Volume changes in binary alloy ordering: A binary classical density functional theory approach

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The chemical ordering transition in a binary alloy is examined using classical density functional theory for a binary mixture. The ordered lattice is assumed to be obtained from the disordered lattice by a volume change only, as in $L1_2$ ordering from a face centered cubic chemically disordered crystal. By using the simplest possible approach to the density functional calculation, a very tractable expansion is obtained which consists of the same terms as the lattice gas formalism, where the lattice is implicitly taken as fixed, plus additional interaction terms and an additional entropy term. This additional entropy term represents a lowest order approximation to the vibrational entropy change.
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I. INTRODUCTION

Chemical ordering transitions in alloys have been studied by a variety of methods, including a lattice gas analog of classical density functional theory [1–4]. Since lattice changes also occur on ordering, it would be valuable to be able to include them along with chemical changes in a similar approach. One approach would involve a set of variables including a global elastic strain tensor along with chemical occupation variables [5]. A question that arises in such an approach is the appropriate form for the ideal (noninteracting) free energy. It has been shown that the occupation variables alone can be treated as a complete system, and that the ideal free energy is the ideal mixing entropy. The occupation variables, plus a global strain tensor, are not a complete system, however. One consistent set of variables is the position and momentum variables for a binary mixture. The approach taken here in developing a lattice gas plus strain tensor formulation of ordering is to look to the classical density functional theory of the binary mixture, and simplify it to the lattice. Since the part of the strain tensor that most directly affects the entropy is the volume, the other terms will be ignored here.

Several forms of classical density functional theory have been used to study the freezing of binary liquids. Since the concern here is the ''entropy'' terms, the simplest form of the theory will be used. Here, instead of looking at the freezing of a liquid, the free energies of two solid structures [the disordered, and the (partially) ordered] are compared. A similar approach was used by Sengupta, Krishnamurthy, and Ramakrishnan to study the fcc-bcc interface [6], and a form of density functional theory was used to study the ordering of hard sphere mixtures [7].

II. CLASSICAL DFT FOR MULTIPLE SPECIES

Classical density functional theory (DFT) of mixtures was used to study the freezing of binary hard sphere and Lennard-Jones fluids [8–13]. Consider a system with a fixed volume V, and m species of classical particles. (The primary interest herein is $m=2$.) The partition function is computed in the grand canonical ensemble at fixed values of V, the temperature T, and the chemical potentials μ_α, $\alpha = 1, \ldots, m$.

Classical DFT guarantees the existence of a functional Ω of the average densities $\rho_\alpha(\vec{r})$ which is minimized by the equilibrium average densities, and which evaluated at the equilibrium densities is equal to the grand potential. For a noninteracting system this can be computed explicitly and is [9]

$$\Omega_{\text{ideal}}[\{\rho_\alpha\}] = \beta^{-1} \sum_\alpha \int_V d\vec{r} \, \rho_\alpha(\vec{r})[\ln(\lambda_\alpha^3 \rho_\alpha(\vec{r})) - \beta\mu_\alpha - 1],$$
(1)

where $\beta = 1/(k_B T)$, and λ_α is the de Broglie thermal wavelength of species α. Note that Eq. (1) is simply the sum over the species of the ideal free energy of each species.

Let $\beta^{-1} V\Phi[\{\rho_\alpha\}] \equiv \Omega[\{\rho_\alpha\}] - \Omega_{\text{ideal}}\{\rho_\alpha\}$ and expand Φ about some particular uniform (liquid) state, with densities $\{\rho_{\alpha 0}\}$. Truncating at second order [14] in the difference in densities, $\delta\rho_\alpha$, and letting $N_\alpha \equiv \int_V d\vec{r} \, \rho_\alpha(\vec{r})$, one obtains as the expansion of the mixed functional for the grand potential:

$$\beta\Omega[\{\rho_\alpha\}] = V\Phi[\{\rho_{\alpha 0}\}] + \sum_\alpha \int_V d\vec{r} \, \rho_\alpha(\vec{r})[\ln(\lambda_\alpha^3 \rho_\alpha(\vec{r})) - 1]$$

$$- \sum_\alpha \beta\mu_\alpha N_\alpha + \sum_\alpha \int_V d\vec{r} C_\alpha^{(1)}(\rho_\alpha(\vec{r}) - \rho_{\alpha 0})$$

$$+ \frac{1}{2} \sum_{\alpha\beta} \int_V d\vec{r}_1 \, d\vec{r}_2 C_{\alpha\beta}^{(2)}(\vec{r}_1, \vec{r}_2)(\rho_\alpha(\vec{r}_1) - \rho_{\alpha 0})$$

$$\times (\rho_\beta(\vec{r}_2) - \rho_{\beta 0}) + O(\delta\rho_\alpha^3).$$
(2)

