

Working Title

Nathan Smith and Nikolas Provatas
McGill Department of Physics
 (Dated: March 22, 2017)

Modeling the liquid in a binary PFC model as regular solution instead of an ideal one leads to lots of interesting features. Look at all those features. We'll even discuss how it can be a contributor to non-classical nucleation pathways. Very sexy.

Keywords: nucleation, growth, phase field crystal

I. INTRODUCTION

II. FREE ENERGY FUNCTIONAL FOR BINARY ALLOYS

To construct a free energy functional for a binary alloy we begin by splitting the free energy into ideal and excess components.

$$\mathcal{F}[\rho_A, \rho_B] = \mathcal{F}_{id}[\rho_A, \rho_B] + \mathcal{F}_{ex}[\rho_A, \rho_B] \quad (1)$$

The ideal component comes from the non-interacting, kinetic part of the Hamiltonian while the excess component comes from the interaction potential part of the Hamiltonian. The ideal component can be computed exactly as,

$$\beta\mathcal{F}_{id}[\rho_A, \rho_B] = \sum_{i=A,B} \int dr \rho_i(r) (\ln(\Lambda_i^3 \rho_i(r)) - 1) \quad (2)$$

Where $\rho_i(r)$ and Λ_i^3 are the density field and thermal de Broglie volume of the i th species. The excess free energy cannot, in general, be computed exactly and thus approximate it by expanding the excess free energy about a uniform reference mixture with densities ρ_A^0 and ρ_B^0 .

$$\begin{aligned} \beta\mathcal{F}_{ex}[\rho_A, \rho_B] = & \beta\mathcal{F}_{ex}^0 + \sum_i \int dr C_i^{(1)}(r) \Delta\rho_i(r) \\ & + \frac{1}{2} \sum_{i,j} \int dr dr' \Delta\rho_i(r') C_{ij}^{(2)}(r, r') \Delta\rho_j(r) + \dots \end{aligned} \quad (3)$$

We now perform a change of variable to solute concentration, c and dimensionless total density, n :

$$n = \Delta\rho/\rho_0 = \frac{\Delta\rho_A + \Delta\rho_B}{\rho_A^0 + \rho_B^0} \quad (4)$$

$$c = \frac{\rho_B}{\rho_A + \rho_B} \quad (5)$$

Under this change of variables the change in ideal free energy from the reference becomes,

$$\begin{aligned} \frac{\beta\Delta\mathcal{F}_{id}[n, c]}{\rho_0} = & \int dr (n+1) \ln(n+1) - n \\ & + (n+1) \left[c \ln\left(\frac{c}{c_0}\right) + (1-c) \ln\left(\frac{1-c}{1-c_0}\right) \right] \end{aligned} \quad (6)$$

Following Greenwood *et al* [cite] if we assume that the concentration field varies over a much longer length scale than the total density, the change in excess free energy from the reference can be written as,

$$\begin{aligned} \frac{\beta\Delta\mathcal{F}_{ex}[n, c]}{\rho_0} = & -\frac{1}{2} \int dr n \left(\int dr' C_{eff}^n n' + C_{eff}^c c' \right) \\ & - \frac{1}{2} \int dr (c - c_0) \left(\int dr' C_{eff}^{c_0 n} n' + C_{eff}^{c c_0} c' \right) \end{aligned} \quad (7)$$

Where the $n - c$ effective correlation functions are,

$$C_{eff}^n = c^2 C_{BB}^{(2)} + (1-c)^2 C_{AA}^{(2)} + 2c(1-c) C_{AB}^{(2)} \quad (8)$$

$$C_{eff}^c = c C_{BB}^{(2)} - (1-c) C_{AA}^{(2)} + (1-2c) C_{AB}^{(2)} \quad (9)$$

$$C_{eff}^{c_0 n} = C_{eff}^c \quad (10)$$

$$C_{eff}^{c c_0} = C_{BB}^{(2)} + C_{AA}^{(2)} - 2C_{AB}^{(2)} \quad (11)$$

A. Simplified Regular Free Energy Functional

Following Greenwood *et al* [cite] we can now expand the ideal free energy about reference density in a Taylor expansion and coarse grain the excess contributions the the free energy. In contrast to Greenwood *et al*, we will not assume that the $k = 0$ mode of the effective concentration-concentration correlation is zero. The effect of eliminating this assumption is to produce a free energy of mixing with a regular solution model instead of an ideal solution. That is to say, there is both an entropy and enthalpy of mixing in the theory.

$$\begin{aligned} \frac{\beta\Delta\mathcal{F}[n, c]}{\rho_0} = & \int dr \frac{n^2}{2} - \eta \frac{n^3}{6} + \chi \frac{n^4}{12} - \frac{1}{2} n C_{eff}^n * n \\ & + \int dr \frac{W_c}{2} |\nabla c|^2 + (n+1) f_{mix}(c) + \frac{1}{2} \epsilon c^2 \end{aligned} \quad (12)$$

ter

B. Model Dynamics

III. EQUILIBRIUM PROPERTIES

A. Syntectic Phase Diagram

B. Precipitation from Solution

IV. APPLICATION

**A. Non-classical nucleation pathways of
precipitation from solution**

B. Anomolous growth of nanoparticles