

Improvements to the Binary Phase Field Crystal Theory with Applications in the Kinetics of Precipitation

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 $\odot\,$ Nathan Smith 2017

Dedication

This thesis is dedicated to my family and friends. You made this research and this time in my life possible.

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Abstract

Two improvements to the binary Structural Phase Field Crystal (XPFC) theory are presented. The first is a general phenomenology for modelling density-density correlation functions and the second extends the free energy of mixing term in the binary XPFC model beyond ideal mixing to a regular solution model. These improvements are applied to study kinetics of precipitation from solution. We see a two-step nucleation pathway similar to recent experimental work [1, 2] in which the solution first decomposes into solute-poor and solute-rich regions followed by nucleation in the solute-rich regions. Additionally, we find a phenomenon not previously described in literature in which the growth of precipitates is accelerated in the presence of uncrystallized solute-rich regions.

Abrégé

Nous présentons deux ameliorations au theorie "Structural Phase Field Crystal" (XPFC) binaire. Le premier decrit une phénoménologie pour une modèle des fonctions de corrélations des densités, et le deuxième augmente la modèle XPFC binaire au delà de la modèle idéale en ajutant une terme au énergie libre de Helmholtz. Ces améliorations sont appliqués aux études kinétiques de la précipité d'une solution. Nous voyons un chemin de nucléation similaire aux éxpériments réçentes [1, 2] dans lequel le solution se sépare en regions avec concentration de soluté bas et élèvé suivi par nucléation dans les régions avec hautes concentrations de soluté. De plus, nous decouvrons une acceleration de l'acroissement du precipité en presence des regions avec une concentration de soluté élèvé. Ce dernier est une phénomène auparavant pas décrit en literature.

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List of Symbols

- * Denotes an inner product (where appropriate) and integration over repeated variables.
- **b** Bold font denotes a vector quantity.
- β The inverse temperature $1/k_bT$ where k_b is Boltzmann's constant.
- ρ The average *number* density N/V. When referred to as a function $\rho(x)$ it is the local number density.

Chapter 1

Introduction

The study of alloys in materials physics is a pursuit of incredibly broad impact since the functional properties of materials depend on their microstructure, which forms through non-equilibrium phase transformations during the process of forming a material. As a result, industries as diverse as those dealing in commercial products based on steel and aluminium to the burgeoning markets dealing in nano-fabrication and optoelectronics are affected by research in alloy materials. One of the most useful paradigms for understanding complex alloy microstructure is that of the binary alloy.

One surprising aspect of binary alloys is the rich diversity of properties and behaviours they display. Because material properties depend on the microstructural details of the material, they have a strong processing path dependence. Grain boundaries, vacancies, dislocations and other microstructural artifacts are all intimately tied to the manufacturing process of the alloy. This means that the study of solids can never be completely separated from the study of solidification. As such, the diversity of material properties and behaviours we see in binary alloys can be directly attributed to the diversity of processes for their construction.

Given the importance of binary systems, it is critical to construct models that can explain the diversity of behaviour we see in them. At the moment, models of alloy solidification can be categorized by the length and time scales they accurately describe. At macroscopic length and time scales, we have continuum methods of heat and mass transport and associated finite element methods of analysis. These methods are appropriate for studying large castings, for example. On length scales $\mathcal{O}(10^{-6}m)$ to $\mathcal{O}(10^{-3}m)$ we use *Phase Field* methods to study phenomena such as dendritic growth and chemical segregation. On still finer length scales from $\mathcal{O}(10^{-9}m)$ to $\mathcal{O}(10^{-6}m)$ and on relatively long timescales, we have the methods of *Phase Field Crystal* (PFC) theory and dislocation dynamics. These methods are appropriate for studying nanoscopic changes that occur on diffusive timescales such as dislocation motion, creep, grain boundary motion and micro segregation. At a still finer scale and on very short time scales ($\mathcal{O}(10^{-12}s)$) we have the methods of molecular dynamics and density functional theory. These methods are appropriate for the study of transport coefficients and interaction potentials.

In this thesis, we'll focus on extending a branch of binary PFC theory known as the binary *XPFC* model –where the "X" in XPFC signifies a class of PFC models constructed to controllably simulate a robust range of metallic and non-metallic crystal symmetries compared to the original PFC models. PFC binary models have been successful in describing a broad selection of phenomena in binary alloys. These successes include eutectic and dendritic solidification [3], the Kirkendall effect [4, 5], solute drag [6], clustering and precipitation [7–9], colloidal ordering in drying suspensions [10], epitaxial growth and island formation [11, 12], and ordered crystals [13] to name a few.

The PFC theory is derived from Classical Density Functional Theory (CDFT) and as such, it can be considered a simplified density functional theory. In practice, two different variants of the PFC theory are used, as alluded to above: the original model developed by Elder *et al* [3] and the Structural Phase Field Crystal (XPFC) model developed by Greenwood *et al.* [14].

The original model was the first PFC theory of binary alloys and contains some important physical properties of binary alloys. However, it is a very reduced form of CDFT and it therefore lacks completeness in its ability to describe binary alloys. Specifically, the original model uses an expansion in concentration that is actually a density difference not a concentration, and the model has a limited ability to describe a realistic or robust range of phase diagrams. The original model also uses a very simplified correlation kernel which limits its ability to describe a variety of crystal lattice structures.

The XPFC model is an improvement that ameliorates the above problems. The concentration is left unexpanded allowing for construction of realistic global phase diagrams instead of local expansions. More significantly, the XPFC model provides a phenomenology for modelling two-point correlation functions that succeeded in describing solidification of a variety of lattice structures, as well as transformations between different crystal lattices. Simplifications of the multi-modal approach first introduced with the XPFC formalism has been used to produce hexagonal, square, kagome, honeycomb, rectangular and other lattices in 2 dimensions [15].

In introducing its phenomenology for modelling correlation functions, the binary XFPC theory tacitly assumes that there is some preferred structure at high concentration and some other structure preferred at low concentration. This assumption can be limiting in situations that have a specific crystalline structure at intermediate concentrations, such as materials with a syntectic phase diagram. At the syntectic point a solid of intermediate concentration solidifies along the interface between a solute rich and solute poor liquid. The XPFC model also assumes no long wavelength correlations in the concentration field which, in practice, means the model has an ideal free energy of mixing. This is another limitation of the XPFC model because the enthalpy of mixing is not generally zero for alloy systems.

The current research as three goals. The first goal is to improve the binary XPFC theory by using a more general phenomenology for modelling pair correlation functions. The second goal is another improvement to the binary XPFC theory which extends the free energy of mixing beyond ideality to account for circumstances when the enthaply of mixing is not negligible. The third goal is to use the new XPFC model derived herein to the elucidate the multi-step nucleation process seen in certain diffusion-limited systems including gold and silver nanoparticles [1].

The remainder of this thesis is divided into 5 chapters:

- Chapter 2 Classical Density Functional Theory (CDFT) is introduced and derived from fundamental principles of quantum statistical mechanics.
- Chapter 3 CDFT theory of solidification is described and discussed. The density functional theory is extended to a dynamic, non-equilibrium theory, and the Phase Field Crystal (PFC) Theory is introduced from it as a simplified density functional theory.
- Chapter 4 Binary PFC theory is derived and previous simplified alloy PFC models are summarized and discussed.
- Chapter 5 Improvements to the XPFC binary alloy theory are derived. This chapter contains novel contributions to the field.
- **Chapter 6** The new XPFC alloy model derived herein is applied to model to the problem of multi-step nucleation of nanoparticles from solution in diffusion limited systems and potential future applications of this model are discussed.

Chapter 2

Introduction to Classical Density Functional Theory

Many physical theories are derived using a succession of approximations. While each approximation yields a theory that is more narrow in scope, it 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.

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 preceed, we'll look at quantum statistical mechanics in the *semiclassical 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 exact free

¹Statistical mechanics is not always described as statistical inference. See works of E. T. Jaynes for details on this approach [16]

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

At a microscopic level, all systems are governed by the fundamental physics of quantum mechanics. Statistical mechanics and in particular quantum statistical mechanics provides a map between this microscopic reality and macroscopic thermodynamic observables. For most applications, quantum statistical mechanics is both intractable to analysis and contains more detail than necessary. 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 *semiclassical limit*.

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

$$Z = \operatorname{Tr}\left[e^{-\beta\hat{H}}\right],\tag{2.1}$$

where,

- \hat{H} is the Hamiltonian $\frac{|\hat{\mathbf{p}}|^2}{2m} + V(\hat{\mathbf{q}})$,
- **p** is set of particle momenta $(p_1, p_2, \dots p_N)$,
- **q** is similarly the set of particles positions, and,
- β is the inverse temperature $1/k_bT$ where k_b is the Boltzmann constant.

Wigner [17], and shortly after, Kirkwood [18] 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,

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

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 [19] and first compute its derivative,

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

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. The new function $W(\mathbf{q}, \mathbf{p})$ encodes the deviation from classical behaviour due to a lack of commutation of the potential and kinetic energy terms in the Hamiltonian. Substituting this redefined form of $I(\mathbf{q}, \mathbf{p})$ into equation 2.3, using the explicit form of the quantum Hamiltonian and after a considerable amount of algebra we find a partial differential equation for W,

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

As in typical in perturbation theories, the solution can be expanded in a power series of a small number, in this case, \hbar , according to $W = 1 + \hbar W_1 + \hbar^2 W_2 + \dots$ By substituting this expansion into $I(\mathbf{q}, \mathbf{p}) = e^{-\beta \mathcal{H}} W(\mathbf{q}, \mathbf{p})$ and $I(\mathbf{p}, \mathbf{q})$ back into equation 2.2 we find a power series expansion for the partition function as well,

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

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

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

Solving equation 2.4 to second order in \hbar and computing the classical averages in equation 2.5 the quantum corrections to the classical partition are computed to second order as²,

$$\langle W_1 \rangle = 0, \tag{2.7}$$

$$\langle W_2 \rangle = -\frac{\beta^3}{24m} \left\langle \left| \nabla_{\mathbf{q}} V \right|^2 \right\rangle.$$
(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,

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

There are a few items of importance in equation 2.9. First of all, the correction is 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 $\mathcal{O}(10^{-4})$ or at its melting temperature the prefactor is $\mathcal{O}(10^{-6})$. 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

²For detailed calculations see [20].

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

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

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,

$$\int' d\Gamma \to \frac{1}{N!} \int d\Gamma \tag{2.11}$$

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

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

Or, in the grand canonical ensemble,

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

Of course, to first order in \hbar , this is exactly the form taught in introductory courses on statistical mechanics and derived by Gibbs³ prior to any knowledge of quantum mechanics [21]. 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. We now apply this semi-classical limit of statistical mechanics to the study of the local density field.

³The \hbar in Gibbs' formula was justified on dimensional grounds and was simply introduced as a scaling factor with units of action $(J \cdot s)$

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,

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

From which the thermodynamic observable is,

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

Where, $\operatorname{Tr}\left[\cdot\right]$ now denotes the classical trace,

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

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

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

where \mathcal{H} is the classical Hamiltonian, μ the chemical potential of the system and $\Xi(\mu, \beta)$ is the grand partition function of the system.

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 an average of the density field, particle number and energy as the macroscopically available information, we can maximize then Gibb's entropy functional,

$$S[f(\mathbf{q}, \mathbf{p})] = -k_b \operatorname{Tr} \left[f(\mathbf{q}, \mathbf{p}) \ln \left(f(\mathbf{q}, \mathbf{p}) \right) \right], \qquad (2.18)$$

subject to the aforementioned constraints (fixed average density, particle number and total energy) to find a probability density function of the form,

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

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

We can combine their Lagrange multipliers into one,

$$f(\mathbf{q}, \mathbf{p}) \propto \exp\left(-\beta(\mathcal{H} - \int \mathrm{d}x\psi(x)\hat{\rho}(x))\right),$$
 (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 in Helmholtz free energy made by virtue of adding particles to the system,

$$\frac{\partial F}{\partial N} = \mu, \tag{2.22}$$

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 where we'll see an analogous equation for the intrinsic chemical potential. The objective of statistical theories is to compute the statistics of some observable (random variable) of choice. Two special sets of statistics provide a complete description of the observable's probability distribution: the *moments* and *cumulants*⁴. The calculation of moments and cumulants can be aided by use of generating functions. In the case of statistical mechanics the generating functions of moments and cumulants have special physical significance. The generating function of moments is closely related to the partition function and the generating function of cumulants is closely related to the associated thermodynamic potential.