Multiplying out the products, and collecting constant and linear terms, this can be rewritten as:

$$\beta\Omega \approx \sum_\alpha \int_V d\vec{r} \, \rho_\alpha(\vec{r})\ln\rho_\alpha(\vec{r}) + Vf_0 + \sum_\alpha D_\alpha N_\alpha$$

$$+ \frac{1}{2} \sum_{\alpha\beta} \int_V d\vec{r}_1 \, d\vec{r}_2 C_{\alpha\beta}^{(2)}(\vec{r}_1, \vec{r}_2)\rho_\alpha(\vec{r}_1)\rho_\beta(\vec{r}_2),$$
(3)

where

$$f_0 = \Phi[\{\rho_{\alpha 0}\}] - \sum_\alpha C_\alpha^{(1)}\rho_{\alpha 0}$$

$$+ \tfrac{1}{2} \sum_{\alpha\beta} \rho_{\alpha 0}\rho_{\beta 0} \int_V d\vec{r}_2\, C_{\alpha\beta}^{(2)}(\vec{0},\vec{r}_2), \qquad (4)$$

$$D_\alpha = -\beta\mu_\alpha + \ln(\lambda_\alpha^3) - 1 + C_\alpha^{(1)} - \sum_\beta \rho_{\beta 0} \int_V d\vec{r}_2\, C_{\alpha\beta}^{(2)}(\vec{0},\vec{r}_2). \qquad (5)$$

By assuming that the uniform fluid at a particular total density and set of concentrations is a local minimum of Ω, D_α could be eliminated in favor of the liquid densities $\{\rho_{\alpha 0}\}$. However, here the task is to compare trial ordered solids with the disordered solid at temperatures well below the melting point. D_α will therefore by retained for now, and later eliminated using the disordered solid as the reference state.

The constant f_0 drops out of the difference in grand potential between two states, and so is irrelevant to determining the transition state and temperature. It can be determined in terms of the pressure of the reference disordered state.

$C_{\alpha\beta}^{(2)}(\vec{r}_1,\vec{r}_2)$ is symmetric in $\alpha\beta$, and depends only on $|\vec{r}_2 - \vec{r}_1|$. (Note that for fixed $\{\mu_\alpha\}$ these liquid direct-correlation functions are needed as a function of temperature in a range including the ordering temperature. In many systems this would involve extrapolation beyond reasonable temperatures for the liquid, and so this computation would not be feasible as written. The purpose here, however, puts more emphasis on understanding the appropriate form of the expansion for the solid, than on a computation using actual liquid data. Given the appropriate form of the expansion stated in terms of the occupation variables and strain tensor, other sources for the parameters are likely to be more suitable to actual numerical work.)

III. DENSITY ANSATZ FOR DISORDERED AND ORDERED SOLID

Consider a fixed volume V. A solid is described in terms of a set of real-space lattice vectors $\{\vec{R}_i\}$, with N sites in the volume V. Making the simplifying assumption that there is exactly one atom per site, $N = \Sigma_\alpha N_\alpha$. In general Ω depends on $\{\vec{R}_i\}$, and an assumption needs to be made as to what possible lattices are being considered. To keep the situation as simple as possible, assume that both the disordered solid and the trial states for the ordered solid have the same lattice structure, so that $\{\vec{R}_i\}$ depends only on N. (Up to an arbitrary choice of origin for the lattice.) So either N, or the lattice constant, or the average total density can be considered as one parameter, and there is one constraint on the vector

$\{N_\alpha\}$. Think of $\rho \equiv N/V$ as the parameter, but N will be written for ρV whenever convenient.

