

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

McGill University

Nathan Smith

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Abstract

Abstract goes here

Dedication

To mum and dad

Declaration

I declare that..

Acknowledgements

I want to thank...

Contents

Chapter 1

Introduction

Chapter 2

Classical Density Functional Theory

2.0.1 Introduction

2.0.2 Deriving the Intrinsic Free Energy Functional

To derive the intrinsic free energy functional we start with the grand partition function for a single component system in the semi-classical limit.

$$\Xi = \sum_{N=0}^{\infty} \frac{e^{N\beta\mu}}{h^{3N}N!} \int d\mathbf{r}^N d\mathbf{p}^N e^{-\beta\mathcal{H}} \quad (2.1)$$

Where the Hamiltonian, \mathcal{H} , has contributions from kinetic energy, interaction potential and an external potential.

$$\mathcal{H} = \sum_{i=1}^N \frac{p_i^2}{2m} + V(r_1, r_2, \dots, r_N) + \sum_{i=1}^N \phi(r_i) \quad (2.2)$$

Note that we explicitly assume that the interactions only depend on the particle positions and not their momenta, this allows us to complete the momentum integral in the partition function.

$$\Xi = \sum_{N=0}^{\infty} \frac{1}{\Lambda^{3N}N!} \int d\mathbf{r}^N e^{-\beta(V(r_1, r_2, \dots, r_N) - \sum_{i=1}^N (\mu - \phi(r_i)))} \quad (2.3)$$

Note now, that we're trying to construct a theory for the density field of our material, $\rho(r)$. The density field is defined as a sum of Dirac delta functions at the positions of the particles. That is, we would like to write the grand partition function in terms the density field and use the grand partition function as a generating functional for the mean, fluctuations and other moments of the density field.

$$\rho(r) \equiv \sum_{i=1}^N \delta^{(3)}(r_i - r) \quad (2.4)$$

We start along this path by noting that the external potential term can be rewritten in terms of the density field as follows,

$$\sum_{i=1}^N (\mu - \phi(r_i)) = \int dr (\mu - \phi(r)) \rho(r) \quad (2.5)$$

In this form, we see that the combination $\mu - \phi(r)$ forms a field that is conjugate to the density field that we will call the *intrinsic chemical potential*, $\psi(r)$. What we mean by conjugate is that repeated functional derivative of the grand partition function will generate correlation functions of the density field.

$$\frac{1}{\beta^N \Xi[\psi(r)]} \frac{\delta^n \Xi[\psi(r)]}{\delta \psi(r_1) \dots \delta \psi(r_n)} = \langle \rho(r_1) \dots \rho(r_n) \rangle \quad (2.6)$$

It is important to note that the partition function has two distinct contributions: one from the ideal contributions to the free energy and one from the interaction term which is called the *excess term*.

$$\Xi[\psi(r)] = \quad (2.7)$$

Chapter 3

Theory of Phase Field Crystal Models

3.1 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.

$$\beta\mathcal{F}_{id}^{tot}[\rho_A, \rho_B] = \beta\mathcal{F}_{id}[\rho_A] + \beta\mathcal{F}_{id}[\rho_B] \quad (3.1)$$

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.

$$\beta\mathcal{F}_{ex} = \beta\mathcal{F}_{ex}^0 - \int dr C_i^{(1)}(r) \Delta\rho_i(r) - \frac{1}{2} \int dr \int dr' \Delta\rho_i(r) C_{ij}^{(2)}(r, r') \Delta\rho_j(r') \quad (3.2)$$

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,

$$\beta\mathcal{F}[\rho_A, \rho_B] = \int dr \left\{ \Delta\rho_i \ln \left(\frac{\Delta\rho_i}{\rho_{i0}} \right) - \Delta\rho_i \right\} - \frac{1}{2} \int dr \int dr' \Delta\rho_i(r) C_{ij}^{(2)}(r, r') \Delta\rho_j(r') \quad (3.3)$$

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,

$$\beta\mathcal{F}[c, \rho] = \tag{3.4}$$

Chapter 4

Chapter Three Title

Chapter 5

Chapter Four Title

Chapter 6

Conclusion

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 [3]. 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.

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.

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

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

¹For considerations far from equilibrium see [2, 4, 1]

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.

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

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.

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

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

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

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 $L(r, r')$.

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

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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 their own right but are also the basis of perturbative techniques. The detail of how to solve this integral can be found in [1] 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.

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