In the case where the observable is the local density field, this is made somewhat more technical by the fact that the density is a function instead of a scalar variable. As such the partition function is more precisely called the partition *functional* as it depends on a function as input. The thermodynamic potential will thus also be a functional. Specifically, the grand canonical partition functional is,

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

As alluded to above, the partition functional is a type of moment generating functional in the sense that repeated (functional) differentiation with respect to the intrinsic chemical potential yields moments of the density field:

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

Similarly, we can construct a thermodynamic potential by taking the logarithm of the partition function. This potential in particular is called the *grand potential functional* in analogy with the grand potential of thermodynamics,

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

⁴See [22] for discussion of moments, cumulants and their importance in statistical mechanics

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

$$-\beta^{-n+1} \frac{\delta^n \Omega[\psi]}{\delta \psi(x_1) \dots \delta \psi(x_n)} = \langle \hat{\rho}(x_1) \dots \hat{\rho}(x_n) \rangle_c$$
(2.26)

Where, $\langle \cdot \rangle_c$, denotes the cumulant average [22].

If we examine the first two cumulants,

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

$$-k_b T \frac{\delta^2 \Omega[\psi]}{\delta \psi(x) \delta \psi(x')} = \left\langle (\hat{\rho}(x) - \rho(x))(\hat{\rho}(x') - \rho(x')) \right\rangle, \qquad (2.28)$$

we notice two remarkable things: 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 invertible⁵. To see this, we compute the Jacobian by combining equation 2.27 and 2.28,

$$\frac{\delta\rho(x)}{\delta\psi(x')} = \beta \left\langle (\hat{\rho}(x) - \rho(x))(\hat{\rho}(x') - \rho(x')) \right\rangle.$$
(2.29)

The right hand side of equation 2.29 is an autocorrelation function and therefore positive semi-definite by the Weiner-Khinchin theorem [23]. This implies that, at least locally, the intrinsic chemical potential can always be written as a functional of the average density, $\psi[\rho(x)]$, and vice versa. Furthermore, because all of the higher order cumulants of the density depend on the intrinsic chemical potential, they too depend only on the average density.

Given the importance of the average density, $\rho(x)$, it follows that we would like to use a thermodynamic potential with a natural dependence on the density. We can construct a generalization of the Helmholtz free energy that has precisely this characteristic by Legendre

⁵The inverse function theorem only implies local invertibility, there is no guarentee of global invertibility. Indeed phase coexistance is a manifestation of this fact where a single intrinsic chemical potential is shared by two phases

transforming the Grand potential,

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

 $\mathcal{F}[\rho(x)]$ is called the *intrinsic free energy functional*.

It can be shown [24] 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,

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

Finally, we may construct an analogous equation to equation 2.22 for the intrinsic chemical potential,

$$\frac{\delta \mathcal{F}}{\delta \rho(x)} = \psi(x), \qquad (2.32)$$

which follows from equation 2.30 assuming equation 2.31. Equation 2.32 implies that the intrinsic chemical potential is the free energy cost of adding density to the location x specifically.

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. It is 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,

$$\Omega_{id}[\psi] = -\frac{k_b T}{\Lambda^3} \int \mathrm{d}x \, e^{\beta\psi(x)} \tag{2.33}$$

$$\mathcal{F}_{id}[\rho] = k_b T \int \mathrm{d}x \left\{ \rho(x) \ln \left(\Lambda^3 \rho(x) \right) - \rho(x) \right\}, \qquad (2.34)$$

Where Λ is the thermal de Broglie wavelength,

$$\Lambda = \sqrt{\frac{2\pi\hbar^2}{mk_bT}}.$$
(2.35)

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

$$\Xi[\psi] = \Xi_{id}[\psi]\Xi_{ex}[\psi], \qquad (2.36)$$

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

$$\Omega = \Omega_{id} + \Omega_{ex} \tag{2.37}$$

$$\mathcal{F} = \mathcal{F}_{id} + \mathcal{F}_{ex}.$$
 (2.38)

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 [25], have been developed to treat the interaction potential systematically, other approximation schemes for the excess free energy are typically more pragmatic, particularly where deriving models that are tractable for the numerical simulation of dynamics is concerned. 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 ,

$$\mathcal{F}_{ex}[\rho] = \mathcal{F}_{ex}[\rho_0] + \left. \frac{\delta \mathcal{F}_{ex}}{\delta \rho(x)} \right|_{\rho_0} * \Delta \rho(x) + \frac{1}{2} \Delta \rho(x') * \left. \frac{\delta^2 \mathcal{F}_{ex}}{\delta \rho(x) \delta \rho(x')} \right|_{\rho_0} * \Delta \rho(x) + \dots, \quad (2.39)$$

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

$$f(x') * g(x') \equiv \int dx' f(x')g(x').$$
 (2.40)

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

$$\frac{\delta^n \mathcal{F}_{ex}[\rho]}{\delta\rho(x_1)\dots\delta\rho(x_n)} = -\beta C^n(x_1,\dots,x_n),$$
(2.41)

the first of which, for a uniform fluid, is the excess contribution to the chemical potential. We may express this as the total chemical potential less the ideal contribution (see equation 2.34),

$$\left. \frac{\delta F_{ex}}{\delta \rho} \right|_{\rho_0} = \mu_0^{ex} = \mu_0 - \mu_{id} = \mu_0 - k_b T \ln\left(\Lambda^3 \rho_0\right).$$
(2.42)

Truncating the expansion in equation 2.39 to second order in $\Delta \rho(x)$ and substituting the linear and quadratic terms from equation 2.42 and 2.41, we can simplify the excess free energy to,

$$\mathcal{F}_{ex}[\rho(r)] = \mathcal{F}_{ex}[\rho_0] + \int dr \left\{ \mu - k_b T \ln \left(\Lambda^3 \rho_0\right) \right\} \Delta \rho(r) - \frac{k_b T}{2} \Delta \rho(r) * C_0^{(2)}(r, r') * \Delta \rho(r'), \quad (2.43)$$

where $C_0^{(2)}(r, r')$ denotes the two-point direct correlation function at the reference state. Combining equation 2.34 with the simplified excess free energy in equation 2.43, we can express total change in free energy, $\Delta \mathcal{F} = \mathcal{F} - \mathcal{F}[\rho_0]$, as,

$$\Delta \mathcal{F}[\rho(r)] = k_b T \int \mathrm{d}r \left\{ \rho(r) \ln\left(\frac{\rho(r)}{\rho_0}\right) - (1 - \beta \mu_0) \Delta \rho(r) \right\} - \frac{k_b T}{2} \Delta \rho(r) * C_0^{(2)}(r, r') * \Delta \rho(r').$$
(2.44)

We find an equivalent expression for the grand potential after a Legendre transform,

$$\Delta\Omega[\rho(r)] = k_b T \int \mathrm{d}r \left\{ \rho(r) \left[\ln \left(\frac{\rho(r)}{\rho_0} \right) + \beta \phi(r) \right] - \Delta\rho(r) \right\} - \frac{k_b T}{2} \Delta\rho(r) * C_0^{(2)}(r, r') * \Delta\rho(r'),$$
(2.45)

where $\phi(r)$ is defined as an external potential, introduced into the system for completeness.

We see that the density functional theory derived here can be 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. It is 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 several parameters to the functional based on the reference fluid. Thankfully, the theory of homogeneous liquids is very well established. This implies we may rely on a broad choice of analytical, numerical or experimental techniques to derive these parameters.

Equation 2.44 establishes an approximate density functional theory for inhomogenous fluids. However, as we will see in the following chapter, the properties of the direct correlation function $C_o^2(r, r')$ also carries information about how the fluid solidifies in the solid state as temperature or density cross into the coexistence.

Chapter 3

Classical Density Functional Theory of Freezing

The classical density functional theories derived in chapter 2 were first established to study inhomogenous fluids. By considering the solid state as an especially extreme case of an inhomogeneous fluid [26], we can use CDFT to study the process of solidification. From the perspective of CDFT, solidification occurs once the density field develops long range periodic structure. While not expressed in precisely this language, this approach dates back as far as 1941 with the early work of Kirkwood and Monroe [27] and was later significantly refined by Yussouff and Ramakrishnan [28].

We'll see that the approach of Youssof and Ramakrishnan was very successful at explaining the solidification in the thermodynamic sense. That is to say, it elucidates the parameters responsible for solidification but not the dynamical pathway responsible for the transition. To discuss the pathway toward equilibrium and the non-equilibrium artifacts introduced along the way into many solids (e.g. grain boundaries, vacancies, dislocations, etc) we proceed to extend the CDFT framework using the Dynamic Density Functional Theory (DDFT). Noting that the full DDFT framework can be intractable in practice, we conclude by introducing a simplified density functional theory called the Phase Field Crystal (PFC) theory.

3.1 Amplitude Expansions

To explore the problem of solidification, we begin with the approximate grand potential established in equation 2.45 with the external potential, $\phi(r)$, set to zero,

$$\beta \Delta \Omega[\rho(r)] = \int dr \left\{ \rho(r) \ln \left(\frac{\rho(r)}{\rho_0} \right) - \Delta \rho(r) \right\} - \frac{1}{2} \Delta \rho(r) * C_0^{(2)}(r, r') * \Delta \rho(r').$$
(3.1)

To make our theory concrete we must choose a suitable reference liquid to set the parameters ρ_0 and $C_0^{(2)}(r, r')$. We will choose the reference liquid to be the liquid at the melting point with density ρ_l .

Scaling out a factor of ρ_l we can rewrite the grand potential in terms of a dimensionless reduced density, $n(r) \equiv (\rho(r) - \rho_l)/\rho_l$,

$$\frac{\beta \Delta \Omega[n(r)]}{\rho_l} = \int dr \left\{ (1+n(r)) \ln \left(1+n(r)\right) - n(r) \right\} - \frac{1}{2} n(r) * \rho_l C_0^{(2)}(r,r') * n(r').$$
(3.2)

To approximate the density profile in the solid state we can expand the density in a plane waves,

$$n(r) = \bar{n} + \sum_{\mathbf{G}} \xi_{\mathbf{G}} e^{i\mathbf{G}r}.$$
(3.3)

Where $\{\mathbf{G}\}\$ is the set of reciprocal lattice vectors in the crystal lattice and the amplitudes, $\xi_{\mathbf{G}}$, serve as order parameters for freezing. \bar{n} is the k = 0, or equivalently the spatial average, of the density profile. In the liquid phase all amplitudes are zero and the average density is uniform, while in the solid phase there are finite amplitudes that describe the periodic profile of the crystal lattice. As we have chosen the reference fluid to be the liquid at the melting point with uniform density ρ_l , \bar{n} is zero for the liquid phase at the melting point (for that reference density) and \bar{n} is the fractional density change of solidification, defined here as η , for the solid phase at the melting point, where

$$\eta = \frac{\rho_s - \rho_l}{\rho_l},\tag{3.4}$$

and in which ρ_s is the macroscopic density of the solid phase.

The amplitudes are constrained by the point group symmetries of the lattice. Grouping the amplitudes of symmetry-equivalent reciprocal lattice vectors together we can write the density profile as,

$$n(r) = \bar{n} + \sum_{\alpha} \left\{ \xi_{\alpha} \sum_{\{\mathbf{G}\}_{\alpha}} e^{i\mathbf{G}\cdot\mathbf{x}} \right\}, \qquad (3.5)$$

Where α is a label running over sets of symmetry-equivalent reciprocal lattice vectors. More precisely, if we apply the projection operator of the totally symmetric representation of the lattice point group to the reciprocal lattice vectors we may label the distinct linear combinations ¹ with α [29]. The members of these distinct linear combinations form the set $\{\mathbf{G}\}_{\alpha}$.

If we insert equation 3.5 into equation 3.2 and integrate over the unit cell of the particular crystal we wish to develop the theory for, we find,

$$\frac{\beta \Delta \Omega_{cell}}{\rho_l} = \int_{cell} dr \left\{ (n(r) + 1) \ln (n(r) + 1) - n(r) \right\} \\ - \frac{1}{2} \left[\bar{n}^2 \rho_l \tilde{C}_0^{(2)}(0) + \sum_{\alpha} \rho_l \tilde{C}_0^{(2)}(\mathbf{G}_{\alpha}) \lambda_{\alpha} |\xi_{\alpha}|^2 \right],$$
(3.6)

Where λ_{α} is the number of reciprocal lattice vectors in the set α and $\tilde{C}_{0}^{(2)}(k)$ is the Fourier transform of the direct correlation function of the reference fluid. The first term in equation 3.6 is convex in all of the amplitudes with a minimum at zero. It is noteworthy, as we will discuss shortly, that the product $\rho_l \tilde{C}_0^{(2)}(\mathbf{G}_{\alpha})$ is a simple function of the structure factor,

¹These linear combinations are all formally equal to zero. It is important to treat opposite vectors (**v** and $-\mathbf{v}$) as distinct for the sake of calculating the set $\{\mathbf{G}\}_{\alpha}$.