As in prior work on the freezing of hard-sphere mixtures [8–13], assume that the density of each species at a site is given by an isotropic Gaussian distribution centered at the site. (In their work on the fcc-bcc interface, the authors of Ref. [6] used a more general form of ''anisotropic Gaussian distributions'' and found that there was significant anisotropy in the bcc density, but very little in the fcc density.) For simplicity assume that this is cut off at the Wigner-Seitz cell about the lattice point. (And very quickly the further assumption will be made that the Gaussian distributions are sharply peaked enough that the integral over the cell is equal to the integral over all space. Thus the assumption is essentially that the Gaussian distributions are sharply enough peaked that there is no overlap between the distributions at different sites.) Referring to the cell at $\vec{R}_i$ as U_i, then, in U_i,

$$\rho_\alpha(\vec{r}) = \lambda_{\alpha i}\exp\{-\gamma_{\alpha i}|\vec{r} - \vec{R}_i|^2\}. \qquad (6)$$

Here, for a binary alloy, N and $\{\lambda_{Ai}\}$, $\{\gamma_{Ai}\}$, and $\{\gamma_{Bi}\}$ ($i = 1 \ldots N$) parametrize the density ansatz, while $\{\lambda_{Bi}\}$ is then fixed by the assumption of one atom per cell. For the disordered solid, $\lambda_{\alpha i}$ and $\gamma_{\alpha i}$ are independent of i, so the parameters are N_d, λ_{Ad}, γ_{Ad}, and γ_{Bd}.

Define

$$c_{\alpha i} \equiv \int_{U_i} d\vec{r}\, \lambda_{\alpha i}\exp\{-\gamma_{\alpha i}|\vec{r} - \vec{R}_i|^2\}. \qquad (7)$$

At this point the limit $\gamma_{\alpha i} \to 0$, $\lambda_{\alpha i} \to \rho_{\alpha 0}$ gives the uniform binary liquid. However, the states to be considered are those with $\gamma_{\alpha i}$ large enough that $\int_{U_i}$ can be approximated by $\int$. For large enough $\gamma_{\alpha i}$,

$$c_{\alpha i} \approx \lambda_{\alpha i}\left(\frac{\pi}{\gamma_{\alpha i}}\right)^{3/2}. \qquad (8)$$

The assumption of one atom per cell then takes the form $\Sigma_\alpha c_{\alpha i} = 1$.

IV. RESULTS AND DISCUSSION

The computation of Ω from Eq. (3) for the trial states described by the density ansatz proceeds as follows: Inserting the density ansatz in the first term of Eq. (3) gives

$$\sum_\alpha \sum_i \left\{ c_{\alpha i}\left(\ln\left(\frac{c_{\alpha i}}{(\pi/\gamma_{\alpha i})^{3/2}}\right) - 3/2\right)\right\} \qquad (9)$$

The last term depends not only on $C_{\alpha\beta}^{(2)}(\vec{r}_1,\vec{r}_2)$ at the lattice points, but also near the lattice points. Assuming that $C_{\alpha\beta}^{(2)}(\vec{r}_1,\vec{r}_2)$ changes slowly enough over the length scale $(1/\gamma_{\alpha i})^{1/2}$ that it can be expanded to second order, the result is

$$\frac{1}{2}\sum_{\alpha\beta}\sum_{ij} c_{\alpha i}c_{\beta j}\left\{ C_{\alpha\beta ij}^{(2)}(p) + \frac{1}{4}\left(\frac{1}{\gamma_{\alpha i}} + \frac{1}{\gamma_{\beta j}}\right)\nabla_{\vec{r}}^2\Big|_{\vec{r}=\vec{R}_{ij}(p)} C_{\alpha\beta}^{(2)}(\vec{r})\right\}, \qquad (10)$$

where

$$C^{(2)}_{\alpha\beta ij}(\rho) \equiv C^{(2)}_{\alpha\beta}(\vec{R}_{ij}(\rho)), \tag{11}$$

$$\vec{R}_{ij}(\rho) \equiv \vec{R}_j(\rho) - \vec{R}_i(\rho). \tag{12}$$

Thus

$$\beta\Omega \approx \sum_\alpha \sum_i \left\{ c_{\alpha i} \ln\left(\frac{c_{\alpha i}}{(\pi/\gamma_{\alpha i})^{3/2}} \right) \right\} + V f_0$$

$$+ \sum_\alpha \left(D_\alpha - \frac{3}{2} \right) N_\alpha + \frac{1}{2} \sum_{\alpha\beta} \sum_{ij} c_{\alpha i} c_{\beta j} C^{(2)}_{\alpha\beta ij}(\rho)$$

$$+ \frac{1}{2} \sum_{\alpha\beta} \sum_{ij} c_{\alpha i} c_{\beta j} \left(\frac{1}{4} \right) \left(\frac{1}{\gamma_{\alpha i}} + \frac{1}{\gamma_{\beta j}} \right) F_{\alpha\beta ij}(\rho), \tag{13}$$

where

$$F_{\alpha\beta ij} \equiv \nabla^2_{\vec{r}}|_{\vec{r} = \vec{R}_{ij}(\rho)} C^{(2)}_{\alpha\beta}(\vec{r}). \tag{14}$$

