

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

Thesis Subtitle

Nathan Frederick Smith

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



Department of Physics
McGill University, Montreal
Canada
??-??-2017

Dedication

Dedication here...

Acknowledgements

Acknowledgements here...

Abstract

English abstract...

Abrégé

French abstract...

Contents

Dedication	i
Acknowledgements	ii
Abstract	iii
Abrégé	iv
1 Introduction	1
2 Fundamentals	2
2.1 Statistical Mechanics in the Semi-classical limit	3
2.1.1 Indistinguishability	5
2.2 Classical Density Functional Theory	6
2.3 Techniques in Density Functional Theory	10
3 Classical Density Functional Theory of Freezing	13
3.1 Amplitude Expansions	13
3.2 Dynamic Density Functional Theory	15
3.3 Phase Field Crystal Theory	16
4 Simplified Binary Phase Field Crystal Models	17
4.1 Original Binary Phase Field Crystal Model	18

4.2	Binary Structural Phase Field Crystal Model	18
4.3	Regular Phase Field Crystal Model	18
5	Applications	21
A	Noise in Nonlinear Langevin Equations	22
A.1	Generalized Einstein Relations in an Arbitrary Model	23
A.2	Example 1 - Model A	24
A.2.1	The partition function route	25
A.2.2	The Equation of Motion Route	26
A.3	Example 2 - Time Dependent Density Functional Theory	27
A.3.1	Pair Correlation from the Partition Functional	27
A.3.2	Linearizing the equation of motion	28
B	Gaussian Functional Integrals	29
C	Binary Correlation Functions	31

List of Figures

List of Tables

Chapter 1

Introduction

[Introduction here....]

Chapter 2

Fundamentals

Many physical theories are derived using a succession of approximations. The utility of this approach is that, while each approximation yields a new theory that is more narrow in scope, the subsequent theory is typically more tractable to either analytical or numerical analysis. Classical Density Functional Theory (CDFT) is derived using this approach and in this chapter we'll examine each approximation and the intermediate theory they supply. In the following chapter, we'll see how CDFT can be used to examine the problem of solidification and how we can derive a more simplified theory, the Phase Field Crystal theory, from it.

CDFT is a theory of statistical mechanics. This means CDFT connects microscopic physics to macroscopic observables using statistical inference¹ instead of attempting to compute microscopic equations of motion. The microscopic physics in this case is most accurately described by many-body quantum mechanics and so the theory of quantum statistical mechanics is a natural starting point in any attempt to calculate thermodynamic observables.

We will see that for our systems of interest that the full quantum statistical theory is completely intractable. To proceed, we'll look at quantum statistical mechanics in the *semi-classical limit*. In the semi-classical limit we'll develop a theory of inhomogenous fluids called Classical Density Functional Theory (CDFT). Finally, we'll see that constructing exactly free

¹Statistical mechanics is not always described as statistical inference. See works of E. T. Jaynes for details on this approach [5]

energy functionals for CDFT is rarely possible and look at an approximation scheme for these functionals.

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 instance, the precise bosonic or fermionic nature of the particles in the system often 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 which is straight forward to generalize to multi-component systems and other ensembles. 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 plane wave solutions,

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

Where, $d\Gamma$ is the phase space measure $d\mathbf{p}d\mathbf{q}/(2\pi\hbar)^N$. To compute the integrand, $I(\mathbf{q}, \mathbf{p})$, we follow Uhlenbeck and Bethe [15] and first compute its derivative,

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

If we then make a change of variables, $I(\mathbf{q}, \mathbf{p}) = e^{-\beta\mathcal{H}}W(\mathbf{q}, \mathbf{p})$, 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 .

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

The solution can be written as a power series in \hbar , $W = 1 + \hbar W_1 + \hbar^2 W_2 + \dots$. 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 quote solution to second order, but details can be found in Landau and Lifshitz [9].

