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

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Abstract

Abstract goes here

Dedication

To mum and dad

Declaration

I declare that..

Acknowledgements

I want to thank...

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2.1 Introduction

To describe the process of solidification we will be using the phase field crystal theory. Phase field crystal theory is a type of classical density functional theory. Work by Youssof and Ramakrishnan[1] and Evans[cite] extended the classical density functional theory of inhomogeneous fluids to the phenomena of solidification in pure materials. While the phase field crystal theory was first produced through purely phenomenological means as a variation on the Swift-Hohenburg model[cite], later work showed that the model can be seen as simplification of the Youssof and Ramakrishnan work on the density functional theory of freezing [cite].

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

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

2.2 Deriving the Intrinsic Free Energy Functional

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

$$\rho(x) = \sum_{i=1}^{N} \delta^{(3)}(x - x_i).$$ (2.1)

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

$$f(\mathbf{r}^N, \mathbf{p}^N, N) = \frac{1}{\Xi[\psi(r)]} \frac{\exp\left\{-\beta\mathcal{H}(\mathbf{r}^N, \mathbf{p}^N) + \beta \int dr \psi(r)\rho(r)\right\}}{h^{3N} N!}.$$ (2.2)

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

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

$$\Xi[\psi(r)] = \sum_{N=0}^{\infty} \frac{1}{h^{3N} N!} \int d\mathbf{r}^N d\mathbf{p}^N \exp\left\{ -\beta \mathcal{H}(\mathbf{r}^N, \mathbf{p}^N) + \beta \int dr \psi(r) \rho(r) \right\}. \tag{2.3}$$

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

$$\Omega[\psi(r)] = -k_b T \ln \Xi[\psi(r)] \tag{2.4}$$

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

$$\frac{\delta \Omega[\psi]}{\delta \psi(r)} = -\langle \rho(r) \rangle \equiv \rho_1(r), \tag{2.5}$$

And the pair correlation function can be expressed as,

$$\frac{\delta^2 \Omega[\psi]}{\delta \psi(r) \delta \psi(r')} = -\beta \langle (\rho(r) - \rho_1(r))(\rho(r') - \rho_1(r')) \rangle. \tag{2.6}$$

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

$$\frac{\delta \rho_1(r)}{\delta \psi(r')} = \beta \langle (\rho(r) - \rho_1(r))(\rho(r') - \rho_1(r')) \rangle, \tag{2.7}$$

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

$$\mathcal{F}[\rho_1(x)] = \Omega[\psi[\rho]] + \int dr \rho_1(r) \psi(r). \tag{2.8}$$

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

$$\frac{\delta \Omega[\rho]}{\delta \rho(r)} = 0. \tag{2.9}$$

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

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

$$\mathcal{F}[\rho] = \mathcal{F}_{id}[\rho] + \mathcal{F}_{ex}[\rho] \tag{2.10}$$

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

$$\mathcal{F}_{id}[\rho] = k_b T \int dr \rho(r) \ln\left(\Lambda^3 \rho(r)\right) - \rho(r). \tag{2.11}$$

Where, Λ, is the thermal deBroglie wavelength,

$$\Lambda = \sqrt{\frac{h^2}{2\pi m k_b T}}. \tag{2.12}$$

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

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

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

$$\mathcal{F}_{ex}[\rho] \approx \mathcal{F}_{ex}[\rho_0] + \int dr \left.\frac{\delta \mathcal{F}_{ex}}{\delta \rho(r)}\right|_{\rho_0} \Delta\rho(r) + \frac{1}{2}\int dr dr' \Delta\rho(r) \left.\frac{\delta^2 \mathcal{F}_{ex}}{\delta \rho(r)\delta\rho(r')}\right|_{\rho_0} \Delta\rho(r') + ... \quad . \tag{2.13}$$

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

$$\frac{\delta^n \mathcal{F}_{ex}[\rho]}{\delta\rho(r_1)...\delta\rho(r_n)} = -\beta C^n(r_1, ..., r_n). \tag{2.14}$$

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

$$\left.\frac{\delta F_{ex}}{\delta\rho}\right|_{\rho_0} = \mu_0^{ex} = \mu_0 - k_b T \ln\left(\Lambda^3 \rho_0\right). \tag{2.15}$$