The equilibrium value of $\gamma_{\alpha i}$ in this approximation is

$$\gamma_{\alpha i} = \frac{1}{6} \sum_\beta \sum_j c_{\beta j} F_{\alpha\beta ij}(\rho). \tag{15}$$

Upon substituting Eq. (15) into Eq. (13), the final term cancels with the $\frac{3}{2}$ in the third term. This substantially simplifies the algebra, so all of the expressions for Ω and $\Delta\Omega$ below assume prior minimization with respect to $\gamma_{\alpha i}$, and when $\gamma_{\alpha i}$ appears it is a shorthand for the right hand side of Eq. (15).

For a binary alloy, c_{Bi} can be eliminated. It will prove helpful to emphasize the relationship between eliminating c_{Ai} or c_{Bi} by using the more symmetrical $m_i \equiv c_{Ai} - \frac{1}{2}$. Thus m_i ranges from $-\frac{1}{2}$ to $\frac{1}{2}$. Then, for a binary alloy,

$$\beta\Omega \approx \sum_{i=1}^N \left\{ \left(\frac{1}{2} + m_i \right) \ln\left(\frac{\frac{1}{2} + m_i}{(\pi/\gamma_{Ai})^{3/2}} \right) \right.$$

$$\left. + \left(\frac{1}{2} - m_i \right) \ln\left(\frac{\frac{1}{2} - m_i}{(\pi/\gamma_{Bi})^{3/2}} \right) \right\} + V f_0 + N(D_2 + \mathcal{G}_2(\rho))$$

$$+ N m_{\mathrm{ave}} (D_1 + \mathcal{G}_1(\rho)) + \frac{1}{2} \sum_{i=1}^N \sum_j m_i m_j C^{(2)}_{ij}(\rho),$$

$$\tag{16}$$

where

$$m_{\mathrm{ave}} \equiv \frac{1}{N} \sum_{i=1}^N m_i, \tag{17}$$

$$C^{(2)}_{ij}(\rho) \equiv C^{(2)}_{AAij}(\rho) + C^{(2)}_{BBij}(\rho) - 2C^{(2)}_{ABij}(\rho), \tag{18}$$

$$\mathcal{G}_1 \equiv \frac{1}{2} \sum_j C^{(2)}_{AAij}(\rho) - C^{(2)}_{BBij}(\rho), \tag{19}$$

$$\mathcal{G}_2 \equiv \frac{1}{8} \sum_j C^{(2)}_{AAij}(\rho) + C^{(2)}_{BBij}(\rho) + 2C^{(2)}_{ABij}(\rho), \tag{20}$$

$$D_2 \equiv \frac{1}{2} (D_A + D_B), \tag{21}$$

$$D_1 \equiv (D_A - D_B), \tag{22}$$

and additionally let

$$\mathcal{G}_3 \equiv \sum_j C^{(2)}_{ij}(\rho) = \sum_j C^{(2)}_{AAij}(\rho) + C^{(2)}_{BBij}(\rho) - 2C^{(2)}_{ABij}(\rho). \tag{23}$$

Now consider a disordered state, specified by a concentration m and an overall density ρ. At at given temperature, this state will be in equilibrium for a pair of chemical potentials μ_A and μ_B. (Now buried in D_1 and D_2.) For this disordered state, the mixed functional for the grand potential per unit volume is

$$\frac{\beta\Omega}{V} \approx \rho \left\{ \left(\frac{1}{2} + m \right) \ln\left(\frac{\frac{1}{2} + m}{(\pi/\gamma_{Ad})^{3/2}} \right) \right.$$

$$\left. + \left(\frac{1}{2} - m \right) \ln\left(\frac{\frac{1}{2} - m}{(\pi/\gamma_{Bd})^{3/2}} \right) \right\}$$

$$+ f_0 + \rho(D_2 + \mathcal{G}_2(\rho))$$

$$+ \rho m(D_1 + \mathcal{G}_1(\rho)) + \rho \frac{1}{2} m^2 \mathcal{G}_3(\rho),$$

$$\tag{24}$$

$$\gamma_{\alpha d}(m, \rho) = \frac{1}{6} \sum_\beta c_\beta \sum_j F_{\alpha\beta ij}(\rho). $$

These can be minimized with respect to ρ and m to obtain the equilibrium density and concentration at a particular μ_A and μ_B, or vice versa.