 $S(k)^2$, namely,

$$\rho_l \tilde{C}_0^2(k) = \frac{S(k) - 1}{S(k)} \quad \forall \ k \neq 0.$$
(3.7)

It follows that solidification must occur when the product $\rho_l \tilde{C}_0^{(2)}(\mathbf{G}_{\alpha})$ (or equivalently, the reference structure factor $S_0(\mathbf{G}_{\alpha})$) is large enough to stabilize a finite amplitude by creating a new minimum away from zero. This phenomenon is shown schematically in figure 3.1 where the grand potential is projected on to a particular ξ_{α} axis and plotted for different values of the reference structure factor. When the reference structure factors are less than some set of critical structure factors (denoted as $S^*(\mathbf{G}_{\alpha})$), only zero amplitude solutions are stable. When the reference structure factors are critical both the zero and non-zero amplitude solutions are stable and we find liquid-solid coexistence. Once the reference structure factors are greater than critical one the periodic crystalline solutions is stable.



Figure 3.1: Schematic view of the grand potential $\beta \Delta \Omega / \rho_l$ projected on to an ξ_{α} axis for three different reference structure factors. To minimize the grand potential, finite ξ_{α} is stable once $S_0(\mathbf{G}_{\alpha}) > S^*(\mathbf{G}_{\alpha})$

Furthermore, equation 3.6 suggests that the set of critical structure factors, $\{S^*(\mathbf{G}_{\alpha})\}_{\alpha}$ are material *independent* as no free parameters remain in the grand potential. As a con-

²This follows from the definition of the structure factor and the Ornstein-Zernike equation

sequence, once we specify the symmetry of the lattice a liquid will solidify into (eg. facecentred-cubic), all materials that undergo this transition should share these parameters at the melting point.

Early numerical evidence of this result was supplied by the Hansen-Verlet criterion [30] which states that for a Lennard-Jones fluid the peak of the structure factor is constant along the melting curve with a value ≈ 2.85 . It has been noted that in comparing experimental evidence of a variety of liquids solidifying to fcc structure, most have a peak value close to 2.8 whereas those solidifying into bcc structures have a peak value around 3.0 [28].

At this level, the CDFT theory of solidification is an infinite order parameter theory of solidification. We can simplify the theory by truncating the number of amplitudes we keep in our expansion of the density. This is justified by noting that only terms from the first few reciprocal lattice families contain the majority of the grand potential energy of solidification[28].

Theory	$\tilde{C}(\mathbf{G}_{[111]})$	$\tilde{C}(\mathbf{G}_{[311]})$	η	Theor	$ ilde{C}(\mathbf{G}_{[110]})$	$\tilde{C}(\mathbf{G}_{[211]})$	η
Ι	0.95	0.0	0.074	Ι	0.69	0.00	0.048
II	0.65	0.23	0.270	II	0.63	0.07	0.052
III	0.65	0.23	0.166	III	0.67	0.13	0.029
Experiment	0.65	0.23	0.148	Exper	riment 0.65	0.23	0.148

(a) Freezing parameters for fcc with comparison to Argon experimental results. (b) Freezing parameters for bcc with comparison to Sodium experimental results.

Table 3.1: Freezing parameters for fcc and bcc systems and comparison to experiment from [28]. Theory I uses one order parameter, theory II uses two order parameters and theory III uses two order parameters with a higher (third) order expansion in the free energy. η is the fractional density change of solidification from equation 3.4

As seen in table 3.1a and table 3.1b theoretical results from a single amplitude theory (theory I in the results) are poor but improve significantly with two order parameters (theory II) or higher order expansions of the free energy (theory III).

3.2 Dynamic Density Functional Theory

In spite of its successes, the CDFT theory of solidification cannot be a general description of solidification as many materials never fully reach equilibrium. The resulting microstructure affects the mechanical properties of the solid. In order to improve our theory we need to examine the pathway systems take to equilibrium so we can understand these microstructural features. We begin with a brief overview of non-equilibrium statistical mechanics.

3.2.1 Overview of Non-equilibrium Statistical Mechanics

Consider a non-equilibrium probability distribution over phase space, $f(\mathbf{q}, \mathbf{p}; t)$. As a function over phase space, its equation of motion is a simple result of classical mechanics,

$$\frac{df}{dt} = \{f, \mathcal{H}\} + \frac{\partial f}{\partial t}.$$
(3.8)

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

$$\{f,g\} = \sum_{i=0}^{N} \frac{\partial f}{\partial q_i} \frac{\partial g}{\partial p_i} - \frac{\partial g}{\partial q_i} \frac{\partial f}{\partial p_i}.$$
(3.9)

Of course, the distribution must remain normalized in time and therefore the total time derivative must be zero,

$$\int d\mathbf{q} d\mathbf{p} f(\mathbf{q}, \mathbf{p}; t) = 1 \to \frac{df}{dt} = 0.$$
(3.10)

Accounting for this conservation law in equation 3.8, the resulting equation of motion is called the *Liouville Equation*,

$$\frac{\partial f}{\partial t} = -\{f, \mathcal{H}\} \tag{3.11}$$

Under appropriate conditions the probability distribution, under the action of the Liouville Equation, will decay to a stable fixed point $f_{eq}(\mathbf{q}, \mathbf{p})$ we call equilibrium,

$$\lim_{t \to \infty} f(\mathbf{q}, \mathbf{p}; t) = f_{eq}(\mathbf{q}, \mathbf{p})$$
(3.12)

Using the non-equilibrium probability distribution, we can also discuss non-equilibrium averages of the density profile and their associated equations of motion. The non-equilibrium density is written in analogy with equation 2.15 by taking of the classical trace of the density operator over with the non-equilibrium distribution,

$$\rho(x,t) = \left\langle \hat{\rho}(x;\mathbf{q}) \right\rangle_{ne} = \operatorname{Tr}\left[\hat{\rho}(x;\mathbf{q}) f(\mathbf{q},\mathbf{p},t) \right].$$
(3.13)

Where $\langle \cdot \rangle_{ne}$ denotes the non-equilibrium average, (i.e., using $f(\mathbf{q}, \mathbf{p}, t)$). Just as the non-equilibrium probability distribution is driven to equilibrium by the Liouville Equation, so too is the density profile by its own equation of motion.

3.2.2 Equation of Motion for the Density

A variety of equations of motion for the density field are known. For instance, we can consider the Navier-Stokes equations of hydrodynamics as one such equation of motion. If we restrict ourselves to diffusion limited circumstances, we may derive a much simpler equation of motion. To achieve this result we use the projection operator method, and assume that the density operator is the only relevant variable. Quoting the result from [23] we find,

$$\frac{\partial \rho(r,t)}{\partial t} = \nabla \cdot \left[\int dr' \,\mathbf{D}(r,r',t) \cdot \nabla' \frac{\delta \mathcal{F}[\rho]}{\delta \rho(r',t)} \right],\tag{3.14}$$

where ∇' denotes differentiation with r', and $\mathbf{D}(r, r', t)$ is the diffusion tensor,

$$\mathbf{D}(r,r',t) = \int_0^\infty \mathrm{d}\tau' \operatorname{Tr}\left[f(\mathbf{q},\mathbf{p},t)\hat{\mathbf{J}}(r,0)\hat{\mathbf{J}}(r',\tau')\right],\tag{3.15}$$

in which $\mathbf{J}(r,t)$ is the local density flux,

$$\hat{\mathbf{J}}(r,t) \equiv \sum_{i}^{N} \frac{p_i}{m_i} \delta(r-q_i).$$
(3.16)

Theories using equation 3.14 and variations thereof are often called *Dynamic Density Functional Theories* (DDFT) or at times *Time Dependent Density Functional Theories* (TDDFT) though we will use the former throughout this work.

The non-equilibrium diffusion tensor presents a significant impediment to integrating this equation of motion so in practice it is often approximated. Following [23], if we assume that the positions evolve more slowly than the velocities and that the momenta of different particles are uncorrelated we can dramatically simplify the diffusion tensor,

$$D(r, r') = D_0 \mathbb{1}\rho(r, t)\delta(r - r').$$
(3.17)

Where D_0 is the diffusion coefficient,

$$D_0 = \frac{1}{3m^2} \int_0^\infty dt \operatorname{Tr} \left[f(\mathbf{q}, \mathbf{p}, t) p_i(0) \cdot p_i(t) \right].$$
(3.18)

Substituting into equation 3.14 we find a simplified equation of motion originally suggested by [31],

$$\frac{\partial \rho(r,t)}{\partial t} = \nabla \cdot \left[D_0 \rho(r,t) \nabla \frac{\delta \mathcal{F}[\rho]}{\delta \rho(r,t)} \right].$$
(3.19)

The equation of motion can also be written as a Langevin equation. In this variant the equation of motion is for the density *operator*, $\hat{\rho}$, and the noise is assumed to obey a
generalized Einstein relation,

$$\frac{\partial \hat{\rho}(x,t)}{\partial t} = \nabla \cdot \left[D_0 \hat{\rho}(x,t) \nabla \left(\frac{\delta \mathcal{F}[\hat{\rho}]}{\delta \hat{\rho}} \right) \right] + \xi(x,t), \qquad (3.20)$$

$$\langle \xi(x,t) \rangle = 0, \tag{3.21}$$

$$\langle \xi(x,t)\xi(x',t')\rangle = -2\nabla \cdot \left[D_0\rho(x,t)\nabla\delta(x-x')\delta(t-t')\right].$$
(3.22)

See Appendix A for more details on generalized Einstein relations and [32] for a detailed discussion about equations 3.19 and 3.20.

At times, the diffusion tensor is assumed to be constant. This is common place in many Phase Field Crystal theories. In light of equation 3.19, this is akin to assuming the density variations are small.

Unfortunately, if we were to use the approximate free energy functional established in equation 2.44 in the DDFT of equation 3.19 or 3.20 we would face a major impediment: the solid state solutions of the density functional theory approach yield sharply peaked solutions at the position of the atoms in the lattice. While this is realistic, they are a major challenge for numerical algorithms that aim to explore long-time microstructure evolution. The challenges are two-fold. First, these sharp peaks require a fine mesh to be resolved resulting in intractably large memory requirement to simulate domains of any non-trivial scale. Second, linear stability analysis of most algorithms demonstrates that the time step size is a monotonically increasing function of the grid spacing, thus only small time steps can be taken on a fine mesh. This further restricts the time scales of microstructure evolution that can be practicality explored to times scales comparable to those of molecular dynamics –perhaps somewhat longer.

One pragmatic solution to this problem is to further approximate the free energy functional of equation 2.44 in such a way as to produce a theory that retains the essential physics of solidification but produces a solid state that is more smoothly peaked. As we will see next, the Phase Field Crystal (PFC) theory, the topic of this thesis, aims to achieve precisely this balance.

3.3 Phase Field Crystal Theory

The phase field crystal theory (PFC) presents a solution to the aforementioned numerical difficulties faced by DDFT methods by approximating the free energy in such a way as to retain the basic features of the theory using a smoother solid state description of density. Starting with the approximate free energy functional of equation 2.44 we proceed as previously by scaling out a factor of the reference density and changing variables to a dimensionless density $n(r) = (\rho(r) - \rho_l)/\rho_l$,

$$\frac{\beta \mathcal{F}[n(r)]}{\rho_l} = \int dr \left\{ (n(r)+1) \ln(n(r)+1) - (1-\beta\mu_0)n(r) \right\} - \frac{1}{2}n(r) * \rho_l C_0^{(2)}(r,r') * n(r').$$
(3.23)

We then Taylor expand the logarithm about the reference density or equivalently n(r) = 0, to fourth order,

$$\frac{\beta \mathcal{F}[n(r)]}{\rho_l} = \int dr \left\{ \frac{n(r)^2}{2} - \frac{n(r)^3}{6} + \frac{n(r)^4}{12} \right\} - \frac{1}{2}n(r) * \rho_l C_0^{(2)}(r, r') * n(r').$$
(3.24)

Where the linear term can be dropped by redefining the density n(r) about its average. Most phase field crystal theories also use a simplified equation of motion as well,

$$\frac{\partial n(r,t)}{\partial t} = M \nabla^2 \left(\frac{\delta \mathcal{F}[n(r)]}{\delta n(r)} \right).$$
(3.25)

As alluded to above, these two simplifications formally make the PFC theory different from CDFT, turning it instead into a type of Ginzburg-Landau type of field theory, where n represents an order parameter that becomes periodic in the solid state. As has been shown in the PFC literature, this apparently gross over-simplification of CDFT manages to correctly reproduce many of the qualitative physics of solidification, such as nucleation, grain boundary misorientation energy, elastic response and dislocations in the solid phase, vacancy diffusion and creep, grain boundary pre-melting, vacancy trapping, and numerous other effects. By progressively improving the parametrization of PFC theories, guided by inspection of the underlying forms, PFC will be able to better quantitatively model the aforementioned processes.

Chapter 4

Simplified Binary Phase Field Crystal Models

In this chapter we will review two current simplified binary PFC models. The first is the original binary PFC model of Elder *et al.* [3] and the second is the binary structural PFC (XPFC) model of Greenwood *et al.* [14]. We begin by establishing background shared by all binary PFC models and move on to summarize and review each.