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

$$\Delta \mathcal{F}[\rho] = k_b T \int dr \rho(r) \ln \left(\frac{\rho(r)}{\rho_0} \right) - (1 - \beta \mu_0) \Delta \rho(r) - \frac{1}{2} \Delta \rho(r) \int dr' C^{(2)}(r, r') \Delta \rho(r') \qquad (2.16)$$

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

$$\rho_1(x) = \rho_0 \exp \left\{ -\beta \phi(r) + \int dr' \Delta \rho_1(r') C^{(2)}(r, r') \right\} \qquad (2.17)$$

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

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Chapter 3

Dynamic Density Functional Theory

3.1   Introduction

Appendix A

Noise in Nonlinear Langevin Equations

When using Langevin equations to study non-equilibrium statistical mechanics the noise strength can be linked to the transport coefficients through a generalization of the Einstein relation. The generalization was first developed by Onsager and Machlup [3]. The typical strategy for deriving such a relationship is to evaluate the equilibrium pair correlation function by two separate methods: the equilibrium partition functional and the equation of motion[1].

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

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

A.1 Generalized Einstein Relations in an Arbitrary Model

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

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

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

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

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

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

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

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

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

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

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

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.

$$\left\langle \hat{\mathbf{a}}(r,t)\hat{\mathbf{a}}^\dagger(r',t') \right\rangle = e^{\mathbf{M}(r,r_1)t} * \left\langle \hat{\mathbf{a}}(r_1,0)\hat{\mathbf{a}}^\dagger(r_2,0) \right\rangle * e^{\mathbf{M}^\dagger(r',r_2)t'}$$
$$+ \int_0^t \int_0^{t'} d\tau d\tau' \, e^{\mathbf{M}(r,r_1)(t-\tau)} * \left\langle \boldsymbol{\xi}(r_1,0)\boldsymbol{\xi}^\dagger(r_2,0) \right\rangle * e^{\mathbf{M}^\dagger(r',r_2)(t'-\tau')} \tag{A.7}$$

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 $\mathbf{M}$ 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 our dynamic correlation function won't contribute to the equilibrium pair correlation. This is as we might expect as the first term holds the contributions to the dynamic correlation function from the initial conditions. The second term can be evalutated by substituting the noise correlation and evaluating the delta function.

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

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

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

A.2   Example 1 - Model A

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

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

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

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

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

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

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

A.2.1 The partition function route

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

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

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

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

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

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

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

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

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

Computing the Pair correlation function in the Gaussian approximation

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

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

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

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

A.2.2   The Equation of Motion Route

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

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

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

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

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

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

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

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

Or equivalently,

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

A.3   Example 2 - Time Dependent Density Functional Theory

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

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

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

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

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

A.3.1   Pair Correlation from the Partition Functional

Just like with the phi^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.

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

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

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

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

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

A.3.2 Linearing the equation of motion

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

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

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

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

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

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

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Appendix B

Gaussian Functional Integrals

Gaussian Functional Integrals

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

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

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 [**Kardar**] 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,

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

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

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

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

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

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

Appendix C

Binary Correlation Functions

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

$$\delta\rho_A\, C_{AA} * \delta\rho_A + \delta\rho_A\, C_{AB} * \delta\rho_B + \delta\rho_B\, C_{BA} * \delta\rho_A + \delta\rho_B\, C_{BB} * \delta\rho_B = \tag{C.1}$$
$$\rho_0 \left(n\, C_{nn} * n + n\, C_{nc} * \delta c + \delta c\, C_{cn} * n + \delta c\, C_{cc} * \delta c \right).$$

We begin by rewriting $\delta\rho_B$,

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

Followed by rewriting $\delta\rho_A$,

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

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

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

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

$$\delta\rho c\, C_{BB} * \delta\rho c = \delta\rho(r)c(r) \int dr' C_{BB}(r - r')\delta\rho(r')c(r')$$

$$\approx \delta\rho(r)c^2(r) \int dr' C_{BB}(r - r')\delta\rho(r'). \tag{C.3}$$

This is because the concentration field can be considered ostensibly constant over the length scale in which $C_{BB}(r)$ varies. Recall that the pair correlation function typically decays to zero on the order of several particle radii. Using this approximation we can rewrite equation C.2 as,

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

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

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

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

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

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