Taking the disordered state (m_d, ρ_d) as the reference (equilibrium) state, and minimizing Eq. (24) to eliminate the chemical potentials, gives

$$-D_1 = \mathcal{G}_1(\rho_d) + m_d \mathcal{G}_3(\rho_d) + \ln\left(\frac{\frac{1}{2} + m_d}{(\pi/\gamma_{Ad})^{3/2}} \right) - \ln\left(\frac{\frac{1}{2} - m_d}{(\pi/\gamma_{Bd})^{3/2}} \right) + \frac{3}{2} \left(\frac{1}{2} + m_d \right) \frac{\partial \ln \gamma_{Ad}}{\partial m} \bigg|_{m_d, \rho_d} + \frac{3}{2} \left(\frac{1}{2} - m_d \right) \frac{\partial \ln \gamma_{Bd}}{\partial m} \bigg|_{m_d, \rho_d}, \tag{25}$$

$$-D_2 = \mathcal{G}_2(\rho_d) + \rho_d \frac{d\mathcal{G}_2}{d\rho}\bigg|_{\rho_d} + m_d\rho_d\frac{d\mathcal{G}_1}{d\rho}\bigg|_{\rho_d} - \frac{1}{2}\,m_d^2\mathcal{G}_3(\rho_d) + \frac{1}{2}\,m_d^2\rho_d\frac{d\mathcal{G}_3}{d\rho}\bigg|_{\rho_d} + \frac{1}{2}\,\ln\!\left(\frac{\frac{1}{2}+m_d}{(\pi/\gamma_{Ad})^{3/2}}\right) + \frac{1}{2}\,\ln\!\left(\frac{\frac{1}{2}-m_d}{(\pi/\gamma_{Bd})^{3/2}}\right)$$

$$-\frac{3}{2}\left(\frac{1}{2}+m_d\right)m_d\frac{\partial\ln\gamma_{Ad}}{\partial m}\bigg|_{m_d,\rho_d} - \frac{3}{2}\left(\frac{1}{2}-m_d\right)m_d\frac{\partial\ln\gamma_{Bd}}{\partial m}\bigg|_{m_d,\rho_d}$$

$$+\frac{3}{2}\left(\frac{1}{2}+m_d\right)\rho_d\frac{\partial\ln\gamma_{Ad}}{\partial\rho}\bigg|_{m_d,\rho_d} + \frac{3}{2}\left(\frac{1}{2}-m_d\right)\rho_d\frac{\partial\ln\gamma_{Bd}}{\partial\rho}\bigg|_{m_d,\rho_d}, \tag{26}$$

$$\frac{\beta\Omega}{V}\bigg|_{m_d,\rho_d} = f_0 - \rho_d^2\frac{d\mathcal{G}_2}{d\rho}\bigg|_{\rho_d} - m_d\rho_d^2\frac{d\mathcal{G}_1}{d\rho}\bigg|_{\rho_d} - \frac{1}{2}\,m_d^2\rho_d^2\frac{d\mathcal{G}_3}{d\rho}\bigg|_{\rho_d} - \frac{3}{2}\left(\frac{1}{2}+m_d\right)\rho_d^2\frac{\partial\ln\gamma_{Ad}}{\partial\rho}\bigg|_{m_d,\rho_d} - \frac{3}{2}\left(\frac{1}{2}-m_d\right)\rho_d^2\frac{\partial\ln\gamma_{Bd}}{\partial\rho}\bigg|_{m_d,\rho_d}, \tag{27}$$

where the formula for D_1 has been used in computing D_2.

For studying the ordering transition, this is the desired result for the disordered state. However, it is interesting to take a detour and ask what this says about the disordered state.

One question to ask is the following: "How does the density vary with concentration at constant pressure?" The pressure (for an equilibrium state) is given by $-p = \Omega/V$. Thus

$$-\beta p = f_0 - \rho_d^2\frac{d\mathcal{G}_2}{d\rho}\bigg|_{\rho_d} - m_d\rho_d^2\frac{d\mathcal{G}_1}{d\rho}\bigg|_{\rho_d} - \frac{1}{2}\,m_d^2\rho_d^2\frac{d\mathcal{G}_3}{d\rho}\bigg|_{\rho_d}$$

$$-\frac{3}{2}\left(\frac{1}{2}+m_d\right)\rho_d^2\frac{\partial\ln\gamma_{Ad}}{\partial\rho}\bigg|_{m_d,\rho_d}$$

