen in a classic paper by E. T. Jaynes [5]

In semi-classical limit, we can build a framework to examine the structure of the density field, using Classical Density Functional Theory (CDFT) [1]. Classical Density Functional Theory. While CDFT supplies the correct setting to discuss microstructure, 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 [16], and, shortly after, Kirkwood [7] 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 [15] 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 [9]. 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,

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

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.

2.2 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 Gibbs² prior to any knowledge of quantum mechanics [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.

2.3 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,

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

²The \hbar in Gibbs' formula was justified on dimensional grounds and was simply a scaling factor with units of action ($J \cdot s$)

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 trace³,

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

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,

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

subject to the aforementioned constraints to find 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 multiplies associated with constraints of average energy, number of particles and density respectively. As you might imagine the constraints

³The classical trace in the grand canonical example in this particular case

of average particle number and density are not independent and 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 Lagrange 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*.

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

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 invertible⁴. To 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 [mention Weiner-Khinchin here?]. 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,

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

2.4 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

⁴The 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

and free energy functional exactly,

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

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

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 [11], 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. Thankfully, the theory of homogeneous liquids, such as our reference liquid, is very well established. This means we may rely on a broad choice of analytical, numerical or experimental techniques to derive these parameters.

Chapter 3

Classical Density Functional Theory of Freezing

The classical density functional theories derived in chapter 2 was first established to study inhomogeneous fluids. Interestingly, one can think of the solid state as an especially extreme case of an inhomogeneous fluid [4]. In this case, we can use CDFT to study the circumstances under which the density field develops long range periodic solutions (ie., solidification). While not expressed in precisely this language, this idea dates back as far as 1941 with the early work of Kirkwood and Monroe [8] and was later significantly refined by Youssof and Ramakrishnan [13].

3.1 Amplitude Expansions

More precisely, if we would like to study the liquid-solid transitions we can expand the density field in a set of plane-waves that span the unit cell of the solid phase,

$$\rho(\mathbf{x}) = \frac{1}{V_{cell}} \sum_i \xi_i e^{i\mathbf{k}_i \cdot \mathbf{x}}. \quad (3.1)$$

In the solid phase, the amplitudes ξ_i become nonzero for $\mathbf{k}_i \neq 0$ and describe the periodic structure of the solid density field. In the liquid, only the $\mathbf{k}_i = 0$ value remains (ie., the density becomes constant). Since the density profile can be reconstructed with knowledge of all the of amplitudes we can rewrite the grand potential as a function of the amplitudes only,

$$\Omega[\rho(x)] = \Omega(\{\xi_i\}), \quad (3.2)$$

From which the equilibrium condition becomes,

$$\frac{\partial \Omega(\{\xi_i\})}{\partial \xi_k} = 0, \quad \forall k. \quad (3.3)$$

Equation 2.42

Add tables from the Youssof and Ramamkrishnan papers to show how successful the theory really was for these static equilibrium thermodynamics. Talk about these amplitudes as the nature order parameters for solidification.

Transition into the short comings of only perfect crystalline descriptions of the solid phase and talk about the factures that influence the mechanical properties of solids (dislocations and grain boundaries etc).

3.2 Dynamics

Here we need to make the point that, while equilibrium results are important, a huge amount of mechanical properties depend on nonequilibrium features such as dislocations, grain boundaries etc. Additionally, these things really depend on the pathway we take to equilibrium.

This is where the free energy functional used by Ramakrishnan as significant set backs. Deriving equations of motion is fine so we can talk about over damped hydrodynamics here and the projection operator stuff. We can also

discuss Archer's work and the distinction between the Langevin equations for the operator versus the mean transport equation.

The problem is that the density profile in equilibrium is essentially a sum of sharply peaked gaussians that are hard to resolve numerically. Want to probe the dislocation dynamics? Best to find a better behaved theory.

3.3 Phase Field Crystal Theory

Introduce PFC. The essential physics of solidifications is retained, and much larger length and timescales can be explored. The assumption here is that we haven't lost the qualitative mechanisms we're interested even if we lost some quantitative agreement with theory.

Chapter 4

Simplified Binary Phase Field Crystal Models

In this chapter we will walk through three simplified binary PFC models. The first is the original binary PFC model, which, while highly successful at modelling a few important phenomena is ultimately limited in scope. The second is the binary structural phase field crystal, or binary XPFC which was successful in modelling a broad spectrum of crystalline structures, but was limited in its ability of model liquid instabilities and a variety of phase diagrams. Finally, we'll see a new contribution to which we will call the regular phase field crystal model which is successful in modeling a broad spectrum of invariant binary reactions and crystalline structures.

