

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

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1 Derivation of the General Binary XPFC Free Energy

In this section we will derive a free energy for a generic binary system starting from basic statistical mechanics. This will stand as a foundation for many applications we will see later. To start we consider a single species system and look at the microscopic origins of the PFC free energy functional. We will see afterwards that generalizing to a multicomponent system relatively simple task.

1.1 Classical density functional theory for a single component

In a many body system in which particles interactions are independent of their velocities, we may split contributions to the free energy into two parts: the ideal and the excess.

1.1.1 The ideal component of the free energy

The ideal component comes from the kinetic energy term in the Hamiltonian and is known exactly.

$$\beta\mathcal{F}_{id}[\rho] = \int dr \rho(r) \{ \ln(\Lambda^3 \rho(r)) - 1 \} \quad (1)$$

Where,

Λ^3 is the thermal DeBroglie volume

$\rho(r)$ is the number density

β is the inverse temperature ($1/k_b T$)

1.1.2 Expansion of the excess free energy

The excess component comes from the interaction term in the Hamiltonian and is often not known exactly and must be modelled. A common technique for modelling the excess free energy is to expand it around uniform fluid reference state. This reference state is characterized by a number density, ρ_0 , and chemical potential μ_0 .

$$\beta \mathcal{F}_{ex}[\rho] = \beta \mathcal{F}_{ex}^0 + \beta \int dr \left. \frac{\delta \mathcal{F}_{ex}}{\delta \rho} \right|_{\rho=\rho_0} \Delta \rho + \beta \frac{1}{2} \int dr \int dr' \Delta \rho(r') \left. \frac{\delta^2 \mathcal{F}_{ex}}{\delta \rho(r) \delta \rho(r')} \right|_{\rho=\rho_0} \Delta \rho(r') + \dots \quad (2)$$

Where,

$\Delta \rho$ is difference from reference density ($\rho(r) - \rho_0$)

\mathcal{F}_{ex}^0 is the free energy of the reference state

The excess free energy is the generating function of direct correlation functions $C^{(n)}(r_1, \dots, r_n)$. In particular this means that direct correlation functions can be written as,

$$C^{(n)}(r_1, \dots, r_n) = -\beta \frac{\delta^{(n)} \mathcal{F}_{ex}[\rho]}{\delta \rho(r_1) \dots \delta \rho(r_n)}, \quad (3)$$

and our previous expansion can be rewritten in terms of these direct correlation functions.

$$\beta \mathcal{F}_{ex}[\rho] = \beta \mathcal{F}_{ex}^0 - \int dr C_0^{(1)}(r) \Delta \rho + \beta \frac{1}{2} \int dr \int dr' \Delta \rho(r') C_0^{(2)}(r, r') \Delta \rho(r') + \dots \quad (4)$$

In the absence of an external field the single particle direct correlation function of the reference system is simply $\beta \mu_0^{ex}$.

1.1.3 Total Free Energy

If we now add in the ideal contribution to the free energy and take advantage of the fact that the excess chemical potential of the reference fluid can be written as the total chemical potential minus the ideal contribution,

$$\mu_0^{ex} = \mu_0 - \mu_0^{id} = \mu_0 - k_b T \ln(\Lambda^3 \rho_0). \quad (5)$$

to find an expression for the total free energy:

$$\beta \mathcal{F}[\rho] = \beta \mathcal{F}_0 + \int dr \left\{ \Delta \rho \ln \left(\frac{\Delta \rho}{\rho_0} \right) - (1 - \mu_0) \Delta \rho \right\} - \frac{1}{2} \int dr \int dr' \Delta \rho(r) C_0^{(2)}(r, r') \Delta \rho(r') \quad (6)$$

1.1.4 Smooth atom approximation and the PFC Free Energy

To construct the phase-field crystal free energy we assume that the density fluctuations, $\Delta\rho(r)$, are small and expand the logarithm term to quartic order in the fluctuations. Furthermore, we nondimensionalize the free energy by scaling out the reference density, ρ_0 , and changing variables to $n(r) = \Delta\rho(r)/\rho_0$.

$$\frac{\beta\mathcal{F}[n]}{\rho_0} = \frac{\beta\mathcal{F}_0}{\rho_0} + \int dr \mu_0 \rho_0 n(r) + \frac{n^2(r)}{2} - \frac{n^3(r)}{6} + \frac{n^4(r)}{12} - \frac{\rho_0}{2} \int dr \int dr' n(r) C_0^{(2)}(r, r') n(r') \quad (7)$$

At this point we note that the constant and linear terms in the free energy can be removed without changing the properties of the functional and we are left with the following minimal free energy functional:

$$\frac{\beta\mathcal{F}}{\rho_0} = \int dr \frac{n^2(r)}{2} - \frac{n^3(r)}{6} + \frac{n^4(r)}{12} - \frac{1}{2} \int dr \int dr' n(r) C^{(2)}(r, r') n(r'). \quad (8)$$

Note, that by convention a factor of the reference density is absorbed into the pair correlation function in the PFC free energy functional.

1.2 Generalizing the Free Energy to Two Components

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

1.2.1 Ideal Free Energy to Two Components

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

$$\beta\mathcal{F}_{id}^{tot}[\rho_A, \rho_B] = \beta\mathcal{F}_{id}[\rho_A] + \beta\mathcal{F}_{id}[\rho_B] \quad (9)$$

Where,

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

1.2.2 Excess Free Energy of a Two Component System

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

$$\beta\mathcal{F}_{ex} = \beta\mathcal{F}_{ex}^0 - \int dr C_i^{(1)}(r) \Delta\rho_i(r) - \frac{1}{2} \int dr \int dr' \Delta\rho_i(r) C_{ij}^{(2)}(r, r') \Delta\rho_j(r') \quad (10)$$

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

1.2.3 Total free energy of a Two Component System

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

$$\beta\mathcal{F}[\rho_A, \rho_B] = \int dr \left\{ \Delta\rho_i \ln \left(\frac{\Delta\rho_i}{\rho_{i0}} \right) - \Delta\rho_i \right\} - \frac{1}{2} \int dr \int dr' \Delta\rho_i(r) C_{ij}^{(2)}(r, r') \Delta\rho_j(r') \quad (11)$$

1.2.4 Changing variables

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

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

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

$$\beta\mathcal{F}[c, \rho] = \quad (12)$$

1.3 Restrictions on the cubic term