4.1 Binary PFC Background

We begin with a multicomponent variant of the approximate free energy functional established in Chapter 2,

$$\beta \mathcal{F}[\rho_A, \rho_B] = \sum_{i=A,B} \int \mathrm{d}r \,\rho_i(r) \ln\left(\frac{\rho_i(r)}{\rho_i^0}\right) - (1 - \beta \mu_i^0) \Delta \rho_i(r) \qquad (4.1)$$
$$- \frac{1}{2} \sum_{i,j=A,B} \Delta \rho_i(r) * C_{ij}^{(2)}(r,r') * \Delta \rho_j(r').$$

It is convenient to change variables to a dimensionless total density, n(r) and local concentration, c(r),

$$n(r) = \frac{\Delta\rho}{\rho_0} = \frac{\Delta\rho_A + \Delta\rho_B}{\rho_A^0 + \rho_B^0}$$
(4.2)

$$c(r) = \frac{\rho_B}{\rho} = \frac{\rho_B}{\rho_A + \rho_B}.$$
(4.3)

Scaling out a factor of the total reference density, ρ_0 we can break the free energy functional in these new variables into three parts,

$$\frac{\beta \mathcal{F}[n,c]}{\rho_0} = \frac{\beta \mathcal{F}_{id}[n]}{\rho_0} + \frac{\beta \mathcal{F}_{mix}[n,c]}{\rho_0} + \frac{\beta \mathcal{F}_{ex}[n,c]}{\rho_0},\tag{4.4}$$

where, \mathcal{F}_{id} , \mathcal{F}_{mix} and \mathcal{F}_{ex} are the ideal, mixing and excess free energies respectively. These are defined as,

$$\frac{\beta \mathcal{F}_{id}[n]}{\rho_0} = \int \mathrm{d}r \,\left\{ (n(r)+1)\ln(n(r)+1) - (1-\beta\mu^0)n(r) \right\}$$
(4.5)

$$\frac{\beta \mathcal{F}_{mix}[n,c]}{\rho_0} = \int \mathrm{d}r \,\left\{ (n(r)+1) \left(c \ln\left(\frac{c}{c_0}\right) + (1-c) \ln\left(\frac{1-c}{1-c_0}\right) \right) \right\},\tag{4.6}$$

where we have introduced $\mu^0 = \mu_A^0 + \mu_B^0$ as the total chemical potential of the reference mixture, and $c_0 = \rho_B^0 / \rho_0$ as the reference concentration. Assuming that the local concentration c(r) varies over much longer length scales than the local density n(r), the excess free energy term becomes

$$\frac{\beta \mathcal{F}_{ex}[n,c]}{\rho_0} = -\frac{1}{2}n(r) * \left[C_{nn}(r,r') * n(r') + C_{nc}(r,r') * \Delta c(r')\right] - \frac{1}{2}\Delta c(r) * \left[C_{cn}(r,r') * n(r') + C_{cc}(r,r') * \Delta c(r')\right],$$
(4.7)

where we have introduced and $\Delta c(r) = c(r) - c_0$ as the deviation of the concentration from the reference. The n - c pair correlations introduced in the excess free energy are,

$$C_{nn} = \rho_0 \left(c^2 C_{BB} + (1-c)^2 C_{AA} + 2c(1-c)C_{AB} \right)$$
(4.8)

$$C_{nc} = \rho_0 \left(cC_{BB} - (1-c)C_{AA} + (1-2c)C_{AB} \right)$$
(4.9)

$$C_{cn} = C_{nc} \tag{4.10}$$

$$C_{cc} = \rho_0 \left(C_{BB} + C_{AA} - 2C_{AB} \right) \tag{4.11}$$

Explicit derivations of these terms can be found in Appendix C. Differences in the various simplified binary PFC theories stem from differing approximations of the terms in the free energy stated in equations 4.5, 4.6 and 4.7.

4.2 Original Binary Phase Field Crystal Model

In the original simplified binary PFC theory, all terms in the free energy are expanded about n(r) = 0 and $c(r) = c_0$ (i.e., about their reference states). For the ideal free energy this results in a polynomial truncated to fourth order,

$$\frac{\beta \mathcal{F}_{id}[n]}{\rho_0} = \int \mathrm{d}r \,\left\{ \frac{n(r)^2}{2} - \eta \frac{n(r)^3}{6} + \chi \frac{n(r)^4}{12} \right\}.$$
(4.12)

The linear term in the expansion is dropped by redefining n about its average and we have added the fitting parameters η and χ to fit the free energy away from the reference parameters. If we assume for simplicity of demonstration $c_0 = 1/2$, the free energy of mixing becomes a simple fourth order polynomial as well,

$$\frac{\beta \mathcal{F}_{mix}[n,c]}{\rho_0} = \int \mathrm{d}r \,\left\{ 2\Delta c(r)^2 + \frac{4\Delta c(r)^4}{3} \right\}. \tag{4.13}$$

Linear couplings to n(r) are dropped by assuming, as we already have, that the concentration field varies on a much longer length scale than the total density and noting that the total density is defined about its average. This argument can also be applied to the linear couplings to n(r) in the excess free energy term, which then leaves only the C_{nn} and C_{cc} terms. Finally, these two terms are approximated with a gradient expansion of the form,

$$C_{nn}(r,r') = (C_0 + C_2 \nabla^2 + C_4 \nabla^4 + \dots) \,\delta(r-r'), \qquad (4.14)$$

$$C_{cc}(r,r') = \left(\epsilon + W_c \nabla^2 + \ldots\right) \delta(r-r').$$
(4.15)

The expansion parameters, C_0, C_2 , and C_4 are all dependent on temperature and concentration. We are required to expand C_{nn} to fourth order because, as noted in chapter 3, the peak of the direct correlation function in Fourier space is the driving force for solidification. The concentration field is correlated over a longer length scale implying that only the short wavevectors are important in C_{cc} so we can expand just to quadratic order, effectively treating c as in the traditional Cahn-Hilliard theory.

Gathering terms, the resulting free energy functional for the original simplified binary PFC model¹ is,

$$\frac{\beta \mathcal{F}[n,c]}{\rho_0} = \int dr \left\{ \frac{1}{2} n(r) \left(1 - C_0 - C_2 \nabla^2 - C_4 \nabla^4 \right) n(r) - \eta \frac{n(r)^3}{6} + \chi \frac{n(r)^4}{12} \right\}$$
(4.16)
+
$$\int dr \left\{ \frac{1}{2} \Delta c(r) \left(4 - \epsilon - W_c \nabla^2 \right) \Delta c(r) + \frac{4 \Delta c(r)^4}{3} \right\}.$$

The strength of the original simplified binary PFC model is that is retains most of the important physics of binary alloys in a very reduced theory. For instance, the simplified model is capable of describing the equilibrium phase diagrams of both eutectic alloys and materials with a solid state spinodal / liquid minimum. Supplied with a diffusive equation of motion, the simplified model can model an impressive diversity of dynamic phenomena

¹The orignal simplified binary PFC model was expressed using slightly different variables. We expand in $\Delta c(r)$ here to facilitate comparison with other theories

including eutectic growth [3], solute segregation [33], dendritic growth [3], epitaxial growth [11, 12] and crack formation [34].

The major limitation of the original simplified model is that the gradient expansion of the density-density correlation function gives only a crude control over the crystal structures that can be formed. In fact, as this theory only controls a single peak in Fourier space it can only solidify into the BCC phase. As noted in chapter 3, the ability to solidify into an arbitrary structure demands control of the density-density correlation function at all reciprocal lattice vectors.

A second limitation of the original simplified model is that it is local in concentration. This means that realistic phase diagrams from 0 to 100% concentration cannot be produced, only local phase diagrams around the reference concentration². The limited concentration range is problematic for comparing to experimental phase diagrams. To obtain relatable and testable results, a major motivation for binary XPFC and this work, we require the entire free energy of mixing term in equation 4.6.

4.3 Original Binary Structural Phase Field Crystal Model

The binary structural phase field crystal theory (XPFC) seeks to remedy the two short comings of the original simplified model. That is, it seeks to reproduce a variety of crystal lattice structure and to construct phase diagrams of a range of concentrations. We'll begin with a derivation of the theory and compare with the original model.

First, the ideal free energy is expanded in precisely the same manner resulting in the same fourth order polynomial,

$$\frac{\beta \Delta \mathcal{F}_{id}[n]}{\rho_0} = \int dr \,\left\{ \frac{n(r)^2}{2} - \eta \frac{n(r)^3}{6} + \chi \frac{n(r)^4}{12} \right\}.$$
(4.12 revisited)

The free energy of mixing is left unexpanded but an overall scale ω is added to fit the mixing

²Indeed, the original model "concentration" was in fact a density difference, not true concentration.

term away from the reference concentration,

$$\frac{\beta \mathcal{F}_{mix}[n,c]}{\rho_0} = \int \mathrm{d}r \,\left\{ \omega(n(r)+1) \left(c \ln\left(\frac{c}{c_0}\right) + (1-c) \ln\left(\frac{1-c}{1-c_0}\right) \right) \right\}. \tag{4.17}$$

This unexpanded free energy of mixing will lead to more accurate global phase diagrams. The excess free energy is approximated using similar assumptions as in the original model (linear couplings are dropped), but the density-density correlation function, C_{nn} , is not expanded. Instead, Greenwood *et al* all assumed that the k = 0 mode of the concentrationconcentration correlation function was zero leaving only the quadratic term in the expansion,

$$C_{cc}(r,r') = \delta(r-r')W_c \nabla^2.$$
(4.18)

Grouping terms together, the complete free energy functional for the binary XPFC model is,

$$\frac{\beta \Delta \mathcal{F}[n,c]}{\rho_0} = \int dr \left\{ \frac{1}{2} n(r) \left(1 - C_{nn}(r,r') \right) * n(r') - \eta \frac{n^3}{6} + \chi \frac{n^4}{12} \right\}$$
(4.19)
$$+ \int dr \left\{ \frac{W_c}{2} \left| \nabla c(r) \right|^2 + \omega f_{mix}(r) \right\}.$$

Where $f_{mix}(r)$ is the local free energy density of mixing,

$$f_{mix}(r) = (n(r) + 1) \left(c(r) \ln \left(\frac{c(r)}{c_0} \right) + (1 - c(r)) \ln \left(\frac{1 - c(r)}{1 - c_0} \right) \right).$$
(4.20)

The density-density correlation function, C_{nn} , is left unexpanded in Fourier space but assumed to have a specific phenomenological form,

$$C_{nn} = \zeta_A(c) C_{AA}(r, r') + \zeta_B(c) C_{BB}(r, r'), \qquad (4.21)$$

where $\zeta_A(c)$ and $\zeta_B(c)$ are interpolation functions, assigned the forms

$$\zeta_A(c) = 1 - 3c^2 + 2c^3 \tag{4.22}$$

$$\zeta_B(c) = \zeta_A(1-c). \tag{4.23}$$

by Greenwood *et al.*

The remaining elemental correlation functions C_{AA} and C_{BB} are modelled using the general XPFC model for correlation functions, which we describe subsequently.

4.3.1 XPFC Correlation Functions

The key insight made by the XPFC model is that the density-density correlation function can be modelled in such a way as to control the crystal lattice structure formed under solidification and to target different structures at different concentrations, and temperatures. Originally delineated for pure systems, the XPFC method for constructing correlation functions is strongly influenced by the methods developed by Ramakrishnan. In particular this means that we need a model correlation function that controls the values specifically at the reciprocal lattice vector positions. We can achieve this with Gaussian peaks centred at the reciprocal lattice vector positions,

$$\tilde{C}(k) = \sum_{\alpha} e^{\frac{T}{T_0}} e^{-\frac{(k-k_\alpha)^2}{2\sigma_\alpha^2}}$$
(4.24)

Where, as in chapter 3, the index α runs over families of point group symmetry-equivalent reciprocal lattice vectors, k_{α} is the length of the reciprocal lattice vectors in α and σ_{α} is the width of the peak. Temperature dependence of the correlation peaks is achieved through the prefactors e^{T/T_0} which gives the correct temperature scaling of the amplitudes at temperatures much higher than the Debye temperature³ as discussed by [13].

³The original XPFC works used a phenomenological prefactor e^{σ^2/C_i} , where σ was considered a model temperature parameter and C_i a constant. That choice was inspired by harmonic analysis in the solid phase

The primary advantages of the XPFC model are two fold: they produce realistic phase diagrams and they model a variety of crystalline lattices. While the former is relatively cosmetic the latter allows for the examination of genuinely novel systems in comparison with the original simplified model. For example, the binary XPFC model has been used to study peritectic systems [14], ordered crystals [13], dislocation-assisted solute clustering and precipitation [7, 8] and solute drag [6]. It is noteworthy, that the above works on clustering have been validated experimentally in binary and ternary alloys.