4.1 Derivation of the General Binary XPFC Free Energy

Now that we've seen the recipe for building a phase-field crystal theory for a single component system the process for building a multicomponent theory proceeds analogously with a few minor changes in perspective. We start again by looking at the ideal and excess contributions

to the free energy.

Ideal Free Energy to Two Components

The kinetic energy terms of each species in the Hamiltonian give rise to separate contributions to the free energy as you might expect. We'll label the two species A and B.

$$\beta\mathcal{F}_{id}^{tot}[\rho_A, \rho_B] = \beta\mathcal{F}_{id}[\rho_A] + \beta\mathcal{F}_{id}[\rho_B] \quad (4.1)$$

Where,

$\beta\mathcal{F}_{id}$ is the same ideal free energy functional as previously

Excess Free Energy of a Two Component System

Our expansion of the excess free energy works just as before but we must sum over the contributions from each species.

$$\beta\mathcal{F}_{ex} = \beta\mathcal{F}_{ex}^0 - \int dr C_i^{(1)}(r) \Delta\rho_i(r) - \frac{1}{2} \int dr \int dr' \Delta\rho_i(r) C_{ij}^{(2)}(r, r') \Delta\rho_j(r') \quad (4.2)$$

Where indices denote species (A or B) and repeated indices are summed over.

Total free energy of a Two Component System

Putting together the excess and ideal terms together and dropping the constant and linear terms as we did previously we find the following total free energy,

$$\beta\mathcal{F}[\rho_A, \rho_B] = \int dr \left\{ \Delta\rho_i \ln \left(\frac{\Delta\rho_i}{\rho_{i0}} \right) - \Delta\rho_i \right\} - \frac{1}{2} \int dr \int dr' \Delta\rho_i(r) C_{ij}^{(2)}(r, r') \Delta\rho_j(r') \quad (4.3)$$

Changing variables

Typically, the concentration is the variable we care about in binary systems so instead of preceeding with the usual phase field crystal approximations at this point we make a change of variables to concentration, c , and total density, ρ .

$$\begin{aligned}\rho &= \rho_A + \rho_B & \rho_0 &= \rho_{0A} + \rho_{0B} \\ c &= \frac{\rho_A}{\rho_A + \rho_B} & c_0 &= \frac{\rho_{0A}}{\rho_{0A} + \rho_{0B}}\end{aligned}$$

Making this change of variables and seperating total density and concentration contribution we find a free energy functional of the form,

$$\beta\mathcal{F}[c, \rho] = \tag{4.4}$$

Chapter 5

Applications

Appendix A

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 [12]. 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.

¹For considerations far from equilibrium see [10, 14, 1]

A.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,

$$\frac{\partial \mathbf{a}(r, t)}{\partial t} = F[\mathbf{a}(r, t)] + \boldsymbol{\xi}(r, t). \quad (\text{A.1})$$

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.

$$\langle \boldsymbol{\xi}(r, t) \rangle = 0 \quad (\text{A.2})$$

$$\langle \boldsymbol{\xi}(r, t) \boldsymbol{\xi}^\dagger(r', t') \rangle = \mathbf{L}(r, r') \delta(t - t') \quad (\text{A.3})$$

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, $\mathbf{a}(r, t) = \mathbf{a}_{eq}(r) + \hat{\mathbf{a}}(r, t)$.

$$\frac{\partial \hat{\mathbf{a}}(r, t)}{\partial t} = \mathbf{M}(r, r') * \hat{\mathbf{a}}(r', t) + \boldsymbol{\xi}(r, t) \quad (\text{A.4})$$

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

$$\mathbf{M}(r, r') * \hat{\mathbf{a}}(r') = \sum_j \int dr' M_{ij}(r, r') \hat{a}_j(r'). \quad (\text{A.5})$$

We can formally solve our linearized equation of motion,

$$\hat{\mathbf{a}}(r, t) = e^{\mathbf{M}(r, r')t} * \hat{\mathbf{a}}(r', 0) + \int_0^t d\tau e^{\mathbf{M}(r, r')(t-\tau)} * \boldsymbol{\xi}(r', \tau), \quad (\text{A.6})$$

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

$$\begin{aligned} \langle \hat{\mathbf{a}}(r, t) \hat{\mathbf{a}}^\dagger(r', t') \rangle &= e^{\mathbf{M}(r, r_1)t} * \langle \hat{\mathbf{a}}(r_1, 0) \hat{\mathbf{a}}^\dagger(r_2, 0) \rangle * e^{\mathbf{M}^\dagger(r', r_2)t'} \\ &+ \int_0^t \int_0^{t'} d\tau d\tau' e^{\mathbf{M}(r, r_1)(t-\tau)} * \langle \boldsymbol{\xi}(r_1, 0) \boldsymbol{\xi}^\dagger(r_2, 0) \rangle * e^{\mathbf{M}^\dagger(r', r_2)(t'-\tau')} \end{aligned} \quad (\text{A.7})$$