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

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

The first order term is zero, because $W_1(\mathbf{q}, \mathbf{p})$ is an odd function of \mathbf{p} . In terms of the Helmholtz 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 items of importance in equation 2.9. First of all the correction inversely proportional to both the temperature and the particle mass. For copper at room tempera-

ture, 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,

$$\mathcal{Z}(\beta) = \frac{1}{N!} \int d\Gamma e^{-\beta\mathcal{H}} + \mathcal{O}(\hbar^2), \quad (2.12)$$

Or, in the grand canonical ensemble,

$$\Xi(\mu, \beta) = \sum_{N=0}^{\infty} \frac{e^{\beta\mu N}}{N!} \int d\Gamma e^{-\beta\mathcal{H}} + \mathcal{O}(\hbar^2) \quad (2.13)$$

Of course, to first order in \hbar , 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.

2.2 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 the sum of Dirac delta functions at the position of each particle,

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

From which the thermodynamic observable is,

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

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

Where, $\text{Tr} [\cdot]$ denotes the classical trace³,

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

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 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 with the insight that,

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

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

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 enery 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

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

[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,

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

2.3 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,

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

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

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,

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

Should we truncate the expansion in equation 2.38 to second order in $\Delta\rho(x)$ and substitute the linear and quadratic terms with equation 2.41 and 2.40 we can simplify the excess free energy to,

$$\mathcal{F}_{ex}[\rho(r)] = \mathcal{F}_{ex}[\rho_0] + \int dr \left\{ \mu - k_b T \ln (\Lambda^3 \rho_0) \right\} \Delta\rho(r) - \frac{k_b T}{2} \Delta\rho(r) * C_0^{(2)}(r, r') * \Delta\rho(r') \quad (2.42)$$

Combining equation 2.33 with the simplified excess free energy in equation 2.42, we can express total change in free energy, $\Delta\mathcal{F} = \mathcal{F} - \mathcal{F}[\rho_0]$, as,

$$\Delta\mathcal{F}[\rho(r)] = k_b T \int dr \left\{ \rho(r) \ln \left(\frac{\rho(r)}{\rho_0} \right) - (1 - \beta\mu_0) \Delta\rho(r) \right\} - \frac{k_b T}{2} \Delta\rho(r) * C_0^{(2)}(r, r') * \Delta\rho(r') \quad (2.43)$$

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.

Equation 2.43 establishes an approximate density functional theory for inhomogenous fluids and, as we will see in the following chapter, for the seemingly disparate phenomena of solidification. We see that it can derived through a series of approximations from a fundamental basis in quantum statistical mechanics and requires no more parameters than the thermodynamic details of a homogeneous reference fluid.

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,

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

Using this technique and the approximate free energy of Equation 2.43 results in good agreement with experiment can be found for equilibrium properties such as the density change of solidification. [table of results from Ramakrishnan?](#) The implication of these results and their success in predicting equilibrium thermodynamic properties points a the amplitudes, ξ_i , as natural and appropriate order parameters from the problem of solidification.

In spite of these successes, CDFT has a major short coming in that it is an equilibrium theory. This short coming cannot be understated in any attempt to be a theory of the mechanical and thermodynamic properties of metal systems. While some mechanical properties are well understood with an understanding of the perfect crystalline state, such as the Young's modulus, the vast majority of mechanical properties of solids is due to their microstructural defects.

Artifacts such as grains boundaries, dislocations and vacancies play key roles not only in the mechanical properties but also the kinetic pathways of certain phase transformations. For instance, dislocations can act to catalyze precipitation in binary alloys [cite Vahid].

The problem that we face is then, how do we examine these defects and microstructural elements but retain some of the positive aspects of CDFT? More specifically, what path does

density profile take to equilibrium?