Figure 4.1: Eutectic phase diagram with metastable projections. Stable coexistance lines are rendered solid whereas metastable projections are dashed.

Unfortunately, by assuming that the k = 0 mode of the concentration-concentration correlation function is zero, the XPFC model restricts its free energy of mixing to an ideal model of mixing. This model of mixing includes only entropic contributions to the free energy. In the solid state, this means that the sole driving force for phase separation is elastic energy as the enthapy of mixing is always zero. This inhibits the modelling of a variety of binary alloy systems, for instance both monotectic and syntectic systems cannot and the Debye-Waller factor. be modelled without a negative enthalpy of mixing. More subtly, in the present XPFC alloy model, even eutectic systems have a negative heat of mixing deep below the eutectic point as the metastable liquid has a spinodal. This phenomenon is shown schematically in figure 4.1, where the metastable projections, including solid and liquid spinodals, are drawn on a hypothetical eutectic phase diagram.

A second disadvantage of the present XPFC model is that the phenomenological form for the correlation function as seen in equation 4.21 implicitly assumes that there are well defined structures at c = 0 and c = 1. This works well for modelling eutectic systems for example, but does not work very well when we expect a solid phase at intermediate concentration. These shortcomings are the motivation for the improvements developed in this thesis which are presented in the following chapter.

Chapter 5

Improvements to the Binary XPFC Model

In this chapter we look at two improvements to the binary XPFC theory. Both of these improvements are novel contributions to the field and significantly extend the scope of the XPFC framework. The improvements, as previously alluded to, are to first, extend the free energy of mixing in the XPFC model to one with an enthalpy of mixing and to second, generalize the phenomenological for of the two-point correlation function in binary alloys.

5.1 Adding an Enthalpy of Mixing

Extending the free energy of mixing beyond ideal mixing is achieved by removing the assumption made by Greenwood *et al.* in deriving the binary XPFC model that the concentrationconcentration correlation function has no k = 0 mode. This is the same approach taken in the original PFC model, though here we keep the ideal mixing term unexpanded as in the original XPFC alloy model. Specifically, the correlation function is expanded as,

$$C_{cc}(r,r') = \delta(r-r') \left(\omega \epsilon + W_c \nabla^2 + \cdots\right), \qquad (5.1)$$

where ϵ is a parameter that is possibly temperature dependent. This form results in a free energy functional of the form,

$$\frac{\beta \Delta \mathcal{F}[n,c]}{\rho_0} = \int dr \left\{ \frac{1}{2} n(r) \left(1 - C_{nn}(r,r') \right) * n(r') - \eta \frac{n^3}{6} + \chi \frac{n^4}{12} \right\}$$
(5.2)
+
$$\int dr \left\{ \frac{W_c}{2} |\nabla c(r)|^2 + \omega f_{mix}(r) \right\},$$

where the local free energy density of mixing, f_{mix} is now,

$$f_{mix}(r) = (n(r)+1)\left(c(r)\ln\left(\frac{c(r)}{c_0}\right) + (1-c(r))\ln\left(\frac{1-c(r)}{1-c_0}\right)\right) + \frac{1}{2}\epsilon(c-c_0)^2.$$
 (5.3)

For simplicity the temperature dependence of the parameter ϵ is taken to be linear about a spinodal temperature T_c ,

$$\epsilon(T) = -4 + \epsilon_0 (T - T_c). \tag{5.4}$$

The resulting model has a free energy of mixing that is equivalent to the regular solution model and, as such, it makes a clear connection to a well used model elsewhere in material science. The regular solution model also supplies the essential physics of a non-negligible enthalpy of mixing.

5.2 Generalizing the Two-Point Correlation Function

To establish a general phenomenology for modelling density-density correlation functions in alloys, note that the density-density correlation function has the form of a linear combination of interpolating functions in concentration, $\zeta(c)$, multiplied by bare correlation functions C(r, r') of individual components,

$$C_{nn}(r, r'; c) = \sum_{i} \zeta_{i}(c) C_{i}(r, r')$$
(5.5)

where the index i is, for the moment, an arbitrary label. For example, in the exact theory that emerges from the original alloy CDFT theory (equation 4.8), we use the labels $\{AA, AB, BB\}$ and have interpolation functions,

$$\zeta_{AA}(c) = \rho_0 (1 - c^2), \tag{5.6}$$

$$\zeta_{AB}(c) = \rho_0 c (1 - c), \tag{5.7}$$

$$\zeta_{BB}(c) = \rho_0 c^2. \tag{5.8}$$

This suggests the following new definition that we introduce herein to generalize the densitydensity correlation function for a binary alloy: Use the labels *i* to enumerate the set of crystal structures known to manifest themselves in an alloy system. The correlation functions, $C_i(r, r')$ are then direct correlation functions that model the crystal structure *i* and the associated interpolation functions $\zeta_i(c)$ define the range of concentrations over which these correlations are valid. In principle, $\zeta_i(c)$ can also be temperature dependent, although we do not consider that case in this thesis.

As a simple example, if we wanted to construct a model of the silver-copper eutectic alloy system, we might start with some model correlation function for pure silver, $C_{\alpha}(r, r')$, and for pure copper, $C_{\beta}(r, r')$. These two structures, the silver rich α phase and the copper rich β phase, are the only two relevant crystalline phases in the system, so to build the full density-density correlation function we just need to choose interpolating functions for each phase. Following Greenwood *et al.* for example, we might choose,

$$\zeta_{\alpha}(c) = 1 - 3c^2 + 2c^3, \tag{5.9}$$

$$\zeta_{\beta}(c) = 1 - 3(1-c)^2 + 2(1-c)^3.$$
(5.10)

To model the α and β correlation functions we use the original XPFC formalism for modelling bare correlation functions (i.e. equation 4.24). The α and β phases are both FCC [35] so we can use an FCC model for the correlation function as in [36].

5.3 Equilibrium Properties of Binary Alloys

These two changes to the XPFC formalism extend the possible systems we can study. In this section we'll explore the equilibrium properties of the improved XPFC free energy functional specialized for three different material phase diagrams: eutectic, syntectic and monotectic.

5.3.1 Eutectic Phase Diagram

While previous PFC models have shown that elastic energy is a sufficient driving force for eutectic solidification, our simplified regular solution XPFC model allows for the examination of the role enthalpy of mixing can play in eutectic solids. For instance, Murdoch and Schuh noted that in nanocrystalline binary alloys, while a positive enthaply of segregation can stabilize against grain growth via solute segregation at the grain boundary, if the enthaply of mixing becomes too large this effect can be negated by second phase formation or even macroscopic phase separation[37].

To specialize our simplified regular model to the case of the binary eutectic, we must choose an appropriate model for the correlation function. Choosing an α phase around c = 0and β phase around c = 1, we can recover the pair correlation function used in the binary XPFC of Greenwood *et al.* with a particular choice of interpolation functions:

$$\zeta_{\alpha}(c) = 2c^3 - 3c^2 + 1 \tag{5.11}$$

$$\zeta_{\beta}(c) = \zeta_{\alpha}(1-c). \tag{5.12}$$

Should we choose, for example, an α and β phase with 2 dimensional hexagonal lattices, differing only by lattice constants, we can produce a phase diagram like that in Fig. 5.1. The phase diagram also depicts the phase diagram of the metastable liquid below the eutectic

point showing the binodal and spinodal lines where the metastable liquid becomes unstable with respect to phase separation. The spinodal line indicates an inflexion point in the free energy of the metastable liquid where the liquid becomes fully unstable with respect to phase separation whereas the binodal line indicates the coexistance curve of the decomposed metastable liquid.



Figure 5.1: Eutectic phase diagram for triangle α and β solid phases and l denotes the liquid. The free energy parameters are $\eta = 2$, $\chi = 1$, $\omega = 0.02$, $\epsilon_0 = 26.6$ and $T_c = 0.15$. The parameters of the structure functions are $\sigma_{10\alpha} = \sigma_{10\beta} = 0.8$, $k_{10\alpha} = 2\pi$, $k_{10\beta} = 4\pi/\sqrt{3}$ and $T_0 = 1$. The horizontal line denotes the eutectic temperature.

It is noted that the phase diagram in Fig. 5.1 and in what follows were done using the same approach that was used in numerous PFC literature [14]. The approach is as follows: a mode expansion for the density is assumed for each crystal phase (zero amplitudes for the liquid phase). For each phase, an amplitude equation analogous to equation 3.6 results, except in this case, it is a function of amplitudes, average density *and* concentration. This coarse grained free energy of each phase is then minimized with respect to the amplitudes,

leaving a free energy density for each phase that is a function only of the average density and concentration. At this juncture, we simplify matters by assuming that the average density is a constant for the system. We then minimize the total free energy of the system with respect to concentration, assuming a conserved total concentration field. This latter step considers separately the coexistence of (1) α -liquid, (2) β -liquid, (3) α - β over different temperature/concentration ranges. Original code was developed to carry our these phase diagram constructions, and implemented using Julia [38], Maxima.jl [39] and the Maxima symbolic computation engine [40].

5.3.2 Syntectic Phase Diagram

Our improved XPFC model also allows for the study of a variety of invariant binary reactions that, to date, have not been studied using phase field crystal models. One such reaction is the syntectic reaction.

The syntectic reaction, $l_1+l_2 \rightarrow \alpha$, consists of solidification at the interface of two liquids. We can achieve this with our model by setting the spinodal temperature, T_c , in equation 5.4 sufficiently high and producing a density-density correlation function that is peaked at a concentration below the spinodal. This can be done by choosing a single interpolation function to be a window function that is centered about an intermediate concentration, c_{α} of the solid phase, α . One obvious choice is,

$$\zeta(c) = e^{-\frac{(c-c_{\alpha})^2}{2\alpha_c^2}}$$
(5.13)

The resulting correlation function for a hexagonal lattice in a syntectic alloy in two dimensions becomes,

$$\tilde{C}_{nn}(k;c) = e^{-\frac{(c-c_{\alpha})^2}{2\alpha_c^2}} e^{-\frac{T}{T_0}} e^{-\frac{(k-k')^2}{2\alpha^2}}$$
(5.14)

A phase diagram that produces a syntectic reaction with an appropriate choice of parameters can be seen in Fig. 5.2.



Figure 5.2: Phase Diagram of Syntectic Alloy with a hexagonal solid phase α . The free energy parameters are $\eta = 2$, $\chi = 1$, $\omega = 0.3$, $\epsilon_0 = 10$ and $T_c = 0.35$. The parameters for the structure function are $\alpha_{10\alpha} = 0.8$, $k_{10\alpha} = 2\pi$ and $T_0 = 1$. The horizontal line denotes the syntectic temperature.

5.3.3 Monotectic Phase Diagram

The monotectic reaction is another invariant binary reaction that has not previously been studied using PFC models. The monotectic reaction, $l_1 \rightarrow \alpha + l_2$, consists of decomposing liquid into a solute poor solid and solute rich liquid. To model a monotectic using our improved XPFC model we hypothesize a solid phase at c = 0 and set the spinodal temperature higher than the solidification temperature. To achieve this, we use a window function peaked around c = 0,

$$\chi_{\alpha}(c) = e^{-\frac{c^2}{2\alpha_c^2}}.$$
 (5.15)

Again considering a simple hexagonal lattice for the α phase, we can produce a phase diagram with a monotectic reaction with an appropriate choice of parameters as in Fig. 5.3.



Figure 5.3: Phase Diagram of Monotectic Alloy with hexagonal α phase. The free energy parameters are $\eta = 2$, $\chi = 1$, $\omega = 0.3$, $\epsilon_0 = 10$, $T_c = 0.35$ and $c_0 = 0.75$. The parameters for the structure function are $\alpha_{10\alpha} = 0.8$, $k_{10\alpha} = 2\pi$ and $T_0 = 1$ and the parameter for the window function is $\alpha_c = 0.4$. The horizontal line indicates the monotectic temperature.

The improvements to the XPFC formalism made in this chapter not only reveal new details in existing systems, but also model new systems that haven't been explored with PFC methods before. They provide a general framework to explore the landscape of other possible binary alloys with an emphasis that the liquid free energy is a crucial element in this complete description. It is also noteworthy that the approach introduced here is extendable in a straightforward way to multi-component alloys if the interpolation functions become multivariate functions of the concentrations.

Chapter 6

Applications

In this chapter we discuss applications of the improved binary XPFC model introduced in Chapter 5 to an application in microstructure evolution. To begin, we introduce a phenomenological set of equations of motion that describe solute and density diffusion in the binary XPFC model. We then apply these to the examination of the process of diffusion limited precipitation from solution. Recent experimental work on the precipitation of gold and silver nanoparticles [1] and on the precipitation of calcium carbonate [2] has demonstrated that the pathway to nucleation can deviate highly from the approximations of Classical Nucleation Theory (CNT). Specifically, both experiments observe spinodal decomposition of the solution prior to nucleation in the solute rich phase. In this chapter, we'll present early findings from our new model that lend support for this dynamical behaviour and, additionally, show that the growth behaviour post-nucleation may be more complex than usual diffusive growth and coarsening typically observed. To conclude we discuss future applications both in the study of precipitation and other areas.