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.

$$\boldsymbol{\Gamma}(r, r') = \lim_{t \rightarrow \infty} \langle \hat{\mathbf{a}}(r, t) \hat{\mathbf{a}}^\dagger(r', t) \rangle = \int_0^\infty dz e^{\mathbf{M}(r, r_1)z} * \mathbf{L}(r_1, r_2) * e^{\mathbf{M}^\dagger(r', r_2)z} \quad (\text{A.8})$$

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

$$\mathbf{M}(r, r_1) * \boldsymbol{\Gamma}(r_1, r') + \boldsymbol{\Gamma}(r, r_1) * \mathbf{M}^\dagger(r_1, r') = -\mathbf{L}(r, r') \quad (\text{A.9})$$

A.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.

$$\beta\mathcal{F}[\phi] = \int dr \left\{ \frac{1}{2} |\nabla\phi(x)|^2 + \frac{r}{2} \phi^2(x) + \frac{u}{4!} \phi^4(x) + h(x)\phi(x) \right\} \quad (\text{A.10})$$

$$\frac{\partial\phi(x, t)}{\partial t} = -\Gamma \left(\frac{\delta\beta\mathcal{F}[\phi]}{\delta\phi(x)} \right) + \xi(x, t) \quad (\text{A.11})$$

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

$$\langle \xi(x, t) \rangle = 0 \quad (\text{A.12})$$

$$\langle \xi(x, t) \xi(x', t') \rangle = L(x - x') \delta(t - t') \quad (\text{A.13})$$

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

A.2.1 The partition function route

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

$$\mathcal{P}_{eq}[\phi] = \frac{e^{-\beta\mathcal{F}[\phi]}}{\mathcal{Z}[h(x)]} \quad (\text{A.14})$$

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

$$\mathcal{Z}[h(x)] = \int \mathcal{D}[\phi] e^{-\beta\mathcal{F}[\phi]} \quad (\text{A.15})$$

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

moment generating function.

$$\frac{1}{\mathcal{Z}[h]} \frac{\delta^n \mathcal{Z}[h]}{\delta h(x_1) \dots \delta h(x_n)} = \langle \phi(x_1) \dots \phi(x_n) \rangle \quad (\text{A.16})$$

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.

$$\beta\mathcal{F}[\Delta\phi] = \int dr \left\{ \frac{1}{2} \Delta\phi(x) \left(r - \nabla^2 + \frac{u}{2} \phi_0^2 \right) \Delta\phi(x) - h(x) \Delta\phi(x) \right\} \quad (\text{A.17})$$

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,

$$\mathcal{Z}[\tilde{h}(k)] \propto \exp \left\{ \frac{1}{2} \int dk \frac{h(k) h^*(k)}{r + \frac{u}{2} \phi_0^2 + |k|^2} \right\}. \quad (\text{A.18})$$

The pair correlation function, $\langle \Delta\tilde{\phi}(k) \Delta\tilde{\phi}^*(k) \rangle$, is then computed using equation A.16.

$$\left\langle \Delta\tilde{\phi}(k) \Delta\tilde{\phi}^*(k') \right\rangle = \frac{2\pi \delta(k + k')}{r + \frac{u}{2} \phi_0^2 + |k|^2} \quad (\text{A.19})$$

A.2.2 The Equation of Motion Route

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

$$\frac{\partial \phi}{\partial t} = -\Gamma \left((r - \nabla^2) \phi(x, t) + \frac{u}{3!} \phi^3(x, t) \right) + \xi(x, t), \quad (\text{A.20})$$

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.

$$\frac{\partial \Delta \tilde{\phi}(k, t)}{\partial t} = -\Gamma \left(\left(r + \frac{u}{2} \phi_0 + |k|^2 \right) \Delta \tilde{\phi}(k, t) \right) + \xi(x, t) \quad (\text{A.21})$$

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

$$M(k, k') = -\Gamma \left(\left(r + \frac{u}{2} \phi_0 + |k|^2 \right) \right) \delta(k + k') \quad (\text{A.22})$$

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

$$L(k, k') = 2\Gamma \delta(k + k'), \quad (\text{A.23})$$

Or equivalently,

$$L(x, x') = 2\Gamma \delta(x - x'). \quad (\text{A.24})$$

A.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,

$$\frac{\partial \rho(r, t)}{\partial t} = D_0 \nabla \cdot \left[\rho(r, t) \nabla \left(\frac{\delta \mathcal{F}[\rho]}{\delta \rho} \right) \right] + \xi(r, t) \quad (\text{A.25})$$

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 $L(r, r')$.

$$\langle \xi(r, t) \rangle = 0 \quad (\text{A.26})$$

$$\langle \xi(r, t) \xi(r', t') \rangle = L(r, r') \delta(t - t') \quad (\text{A.27})$$