3.2 Dynamic Density Functional Theory

We can extend our density functional theory to a dynamical model using techniques from non-equilibrium statistical mechanics. We begin by considering some non-equilibrium probability distribution over phase space, $f(\mathbf{q}, \mathbf{p}, t)$, and its equation of motion,

$$\frac{\partial f(\mathbf{q}, \mathbf{p}, t)}{\partial t} = -\{f, \mathcal{H}\}. \quad (3.4)$$

Where, $\{\cdot, \cdot\}$, denotes the Poisson bracket,

$$\{f, g\} = \sum_{i=0}^N \frac{\partial f}{\partial q_i} \frac{\partial g}{\partial p_i} - \frac{\partial g}{\partial q_i} \frac{\partial f}{\partial p_i}. \quad (3.5)$$

Equation 3.4 is called the *Liouville Equation*. Under appropriate conditions the probability distribution will decay to the equilibrium fixed point,

$$\lim_{t \rightarrow \infty} f(\mathbf{q}, \mathbf{p}, t) = f_{eq}(\mathbf{q}, \mathbf{p}) \quad (3.6)$$

Using the non-equilibrium probability distribution, we can also discuss non-equilibrium averages of the density profile and their associated equations of motions. The non-equilibrium density is written in analogy with equation 2.15,

$$\rho(x, t) = \langle \hat{\rho}(x; \mathbf{q}) \rangle_{ne} = \text{Tr} [\hat{\rho}(x; \mathbf{q}) f(\mathbf{q}, \mathbf{p}, t)]. \quad (3.7)$$

Where, $\langle \cdot \rangle_{ne}$, denotes the non-equilibrium average. Thusly, just as the non-equilibrium probability distribution is driven to equilibrium by the Liouville Equation, so too will the density profile by its own equation of motion. Under the approximation that direct correlation function decays to equilibrium more quickly than the density profile we can write

the equation of motion as[Cite Evans and Tarazona here and Archer for the distinction between these two equations? Perhaps Espanol as well for the projection operator derivation],

$$\frac{\partial \rho(x, t)}{\partial t} = \nabla \cdot \left[D_0 \rho(x, t) \nabla \left(\frac{\delta \mathcal{F}[\rho]}{\delta \rho(x, t)} \right) \right] \quad (3.8)$$

Or, equivalently, we may write an equation of motion for the operator itself, $\hat{\rho}$, as,

$$\frac{\partial \hat{\rho}(x, t)}{\partial t} = \nabla \cdot \left[D_0 \hat{\rho}(x, t) \nabla \left(\frac{\delta \mathcal{F}[\hat{\rho}]}{\delta \hat{\rho}} \right) \right] + \xi(x, t). \quad (3.9)$$

Where, $\xi(x, t)$ is a Gaussian random driving force with zero average and variance is,

$$\langle \xi(x, t) \xi(x', t') \rangle = -2 \nabla \cdot [D_0 \rho(x, t) \nabla \delta(x - x') \delta(t - t')], \quad (3.10)$$

Due to a generalized Einstein relation¹ for the Langevin equation in equation 3.9.

Equations similar to those seen here and extensions thereof fall under the category of *Dynamic Density Functional Theory*(DDFT).

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 in even if we lost some quantitative agreement with theory.

¹See Appendix A for details on generalized Einstein relations for nonlinear Langevin equations

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 Original Binary Phase Field Crystal Model

To derive the original binary PFC model, we begin with a multicomponent variant of equation 2.43,

$$\beta\mathcal{F}[\rho_A, \rho_B] = \sum_{i=A,B} \int dr \rho_i \ln \left(\frac{\rho_i}{\rho_i^0} \right) - (1 - \mu_i^0) \Delta \rho_i \quad (4.1)$$

$$- \frac{1}{2} \sum_{i,j=A,B} \int dr dr' \Delta \rho_i(r) C_{ij}^{(2)}(r, r') \Delta \rho_j(r'). \quad (4.2)$$

As noted in chapter 3, we can produce a PFC model by approximating the ideal component of the free energy.