6.0.1 XPFC Dynamics

To examine applications of our improvements to the XPFC model we begin by considering equations of motion. Following [14], we use conservative dynamics for both n(x, t) and c(x, t).

$$\frac{\partial n(x,t)}{\partial t} = M_n \nabla^2 \left(\frac{\delta \beta \Delta \mathcal{F} / \rho_0}{\delta n(x,t)} \right) + \xi_n(x,t), \tag{6.1}$$

$$\frac{\partial c(x,t)}{\partial t} = M_c \nabla^2 \left(\frac{\delta \beta \Delta \mathcal{F} / \rho_0}{\delta c(x,t)} \right) + \xi_c(x,t), \tag{6.2}$$

where M_n and M_c are the solute and density mobilities. The noise terms $\xi_n(x,t)$ and $\xi_c(x,t)$ model thermal fluctuations. Their dynamics follow the fluctuation-dissipation theorem, the theory of which is derived in the Appendix A. These equations of motion are largely phenomenological as, strictly speaking, there is no reason that the local concentration should be conserved. This conservation can be justified in the limit that the total density does not deviate far from the reference. When this is the case we have $c \equiv \rho_B/\rho \approx \rho_B/\rho_0$ which is conserved. For simplicity, we will carry out simulations in this chapter in this limit.

6.1 Multi-Step Nucleation of Nanoparticles in Solution

Many nanoparticle solutions are formed by precipitation from solution and their size distribution (polydispersity index) is of key importance to their application. Therefore, a precise understanding of the kinetic pathway of precipitation is of crucial importance in designing synthesis techniques of highly mono-disperse nanoparticles.

As stated above, recent experimental work has shown that precipitation from a solution can follow a pathway vary different from that assumed by Classical Nucleation Theory (CNT) [1, 2]. CNT assumes that, for binary systems, changes in composition occur simultaneously with changes in order. In contrast, these experimental findings suggest that in certain systems changes in composition can precede changes in order via spinodal decomposition. While there is some dispute about whether or not to call this process a non-classical *nucleation* pathway [41, 42], the observed pathway to precipitation raises several questions about its classification, regardless of semantics.

6.1.1 Classical and Non-classical Nucleation Theories

In CNT, the rate of formation of post-critical can be written as an Arrhenius equation,

$$J = \frac{\partial n^*}{\partial t} = A e^{-\beta \Delta G^{\ddagger}}, \tag{6.3}$$

where,

A is a constant prefactor,

 ΔG^{\ddagger} is the Gibbs free energy of a critical nucleus and,

 n^* is the number of critical nuclei.

Following [43], the probability of nucleation of a droplet of volume V, $f_{nuc}(t)$, is then,

$$f_{nuc}(t) = \left\langle \frac{N_{cry}}{N_{total}} \right\rangle = 1 - e^{-JVt}, \tag{6.4}$$

where N_{cry} and N_{total} are the number of crystalline droplets and the total number of droplets respectively.

CNT assumes that there is a single critical state which is specified by the thermodynamic parameters of the target phase at a critical radius R^* . This naive approach dramatically underestimates the time required to assemble a critical nucleus due to its simplistic parametrization of the kinetic pathway [43–45].

Improvements to CNT can be made to the model by increasing the parameter space describing the nucleation process. Considering both radius and density of the critical nucleus [44] gives good agreement with nucleation of globular proteins, for example. One problem with this approach is the selection of appropriate parameters. There is no guarantee that a finite set parameters will describe the kinetic pathway taken by a nucleus and if we are without a fundamental technique for calculating the chosen parameters we have little way of knowing if our theory is accurate or simply over-fit. In [45], for example, nucleation data is fit to the functional form instead of using calculated or otherwise measured parameters.

Statistical field theories such as the XPFC alloy model can help provide an answer to this problem by taking an unbiased approach to nucleation process within the context of CDFT. The critical state, and entire kinetic pathway, can be examined free of any particular parametrization. The equations of motion can be integrated numerically for an ensemble systems and nucleation details measured from the computed results. Moreover, unlike other numerical approaches to nucleation like molecular dynamics or formal density functional theory, the PFC model can examine nucleation on diffusive time scales.

6.1.2 XPFC Modelling of Precipitation

To construct an appropriate free energy functional for a system analogous to gold nanoparticles studied by Loh *et al.* [1] we consider the structure of its equilibrium phase diagram. Precipitation is indicative of a simple liquid-solid coexistance curve. The presumed presence of spinodal decomposition under certain circumstances indicates that it is a metastable liquid spinodal submerged beneath the liquid-solid coexistance curve [41]. We assume that there must exist conditions under which the spinodal decomposition of the metastable liquid phase occurs more rapidly than nucleation directly from solution (ie., classical nucleation).

Producing a phase diagram in our XPFC model with these characteristics is very similar to modelling a monotectic system with the exception that the spinodal temperature T_c must be low enough to hide the entire liquid spinodal below the coexistance curve. We will also centre the interpolation function $\zeta_{\alpha}(c)$ about c = 1 so that the nanocrystalline solid α is favoured at large concentration. The resulting density-density correlation function for a 2 dimensional hexagonal precipitate would thus be,

$$\tilde{C}_{nn}(k;c) = \exp\left\{-\frac{(c-1)^2}{2\sigma_c^2}\right\} \exp\left\{\frac{T}{T_0}\right\} \exp\left\{-\frac{(k-k_{10})^2}{2\sigma^2}\right\},$$
(6.5)

where,

 σ_c is the width of the interpolation function $\zeta_{\alpha}(c)$, which controls the solvent solubility in the precipitate in this case and,

 k_{10} is the length of the [10] reciprocal lattice vector of the preciptate in equilibrium.

An example phase diagram of a system with sample parameters in equation 6.5 is shown in figure 6.1. The metastable binodal (coexistence) and spinodal curves are depicted below the coexistence curve.



Figure 6.1: Phase Diagram of a Precipitating Solution with hexagonal α phase solid. The free energy parameters are $\eta = 2$, $\chi = 1$, $\omega = 0.3$, $\epsilon_0 = 30$, $T_c = 0.15$ and $c_0 = 0.5$. The parameters for the correlation function from equation 6.5 are $\sigma = 0.8$, $k_{10} = 2\pi$, $T_0 = 1$ and $\sigma_c = 0.5$.

6.1.3 Dynamics of Precipitation: Results and Discussion

We examined the precipitation process in a system that follows the XPFC model with corresponding equilibrium phase diagram in figure 6.1. The situation examined corresponded to a quench to a temperature below the metastable spinodal curve. The spinodal curve marks an inflection point in the liquid free energy meaning the metastable liquid becomes fully unstable and decomposes into regions of differing concentration as a result. A typical microstructure evolution sequence results for a typical quench of a uniform solution of c = 0.3from the liquid phase to a temperature $T/T_0 = 0.07$ is shown in figure 6.2. Frames (a)-(c) show the initial deeposition of the liquid, once below the spinodal temperature, into two regions of high and low compositions. Frames (d)-(f) show that once the concentration in the solute-rich regions of the decomposed liquid occurs, nucleation of the solid phase begins to occur in these confined liquid volumes. Once nucleated, the solid regions start/continue to grow at the expense of the liquid phase. Finally, in frames (g)-(i), the nucleated nanoparticles undergo growth and coarsening. This simulation is a typical example where the nucleation of precipitates in preceded by spinodal decomposition, which is consistent with the the experimental findings mentioned above for the nanoparticle and calcium carbonate systems [1, 2]. While one simulation sequence is show here, this scenario was typical of all ensembles we ran and from which we gathered statistics for the data shown below. As mentioned above, we observed that once any solute-rich regions crystallize, their growth is accelerated at the expense of uncrystallized solute-rich regions. We refer to this phenomenon as *sacrificial* growth (frames (d)-(f) in figure 6.2)).







Figure 6.2: Various stages of precipitation of nanoparticles from solution. All thermodynamic parameters are shared with figure 6.1. The initial condition is a uniform solution quenched abruptly to T = 0.07. The initial condition has concentration c = 0.3 and relative density is set to n = 0.05. Mobilities M_n and M_c are set to 1 and W_c is set to 3.0. Numerical parameters are grid spacing $\Delta x = 0.125$ on a 1024 by 1024 lattice with time step size $\Delta t = 0.0025$. Sub-figures (a) - (c) show spinodal decomposition of the liquid into solute right and solute poor regions. Sub-figures (d) - (f) show nucleation of the solid and solid growth at the expense of liquid regions. The remaining sub-figures show only nanoparticle growth and coarsening.

To quantify the phenomenon shown in figure 6.2, we examine the mean radius $\langle R(t) \rangle$ of solute-rich domains as a function of time, and average the results over an ensemble of 120 quenches analogous to those shown in figure 6.2. Here we define the mean radius as the square root of the mean area,

$$\langle R(t) \rangle = \sqrt{\langle A(t) \rangle}.$$
 (6.6)

The results obtained are not expected to depend on the precise definition of R(t).

In purely diffusive growth the mean radius should scale as $\langle R(t) \rangle \sim t^{1/2}$, while at the late stages of growth, where coarsening occurs, the growth rate is expected to follow $\langle R(t) \rangle \sim t^{1/3}$ dynamics. In figure 6.3 we plot $\langle R(t) \rangle$ on a log-log graph. Lines corresponding to the diffusive growth exponent are also drawn for comparison to numerical results. The data show that for early times, crystalline regions grow at a hyper-diffusive rate.



Figure 6.3: Droplet growth $\langle R(t) \rangle$ Versus time. Black line show $\sim t^{1/2}$ growth. Insets show early hyper-diffusive growth of crystalline nanoparticles and late stage hypo-diffusive growth.

This decays to hypo-diffusive after uncrystallized regions have disappeared and coarsening takes over the kinetics of precipitation.

During sacrificial growth period referred to above, we observe that nucleation is suppressed in the remaining uncrystallized solute-rich regions. When both crystallized and uncrystallized solute-rich regions exist, solute is segregated into crystallized regions because of the difference in chemical potential. Constricted by surface tension and deprived of solute, these remaining droplets have a far slower nucleation rate (thermodynamic driving force) than when no crystallized regions exist. This can be seen more quantitatively by examining the fraction of uncrystallized droplets versus time. This is shown in figure 6.4 for the case corresponding to the data in figure 6.2. At $\sim 50\%$ crystallization, we see a pronounced reduction in the nucleation rate as the diffusive process of sacrificial growth dominates, consistent with our expected hypothesis above.



Figure 6.4: Fraction of uncrystallized droplets in time.

6.2 Outlook and Future Applications

The results presented here describe the behaviour of a quench followed by multi-step precipitation process of relevance to the precipitation of gold nano-particles observed in recent experiments. It is noteworthy that the predicted results were done within a single framework and set parameters corresponding to the improved XPFC alloy model introduced in this thesis. The dynamical results shown here point to a richness in the landscape of kinetic pathways to precipitation. One direction for future application of the improved XPFC framework is to explore more of this landscape and to determine the effect of quench parameter and solution concentration in nucleation kinetics, as well as the polydispersity of precipitated particles, key features of interest to experimental investigations of this topic.

Chapter 7

Conclusion

The goal of the current research was threefold. The first two goals were to present two extensions to the binary XPFC theory. The first extension we presented was the addition of an enthalpy of mixing to account for non-ideal mixing and second was a general phenomenology for modelling density pair correlation functions. In Chapter 5 we saw these two extensions derived in detail and explored the new landscape of equilibrium phase diagrams they result in. We also noted that metastable features of the phase diagram can be reproduced such a submerged metastable liquid spinodal below the eutectic point in a eutectic material.

The final goal was to apply these improvements to the study of multi-step nucleation pathways in precipitation. In Chapter 6 we constructed a simplified model of precipitation and showed that a submerged metastable liquid spinodal can indeed result in a multi-step nucleation pathway like those observed experimentally in silver and gold nanoparticles [1].

Beyond the study of precipitation there are other processes in which our improvements to the XPFC alloy model may prove insightful. Investigating the effects of elasticity on monotectic and syntectic nucleation and growth are one clear direction that can now be studied given the capacity to model the equilibrium phase diagrams and kinetics of these materials. As previously noted, the problem of stability of nanocrystalline binary alloys is another topic of importance that has been shown to depend on the enthalpy of mixing of the system [37].

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 [46]. 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 with a ϕ^4 theory and Time Dependent Density Functional Theory (TDDFT) with a general Helmholtz free energy.