A.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.

$$\mathcal{F}[\rho] = \mathcal{F}_{eq} + \beta \int dr \left(\frac{\delta \mathcal{F}[\rho]}{\delta \rho(r)} \right) \Big|_{\rho_{eq}} \Delta \rho(r) + \frac{1}{2} \int dr \int dr' \Delta \rho(r) \left(\frac{\delta^2 \mathcal{F}[\rho]}{\delta \rho(r) \delta \rho(r')} \right) \Big|_{\rho_{eq}} \Delta \rho(r') \quad (\text{A.28})$$

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.

$$\mathcal{F}[\rho] = \frac{1}{2} \int dr \int dr' \Delta\rho(r) \Gamma^{-1}(r, r') \Delta\rho(r') \quad (\text{A.29})$$

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,

$$\langle \Delta\rho(r) \Delta\rho(r') \rangle = \Gamma(r, r') \quad (\text{A.30})$$

A.3.2 Linearizing the equation of motion

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

$$\frac{\partial \Delta\rho(r, t)}{\partial t} = D_0 \nabla \cdot [\rho_{eq}(r) \nabla (\Gamma^{-1}(r, r') * \Delta\rho(r', t))] + \xi(r, t) \quad (\text{A.31})$$

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

$$M(r, r') = D_0 \nabla \cdot [\rho_{eq}(r) \nabla (\Gamma^{-1}(r, r'))] \quad (\text{A.32})$$

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

$$L(r, r') = -2D_0 \nabla \cdot (\rho_{eq}(r) \nabla) \delta(r - r') \quad (\text{A.33})$$

Appendix B

Gaussian Functional Integrals

Gaussian Functional Integrals

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

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

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 [6] and are repeated here for the convenience of the reader.

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

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

For which the solution is,

$$\mathcal{Z}[\mathbf{h}] = \sqrt{\frac{2\pi}{\det(\mathbf{K})}} \exp \left\{ \frac{1}{2} \sum_i \sum_j h_i \mathbf{K}_{ij}^{-1} h_j \right\}. \quad (\text{B.3})$$

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

$$\mathcal{Z}[h(x)] \propto \exp \left\{ \int dx \int dx' \left[\frac{1}{2} h(x) \mathbf{K}^{-1}(x, x') h(x') \right] \right\} \quad (\text{B.4})$$

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

$$\int dx' \mathbf{K}(x, x') \mathbf{K}^{-1}(x', x'') = \delta(x - x''). \quad (\text{B.5})$$

Ultimately, we don't need to worry about the constant of proportionality in equation B.4 because we'll be dividing this contribution when calculating correlation functions.

Appendix C

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,

$$\begin{aligned} \delta\rho_A C_{AA} * \delta\rho_A + \delta\rho_A C_{AB} * \delta\rho_B + \delta\rho_B C_{BA} * \delta\rho_A + \delta\rho_B C_{BB} * \delta\rho_B = \\ \rho_0 (n C_{nn} * n + n C_{nc} * \delta c + \delta c C_{cn} * n + \delta c C_{cc} * \delta c). \end{aligned} \quad (\text{C.1})$$

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 $\delta\rho_B C_{BB} * \delta\rho_B$:

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

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,

$$\begin{aligned}\delta\rho c C_{BB} * \delta\rho c &= \delta\rho(r)c(r) \int dr' C_{BB}(r - r') \delta\rho(r')c(r') \\ &\approx \delta\rho(r)c^2(r) \int dr' C_{BB}(r - r') \delta\rho(r').\end{aligned}\tag{C.3}$$

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 C.2 as,

$$\begin{aligned}
\delta\rho_B C_{BB} * \delta\rho_B &= \delta\rho (c^2 C_{BB}) * \delta\rho \\
&+ \rho_0 \delta c (c C_{BB}) * \delta\rho c \\
&+ \rho_0 \delta\rho (c C_{BB}) * \delta c \\
&+ \rho_0^2 \delta c C_{BB} * \delta c.
\end{aligned} \tag{C.4}$$

Repeating this procedure with the remaining three terms and then regrouping we can easily identify the required pair correlations.¹

$$C_{nn} = \rho_0 (c^2 C_{BB} + (1-c)^2 C_{AA} + 2c(1-c) C_{AB}) \tag{C.5}$$

$$C_{nc} = C_{cn} = \rho_0 (c C_{BB} - (1-c) C_{AA} + (1-2c) C_{AB}) \tag{C.6}$$

$$C_{cc} = \rho_0 (C_{BB} + C_{AA} - 2C_{AB}) \tag{C.7}$$

¹Note that we may also take advantage of the fact that $C_{AB} = C_{BA}$.

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