4.2 Binary Structural Phase Field Crystal Model

4.3 Regular Phase Field Crystal Model

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.

$$\beta\mathcal{F}_{id}^{tot}[\rho_A, \rho_B] = \beta\mathcal{F}_{id}[\rho_A] + \beta\mathcal{F}_{id}[\rho_B] \quad (4.3)$$

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.

$$\beta\mathcal{F}_{ex} = \beta\mathcal{F}_{ex}^0 - \int dr C_i^{(1)}(r) \Delta\rho_i(r) - \frac{1}{2} \int dr \int dr' \Delta\rho_i(r) C_{ij}^{(2)}(r, r') \Delta\rho_j(r') \quad (4.4)$$

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,

$$\beta\mathcal{F}[\rho_A, \rho_B] = \int dr \left\{ \Delta\rho_i \ln \left(\frac{\Delta\rho_i}{\rho_{i0}} \right) - \Delta\rho_i \right\} - \frac{1}{2} \int dr \int dr' \Delta\rho_i(r) C_{ij}^{(2)}(r, r') \Delta\rho_j(r') \quad (4.5)$$

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 separating total density and concentration contribution we find a free energy functional of the form,

$$\beta\mathcal{F}[c, \rho] = \tag{4.6}$$

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.

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

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.

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

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

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

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 off the kernel $M(r, r')$ from the linearized equation.

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

Plugging into the generalized Einstein relation, we find that 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 $C_{AB} = C_{BA}$.

Bibliography

- [1] Ronald Forrest Fox and George E. Uhlenbeck. Contributions to non-equilibrium thermodynamics. i. theory of hydrodynamical fluctuations. *Physics of Fluids*, 13(8):1893–1902, 1970.
- [2] J. Willard Gibbs. *Elementary principles in statistical mechanics*. 1960.
- [3] Jean-Pierre Hansen and Ian R. McDonald. Appendix b: Two theorems in density functional theory. In Jean-Pierre Hansen and Ian R. McDonald, editors, *Theory of Simple Liquids (Fourth Edition)*, pages 587 – 589. Academic Press, Oxford, fourth edition edition, 2013.
- [4] Jean-Pierre Hansen and Ian R. McDonald. Chapter 6 - inhomogeneous fluids. In Jean-Pierre Hansen and Ian R. McDonald, editors, *Theory of Simple Liquids (Fourth Edition)*, pages 203 – 264. Academic Press, Oxford, fourth edition edition, 2013.
- [5] E. T. Jaynes. Information theory and statistical mechanics. *Phys. Rev.*, 106:620–630, May 1957.
- [6] M. Kardar. *Statistical Physics of Fields*. June 2006.
- [7] John G. Kirkwood. Quantum statistics of almost classical assemblies. *Phys. Rev.*, 44:31–37, Jul 1933.
- [8] John G. Kirkwood and Elizabeth Monroe. Statistical mechanics of fusion. *The Journal of Chemical Physics*, 9(7):514–526, 1941.

- [9] L.D. LANDAU and E.M. LIFSHITZ. Chapter iii - the gibbs distribution. In L.D. LANDAU and E.M. LIFSHITZ, editors, *Statistical Physics (Third Edition, Revised and Enlarged)*, pages 79 – 110. Butterworth-Heinemann, Oxford, third edition, revised and enlarged edition, 1980.
- [10] Melvin Lax. Fluctuations from the nonequilibrium steady state. *Rev. Mod. Phys.*, 32:25–64, Jan 1960.
- [11] Joseph E. Mayer and Elliott Montroll. Molecular distribution. *The Journal of Chemical Physics*, 9(1):2–16, 1941.
- [12] L. Onsager and S. Machlup. Fluctuations and irreversible processes. *Phys. Rev.*, 91:1505–1512, Sep 1953.
- [13] T. V. Ramakrishnan and M. Yussouff. First-principles order-parameter theory of freezing. *Phys. Rev. B*, 19:2775–2794, Mar 1979.
- [14] David Ronis, Itamar Procaccia, and Jonathan Machta. Statistical mechanics of stationary states. vi. hydrodynamic fluctuation theory far from equilibrium. *Phys. Rev. A*, 22:714–724, Aug 1980.
- [15] George E. Uhlenbeck and Erich Beth. The quantum theory of the non-ideal gas i. deviations from the classical theory. *Physica*, 3(8):729 – 745, 1936.
- [16] E. Wigner. On the quantum correction for thermodynamic equilibrium. *Phys. Rev.*, 40:749–759, Jun 1932.