¹For considerations far from equilibrium see [47-49]

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,

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

Where, **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,

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

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

This assumption is justified by positing that the stochastic driving force is the aggregated affect of many random microscopic processes that satisfy the central limit theorem so we may assume a Gaussian form. 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, $\mathbf{a}(r,t) = \mathbf{a}_{eq}(r) + \hat{\mathbf{a}}(r,t)$.

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

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

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

We can formally solve our linearized equation of motion,

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

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

$$\left\langle \hat{\mathbf{a}}(r,t)\hat{\mathbf{a}}^{\dagger}(r',t') \right\rangle = e^{\mathbf{M}(r,r_{1})t} * \left\langle \hat{\mathbf{a}}(r_{1},0)\hat{\mathbf{a}}^{\dagger}(r_{2},0) \right\rangle * e^{\mathbf{M}^{\dagger}(r',r_{2})t'} + \int_{0}^{t} \int_{0}^{t'} d\tau d\tau' e^{\mathbf{M}(r,r_{1})(t-\tau)} * \left\langle \boldsymbol{\xi}(r_{1},0)\boldsymbol{\xi}^{\dagger}(r_{2},0) \right\rangle * e^{\mathbf{M}^{\dagger}(r',r_{2})(t'-\tau')}.$$
(A.7)

To evaluate the equilibrium correlation function we take the limit as each time goes to infinity together $(t = t' \to \infty)$. It is important to note that every eigenvalue of **M** must be negative for our solution to decay to equilibrium in the long time limit (eg. $lim_{t\to\infty}\hat{\mathbf{a}}(r,t) = 0$) and as such the first term in equation A.7 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 from equation A.3 and evaluating the delta function.

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

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

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

As we can see from equation A.9, near equilibrium the noise correlation function is a simple function of the pair correlation function, $\Gamma(r, r')$ and the linearized transport coefficient $\mathbf{M}(r, r')$.

As a simple check we apply our result to the original work of Einstein. Recall that in
the over damped limit the equation of motion for the velocity for a 1 dimensional Brownian particle is,

$$\frac{\partial v(t)}{\partial t} = -\gamma v(t) + \xi(t). \tag{A.10}$$

This equation is alread linear so we can pick off the linearized transport coefficient as $-\gamma$. The pair correlation function in equilibrium is given by equipartition theorem as,

$$\left\langle v^2 \right\rangle = \frac{k_b T}{m}.\tag{A.11}$$

Simply applying equation A.9 we find,

$$\langle \xi(t)\xi(t')\rangle = 2\frac{k_b T\gamma}{m}\delta(t-t'), \qquad (A.12)$$

As expected. Satisfied that equation A.9 reduces to the correct result for the base case we proceed to examine two examples that are guininely nonlinear field theories.

A.2 Example 1 - Model A

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

$$\beta \mathcal{F}[\phi] = \int dr \left\{ \frac{1}{2} |\nabla \phi(x)|^2 + \frac{r}{2} \phi^2(x) + \frac{u}{4!} \phi^4(x) + h(x)\phi(x) \right\}$$
(A.13)

$$\frac{\partial \phi(x,t)}{\partial t} = -\Gamma\left(\frac{\delta\beta\mathcal{F}[\phi]}{\delta\phi(x)}\right) + \xi(x,t) \tag{A.14}$$

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

$$\langle \xi(x,t) \rangle = 0 \tag{A.15}$$

$$\langle \xi(x,t)\xi(x',t')\rangle = L(x-x')\delta(t-t') \tag{A.16}$$

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.

$$\mathcal{P}_{eq}[\phi] = \frac{e^{-\beta \mathcal{F}[\phi]}}{\mathcal{Z}[h(x)]} \tag{A.17}$$

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

$$\mathcal{Z}[h(x)] = \int \mathcal{D}[\phi] e^{-\beta \mathcal{F}[\phi]}$$
(A.18)

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

$$\frac{1}{\mathcal{Z}[h]} \frac{\delta^n \mathcal{Z}[h]}{\delta h(x_1) \dots \delta h(x_n)} = \langle \phi(x_1) \dots \phi(x_n) \rangle \tag{A.19}$$

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.

$$\beta \mathcal{F}[\Delta \phi] = \int dr \left\{ \frac{1}{2} \Delta \phi(x) \left(r - \nabla^2 + \frac{u}{2} \phi_0^2 \right) \Delta \phi(x) - h(x) \Delta \phi(x) \right\}$$
(A.20)

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,

$$\mathcal{Z}[\tilde{h}(k)] \propto \exp\left\{\frac{1}{2} \int dk \, \frac{h(k)h^*(k)}{r + \frac{u}{2}\phi_0^2 + |k|^2}\right\}.$$
(A.21)

The pair correlation function, $\langle \Delta \tilde{\phi}(k) \Delta \tilde{\phi}^*(k) \rangle$, is then computed using equation A.19.

$$\left\langle \Delta \tilde{\phi}(k) \Delta \tilde{\phi}^*(k') \right\rangle = \frac{2\pi \delta(k+k')}{r + \frac{u}{2}\phi_0^2 + |k|^2} \tag{A.22}$$

A.2.2 The Equation of Motion Route

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

$$\frac{\partial\phi}{\partial t} = -\Gamma\left((r - \nabla^2)\phi(x, t) + \frac{u}{3!}\phi^3(x, t)\right) + \xi(x, t),\tag{A.23}$$

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.

$$\frac{\partial \Delta \tilde{\phi}(k,t)}{\partial t} = -\Gamma \left((r + \frac{u}{2}\phi_0 + |k|^2) \Delta \tilde{\phi}(k,t) \right) + \xi(x,t)$$
(A.24)

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

$$M(k,k') = -\Gamma\left(\left(r + \frac{u}{2}\phi_0 + |k|^2\right)\right)\delta(k+k')$$
(A.25)

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

$$L(k,k') = 2\Gamma\delta(k+k'), \tag{A.26}$$

Or equivalently,

$$L(x, x') = 2\Gamma\delta(x - x'). \tag{A.27}$$

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,

$$\frac{\partial \rho(r,t)}{\partial t} = D_0 \nabla \cdot \left[\rho(r,t) \nabla \left(\frac{\delta \mathcal{F}[\rho]}{\delta \rho} \right) \right] + \xi(r,t)$$
(A.28)

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').

$$\langle \xi(r,t) \rangle = 0 \tag{A.29}$$

$$\langle \xi(r,t)\xi(r',t')\rangle = L(r,r')\delta(t-t') \tag{A.30}$$

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.

$$\mathcal{F}[\rho] = \mathcal{F}_{eq} + \beta \int dr \left(\frac{\delta \mathcal{F}[\rho]}{\delta \rho(r)} \right) \Big|_{\rho_{eq}} \Delta \rho(r) + \frac{1}{2} \int dr \int dr' \Delta \rho(r) \left(\frac{\delta^2 \mathcal{F}[\rho]}{\delta \rho(r) \delta \rho(r')} \right) \Big|_{\rho_{eq}} \Delta \rho(r')$$
(A.31)

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.

$$\mathcal{F}[\rho] = \frac{1}{2} \int dr \int dr' \Delta \rho(r) \Gamma^{-1}(r, r') \Delta \rho(r')$$
(A.32)

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,

$$\langle \Delta \rho(r) \Delta \rho(r') \rangle = \Gamma(r, r')$$
 (A.33)

A.3.2 Linearing the equation of motion

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

$$\frac{\partial \Delta \rho(r,t)}{\partial t} = D_0 \nabla \cdot \left[\rho_{eq}(r) \nabla \left(\Gamma^{-1}(r,r') * \Delta \rho(r',t) \right) \right] + \xi(r,t)$$
(A.34)

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

$$M(r, r') = D_0 \nabla \cdot \left[\rho_{eq}(r) \nabla \left(\Gamma^{-1}(r, r') \right) \right]$$
(A.35)

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').

$$L(r,r') = -2D_0 \nabla \cdot (\rho_{eq}(r)\nabla) \,\delta(r-r') \tag{A.36}$$

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,

$$\mathcal{Z}[h(x)] = \int \mathcal{D}[\phi] \exp\left\{-\int dx \int dx' \left[\frac{1}{2}\phi(x)\mathbf{K}(x,x')\phi(x')\right] + \int dx \left[h(x)\phi(x)\right]\right\}.$$
 (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 [50] and are repeated here for the convenience of the reader.

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

$$\mathcal{Z}[\mathbf{h}] = \int \prod_{i} dx_{i} \exp\left\{-\frac{1}{2} \sum_{i} \sum_{j} x_{i} \mathbf{K}_{ij} x_{j} + \sum_{i} h_{i} x_{i}\right\},\tag{B.2}$$

For which the solution is,

$$\mathcal{Z}[\mathbf{h}] = \sqrt{\frac{2\pi}{\det(\mathbf{K})}} \exp\left\{\frac{1}{2}\sum_{i}\sum_{j}h_{i}\mathbf{K}_{ij}^{-1}h_{j}\right\}.$$
(B.3)

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

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

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

$$\int dx' \mathbf{K}(x, x') \mathbf{K}^{-1}(x', x'') = \delta(x - x'').$$
(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 we often change variables from ρ_A and ρ_B to nand c. This change of variable is helpful in identifying the results of the PFC theory with established results in the field as concentration and total density are more commonly used in the field of material science. Computing the bulk terms (ie., $\Delta \mathcal{F}_{mix}[n, c]$ and $\Delta \mathcal{F}_{id}[n]$ from equation 4.6 and 4.5 is a matter of substitution and simplification but computing the change of variables for excess free energy 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,

$$\Delta \rho_A * \rho_0 C_{AA} * \Delta \rho_A + 2\Delta \rho_A * \rho_0 C_{AB} * \Delta \rho_B + \Delta \rho_B * \rho_0 C_{BB} * \Delta \rho_B$$
(C.1)
= $n * C_{nn} * n + 2n * C_{nc} * \Delta c + \Delta c * C_{cc} * \Delta c,$

Where f * C * g is shorthand for,

$$\int dr \int dr' f(r)C(r,r')g(r).$$
 (C.2)

We begin by rewriting $\Delta \rho_B$,

$$\Delta \rho_B = \rho c - \rho_0 c_0$$
$$= \rho c - \rho c_0 + \rho c_0 - \rho_0 c_0$$
$$= \Delta \rho c + \rho_0 \Delta c,$$

And likewise $\Delta \rho_A$,

$$\Delta \rho_A = \rho(1-c) - \rho_0(1-c_0)$$
$$= \Delta \rho(1-c) - \rho_0 \Delta c.$$

With those forms established, we demonstrate the general process by computing one term in equation C.1: $\Delta \rho_B * C_{BB} * \Delta \rho_B$. We begin by expanding $\Delta \rho_B$

$$\Delta \rho_B * C_{BB} * \Delta \rho_B = (\Delta \rho c + \rho_0 \Delta c) * C_{BB} * (\Delta \rho c + \rho_0 \Delta c)$$

= $\Delta \rho c * C_{BB} * (\Delta \rho c)$
+ $\rho_0 \Delta c * C_{BB} * (\Delta \rho c)$
+ $\rho_0 (\Delta \rho c) * C_{BB} * \Delta c$
+ $\rho_0^2 \Delta c * C_{BB} * \Delta c.$ (C.3)

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,

$$\Delta \rho c C_{BB} * \Delta \rho c = \Delta \rho(r) c(r) \int dr' C_{BB}(r - r') \Delta \rho(r') c(r')$$
$$\approx \Delta \rho(r) c^2(r) \int dr' C_{BB}(r - r') \Delta \rho(r'). \tag{C.4}$$

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.3 as,

$$\Delta \rho_B C_{BB} * \Delta \rho_B = \Delta \rho \left(c^2 C_{BB} \right) * \Delta \rho$$

$$+ \rho_0 \Delta c \left(c C_{BB} \right) * \Delta \rho c$$

$$+ \rho_0 \Delta \rho \left(c C_{BB} \right) * \Delta c$$

$$+ \rho_0^2 \Delta c C_{BB} * \Delta c.$$
(C.5)

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

$$C_{nn} = \rho_0 \left(c^2 C_{BB} + (1-c)^2 C_{AA} + 2c(1-c) C_{AB} \right)$$
(C.6)

$$C_{nc} = C_{cn} = \rho_0 \left(c \, C_{BB} - (1 - c) \, C_{AA} + (1 - 2c) \, C_{AB} \right) \tag{C.7}$$

$$C_{cc} = \rho_0 \left(C_{BB} + C_{AA} - 2C_{AB} \right)$$
(C.8)

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

Appendix D

Algorithms

This Appendix presents a general approach to integrating nonlinear stochastic partial differential equations. An integration scheme for the binary XPFC equations of motion is presented as a particular application.

