Working Title

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Modelling 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.

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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.

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

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

$$\beta\mathcal{F}[\rho_A, \rho_B] = \sum_i \int \mathrm{d}r \rho_i(r) \left(\ln\left(\Lambda_i^3 \rho_i(r)\right) - 1\right) \tag{2}$$

Where the sum runs over components, A and B, and Λ_i^3 is the thermal de Broglie volume. 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.

$$\begin{aligned}\beta\mathcal{F}_{ex}[\rho_A, \rho_B] = \beta\mathcal{F}_{ex}^0 + \int \mathrm{d}r C_i^{(1)}(r)\delta\rho_i(r) \\ + \frac{1}{2}\int \mathrm{d}r \int dr' \delta\rho_i(r) C_{ij}^{(2)}(r, r')\delta\rho_j(r')\end{aligned} \tag{3}$$

Where, summation over repeated indices is implied. We now perform a change a variable to solute concentration, c, and dimensionless total density, n.

$$n = \frac{\delta\rho}{\rho^0} = \frac{\delta\rho_A + \delta\rho_B}{\rho_A^0 + \rho_B^0} \tag{4}$$

$$c = \frac{\rho_B}{\rho_A + \rho_B} \tag{5}$$

Under this change of variables, the ideal free energy separates cleanly into total density and ideal free energy of mixing term as we might expect.

$$\begin{aligned}\frac{\beta\mathcal{F}_{id}[n, c]}{\rho^0} = \int \mathrm{d}r\,(n+1)\ln(n+1) - n \\ \int \mathrm{d}r\,(n+1)\left[c\ln\left(\frac{c}{c_0}\right) + (1-c)\ln\left(\frac{1-c}{1-c_0}\right)\right]\end{aligned} \tag{6}$$

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,

$$\begin{aligned}\frac{\beta\mathcal{F}_{ex}[n, c]}{\rho^0} = -\frac{1}{2}\int \mathrm{d}r n(r)\left(\int \mathrm{d}r' C_{eff}^n n' + C_{eff}^c c'\right) \\ -\frac{1}{2}\int \mathrm{d}r (c - c^0)\left(\int \mathrm{d}r' C_{eff}^{c_0 n} n' + C_{eff}^{cc_0} c'\right)\end{aligned} \tag{7}$$

where the effective pair correlation functions C_{eff} are,

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

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

$$C_{eff}^{c_0 n} = C_{eff}^c \tag{10}$$

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

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 to 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* enthaply of mixing in the theory.

$$\begin{aligned}\frac{\beta\Delta\mathcal{F}[n, c]}{\rho_0} = \int \mathrm{d}r \frac{n^2}{2} - \eta\frac{f^3}{6} + \chi\frac{n^4}{12} - \frac{1}{2}nC_{eff}^n * n \\ + \int \mathrm{d}r \frac{W_c}{2}\left|\nabla c\right|^2 + (n+1)f_{mix}(c) + \frac{1}{2}\epsilon(c - c_0)^2\end{aligned} \tag{12}$$