D.1 Semi-Implicit Spectral Methods for Systems of First Order PDEs

To start, we consider the general case of time stepping a system of non-linear first-order PDE's. Specifically, we are going to look at a set of stochastic non-linear PDE's,

$$\frac{\partial \overline{\psi}(x,t)}{\partial t} = \mathcal{G}\left[\overline{\psi}(x,t)\right] + \overline{\xi}(x,t), \tag{D.1}$$

Where,

 $\overline{\psi}(x,t)$ is a vector of our fields of interest (ex: (n, c)) and we've used $\overline{\cdot}$ to denote a vector,

 \mathcal{G} is some driving force for our fields and,

 $\overline{\xi}(x,t)$ is the stochastic driving force with variances given by a generalized Einstein relationship.

To develop a semi-implicit method we start by splitting the functional \mathcal{G} into linear and non-linear components,

$$\frac{\partial \psi(x,t)}{\partial t} = \overline{\overline{\mathcal{L}}}(x,x') * \overline{\psi}(x',t) + \mathcal{NL}\left[\overline{\psi}\right] + \overline{\xi}(x,t)$$
(D.2)

Where,

- $\overline{\overline{\mathcal{L}}}$ denotes the linear contribution and $\overline{\overline{\cdot}}$ denotes a matrix,
- * matrix multiplication and integration over the repeated variable and,
- \mathcal{NL} is the non-linear component of the the functional \mathcal{G} .

In a special set of PDE's the kernel $\overline{\overline{\mathcal{L}}}$ is translationally invariant. When this is the case, the convolution theorem can be used to write the linear functional as an algebraic product in Fourier space.

$$\frac{\partial \psi(k,t)}{\partial t} = \overline{\overline{\mathcal{L}}}(k)\overline{\psi}(k,t) + \mathcal{F}\left[\mathcal{NL}\left[\overline{\psi}\right]\right] + \overline{\xi}(k,t) \tag{D.3}$$

Where, $\mathcal{F}[\cdot]$ denotes a Fourier transform. We now consider our fields on a discrete grid with Δk spacing between Fourier modes and Δt spacing between times such that we might define,

$$\overline{\psi}_{j}^{n} \equiv \overline{\psi}(j\Delta k, n\Delta t). \tag{D.4}$$

To develop a generic approach to time stepping we consider evaluating our field between grid points in time (eg. at $\overline{\psi}_j^{n+\gamma}$ where $\gamma \in [0, 1]$).



Figure D.1: Schematic of time step

To first order we can approximate this value as a linear interpolation of the value at nand the value at n + 1.

$$\overline{\psi}_j^{n+\gamma} = (1-\gamma)\overline{\psi}_j^n + \gamma\overline{\psi}_j^{n+1} \tag{D.5}$$

We can also approximate the time derivative $\partial_t \overline{\psi}$ as,

$$\frac{\partial \overline{\psi}}{\partial t} = \frac{\overline{\psi}_j^{n+1} - \overline{\psi}_j^n}{\Delta t} + \frac{1 - 2\gamma}{2} \frac{\partial^2 \overline{\psi}}{\partial t^2} \Delta t + \dots$$
(D.6)

Deriving different integration schemes is done by evaluating the equation of motion for various values of γ . For example, to recover simple Euler stepping we can evaluate the equation of motion with $\gamma = 0$. The semi-implicit scheme relays on evaluating the non-linear component of the equation of motion at $\gamma = 0$ while the rest of the equation is evaluated at $\gamma = 1$. In this treatment we will evaluate the non-linear component at $\gamma = 0$ but we will leave the rest of the equation unevaluated so that γ can be choosen freely at the end. Substituting these results into equation of motion we find the following result,

$$\frac{\overline{\psi}_{j}^{n+1} - \overline{\psi}_{j}^{n}}{\Delta t} + \frac{1 - 2\gamma}{2} \frac{\partial^{2} \overline{\psi}}{\partial t^{2}} \Delta t = \overline{\mathcal{L}} \left((1 - \gamma) \overline{\psi}_{j}^{n} + \gamma \overline{\psi}_{j}^{n+1} \right) + \mathcal{F} \left[\mathcal{NL} \left[\overline{\psi}_{j}^{n} \right] \right] + \overline{\xi}_{j}^{n+\gamma}$$
(D.7)

Separating t = n + 1 terms on the left and t = n terms on the right,

$$\left(\mathbb{1} - \Delta t\gamma \overline{\overline{\mathcal{L}}}\right) \overline{\psi}_{j}^{n+1} = \left(\mathbb{1} + \Delta t(1-\gamma)\overline{\overline{\mathcal{L}}}\right) \overline{\psi}_{j}^{n} + \Delta t \mathcal{F} \left[\mathcal{NL}\left[\overline{\psi}_{j}^{n}\right]\right] + \Delta t \overline{\xi}_{j}^{n+\gamma} - \frac{1-2\gamma}{2} \frac{\partial^{2} \overline{\psi}}{\partial t^{2}} \Delta t^{2}$$

$$(D.8)$$

Finally, we can isolate $\overline{\psi}_{j}^{n+1}$ by left multiplying by $\left(\mathbb{1} - \gamma \Delta t \overline{\overline{\mathcal{L}}}\right)^{-1}$,

$$\overline{\psi}_{j}^{n+1} = \left(\mathbb{1} - \Delta t\gamma \overline{\overline{\mathcal{L}}}\right)^{-1} \left(\left(\mathbb{1} + \Delta t(1-\gamma)\overline{\overline{\mathcal{L}}}\right) \overline{\psi}_{j}^{n} + \Delta t\mathcal{F}\left[\mathcal{NL}\left[\overline{\psi}_{j}^{n}\right]\right] + \Delta t\overline{\xi}_{j}^{n+\gamma} - \frac{1-2\gamma}{2} \frac{\partial^{2}\overline{\psi}}{\partial t^{2}} \Delta t^{2} \right)$$
(D.9)

The final term on the right hand side emphasizes that if we choose $\gamma = 1/2$ we will have a algorithm that is accurate to second order in time (this is a kind of Crank-Nicolson method). If we choose $\gamma = 1$ we recover a semi-implicit method.

D.2 Applications to the Binary XPFC Model

The binary XPFC model is a good example of a system of first order PDE's like those discussed in the previous discussion. The equations of motion in real space are,

$$\frac{\partial c(x,t)}{\partial t} = M_c \nabla^2 \left((\omega \epsilon - W_c \nabla^2) c + \omega (1+n) \frac{\partial \Delta F_{mix}(c)}{\partial c} - \frac{1}{2} n \left(\frac{\partial C_{eff}}{\partial c} * n \right) \right) + \xi_c(x,t)$$
(D.10)

$$\frac{\partial n(x,t)}{\partial t} = M_n \nabla^2 \left(\left(1 - C_{eff} *\right) n - \frac{\eta}{2} n^2 + \frac{\chi}{3} n^3 + \omega \Delta F_{mix} \right) + \xi_n(x,t)$$
(D.11)

Where,

 ΔF_{mix} is the ideal free energy of mixing $c \log\left(\frac{c}{c_0}\right) + (1-c) \log\left(\frac{1-c}{1-c_0}\right)$

With reference to the formalism we've already established our task is now to separate out the linear and non-linear components of these equations of motion. To do this, we expand the concentration and density around constant references c_* and n_* . Doing so leads to an expression of $\overline{\overline{\mathcal{L}}}$,

$$\overline{\overline{\mathcal{L}}} = \begin{bmatrix} -M_c k^2 \left(\omega \left(\epsilon - \frac{1}{c_*^2 - c_*} \right) + W_c k^2 \right) & -M_c k^2 \omega \log \left(\frac{(c_0 - 1)c_*}{c_0(c_* - 1)} \right) \\ -M_n k^2 \omega \log \left(\frac{(c_0 - 1)c_*}{c_0(c_* - 1)} \right) & -M_n k^2 \left(1 - C_{eff} |_{c_*}(k) \right) \end{bmatrix}$$
(D.12)

Important to note in the structure of $\overline{\mathcal{L}}$ is that it is diagonal in the limit of small ω . In the approximation that it is diagonal, previous algorithms for the binary XPFC model are recovered where, to linear order, concentration and density may be independently integrated. Another interesting case is that of $M_n = M_c$ where the matrix is symmetric and thus has orthogonal eigenvectors. We proceed by considering this simplified case where the concentration and density are weakly coupled at the linear order and may be integrated seperately.

D.2.1 Algorithm for the Concentration c(x,t)

The concentration equation of motion is,

$$\partial_t \tilde{c} = -M_c k^2 \left(\omega \epsilon \tilde{c} + W_c k^2 \tilde{c} + \mathcal{F} \{ NL(c) \} \right) + \tilde{\xi}.$$
 (D.13)

Where NL(c) is the non-linear term and ξ is the drive noise.

$$NL(c) = \omega(1+n) \left(\ln\left(\frac{c}{c_0}\right) - \ln\left(\frac{1-c}{1-c_0}\right) \right) - \frac{1}{2}n \left(C_{eff}^n * n\right)$$
(D.14)

Now if we think about the solution to this equation at time $t^{n+\xi}$ time between t^n and t^{n+1} we express the solution as an interpolation between the solutions at the earlier and later times.

$$\tilde{c}_{k}^{n+\xi} = (1-\xi)\tilde{c}_{k}^{n} + \xi\tilde{c}_{k}^{n+1}$$
(D.15)

We also find that we can express the time derivative as finite difference plus a correction term.

$$\partial_t \tilde{c} = \frac{\tilde{c}_k^{n+1} - \tilde{c}_k^n}{\Delta t} + \frac{1 - 2\xi}{2} \frac{\partial^2 \tilde{c}}{\partial t^2} \Delta t + \dots$$
(D.16)

Using each of these ideas we can rewrite the equation of motion completely, with the exception of the nonlinear term, which we evaluate a the time t^n in keeping with many of the semi-implicit methods published.

$$\frac{\tilde{c}_k^{n+1} - \tilde{c}_k^n}{\Delta t} + \frac{1 - 2\xi}{2} \frac{\partial^2 \tilde{c}}{\partial t^2} \Delta t = \Lambda(k) \left[(1 - \xi) \tilde{c}_k^n + \xi \tilde{c}_k^{n+1} \right] - M_c k^2 \mathcal{F}\{NL(c^n)\} + \tilde{\xi}_k^n \quad (D.17)$$

where,

$$\Lambda(k) = -M_c k^2 \left(\omega \epsilon + W_c k^2\right). \tag{D.18}$$

Moving future times to the left and past times to the right we find,

$$\tilde{c}_k^{n+1} = \hat{P}\tilde{c}_k^n + \hat{Q}\mathcal{F}\{NL(c^n)\}_k + \hat{L}\tilde{\xi}_k^n + \frac{2\xi - 1}{2}\frac{\partial^2 \tilde{c}}{\partial t^2}\Delta t^2$$
(D.19)

Where the operators \hat{P} , \hat{Q} and \hat{L} are,

$$\hat{P} = 1 + \frac{\Delta t \Lambda(k)}{1 - \xi \Delta t \Lambda(k)} \tag{D.20}$$

$$\hat{Q} = -\frac{M_c k^2 \Delta t}{1 - \Delta t \xi \Lambda(k)} \tag{D.21}$$

$$\hat{L} = \frac{\Delta t}{1 - \Delta t \xi \Lambda(k)} \tag{D.22}$$

Different values of ξ lead to different integration schemes. The $\xi = 0$ corresponds to euler time stepping in fourier space, while $\xi = 1$ yields the often used semi-implicit fourier method. There is an import case in which we choose $\xi = 1/2$ where the algorithm becomes accurate to second order in time. This is the Crank-Nicholson fourier method.

D.2.2 Algorithm for the Total Density n(x,t)

We can develop an algorithm for the equation of motion for the total density in the same way that we did with concentration. The equation of motion for the total density in fourier space looks like,

$$\partial_t \tilde{n}(k,t) = -M_n k^2 \left(\tilde{n} + \mathcal{F}\{NL(n)\} \right) + \tilde{\xi}$$
(D.23)

Where now the nonlinear term is,

$$NL(n) = -\eta \frac{n^2}{2} + \chi \frac{n^3}{3} + \Delta f_{mix}(c) - C_{eff}^n * n$$
 (D.24)

Note that the convolution term is nonlinear because of an implicit dependance on the concentration. Now, in principle, you could compute that pair correlation function every time step for a more accurate linear propagator, but here we will not consider that.

Here again, we find the same structure as previously:

$$\tilde{n}_k^{n+1} = \hat{P}\tilde{n}_k^n + \hat{Q}\mathcal{F}\{NL(n^n)\}_k + \hat{L}\tilde{\xi}_k \tag{D.25}$$

Here, the operators \hat{P} , \hat{Q} and \hat{L} are:

$$\hat{P} = 1 - \frac{\Delta t M_n k^2}{1 + \xi \Delta t M_n k^2} \tag{D.26}$$

$$\hat{Q} = -\frac{M_c k^2 \Delta t}{1 + \Delta t \xi M_n k^2} \tag{D.27}$$

$$\hat{L} = \frac{\Delta t}{1 + \Delta t \xi M_n k^2} \tag{D.28}$$

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