$$-\frac{3}{2}\left(\frac{1}{2}-m_d\right)\rho_d^2\frac{\partial\ln\gamma_{Bd}}{\partial\rho}\bigg|_{m_d,\rho_d}, \tag{28}$$

and switching back from m to c for a moment, this is

$$\beta p = -f_0 + \frac{1}{2}\,\rho^2\left\{c_A^2\frac{d\mathcal{G}_{AA}}{d\rho} + c_B^2\frac{d\mathcal{G}_{BB}}{d\rho} + 2c_Ac_B\frac{d\mathcal{G}_{AB}}{d\rho}\right\}$$

$$+\frac{3}{2}\,c_A\rho^2\frac{\partial\ln\gamma_{Ad}}{\partial\rho} + \frac{3}{2}\,c_B\rho^2\frac{\partial\ln\gamma_{Bd}}{\partial\rho}. \tag{29}$$

$$\mathcal{G}_{\alpha\beta} \equiv \sum_j\,C^{(2)}_{\alpha\beta ij}(\rho). \tag{30}$$

For a given p, m, and T, this equation implicitly gives the equilibrium density of the disordered solid, assuming it exists.

Some insight into this equation can be gained by imagining that $\mathcal{G}_{\alpha\beta}$ is dominated by nearest-neighbor contributions. One then expects that for a single species the equilibrium density is given by a density near the minimum of $\mathcal{G}_{AA}$. (That is, the nearest-neighbor distance in the solid is approximately equal to the distance at which the liquid's direct correlation function has its main peak.) If the two species are significantly different in size, it is plausible to assume that the terms involving $\mathcal{G}_{\alpha\beta}$ in Eq. (29) are more important than

those involving $\gamma_{\alpha d}$. Suppose the latter are small. At the pressure where $\beta p + f_0 = 0$, the density corresponding to this pressure is given by

$$0 = c_A^2\frac{d\mathcal{G}_{AA}}{d\rho} + c_B^2\frac{d\mathcal{G}_{BB}}{d\rho} + 2c_Ac_B\frac{d\mathcal{G}_{AB}}{d\rho}. \tag{31}$$

Further simplifying by assuming $C^{(2)}_{AB}(\vec{r}) = (C^{(2)}_{AA}(\vec{r}) + C^{(2)}_{BB}(\vec{r}))/2$, this reduces to

$$0 = c_A\frac{d\mathcal{G}_{AA}}{d\rho} + (1-c_A)\frac{d\mathcal{G}_{BB}}{d\rho}. \tag{32}$$

Considering nearest-neighbor contributions only, and assuming that both $C^{(2)}_{AA}(\vec{r})$ and $C^{(2)}_{BB}(\vec{r})$ can be expanded as quadratics about their minima over the relevant region,

$$\mathcal{G}_{AA}(r_{nn}) = K_A + \tfrac{1}{2}k_A(r_{nn}-r_A)^2,$$

$$\mathcal{G}_{BB}(r_{nn}) = K_B + \tfrac{1}{2}k_B(r_{nn}-r_B)^2, \tag{33}$$

where r_{nn} is the nearest-neighbor distance corresponding to a given density, then Eq. (33) gives

$$r_{nn} = \frac{c_Ak_A}{c_Ak_A+(1-c_A)k_B}\,r_A + \frac{(1-c_A)k_B}{c_Ak_A+(1-c_A)k_B}\,r_B. \tag{34}$$

If $k_A = k_B$, this makes r_{nn} linear in concentration.

Returning to the analysis of the ordering transition, the next step is to compute the difference in Ω between a trial state and an equilibrium disordered state. At the transition, both the reference disordered state and the (partially) ordered state at the transition will be global minima of Ω, and the difference in Ω will be zero. Hopefully the approximation of Ω is good enough, and the range of trial states provided by the density ansatz is generous enough, that the solution provided will approximate the actual transition. Only trial states with $\gamma_{\alpha i}$, given by the last line of Eq. (16), need to be considered. The trial states are therefore considered as a function of ρ and $\{m_i\}$. m_d, ρ_d, γ_{Ad}, and γ_{Bd} refer to the equilibrium states for the given chemical potentials and temperature. Combining Eqs. (16) and (25)–(27),

$$\Delta\beta\Omega \approx \sum_{i=1}^{N}\left\{\left(\frac{1}{2}+m_i\right)\ln\left(\frac{\frac{1}{2}+m_i}{\frac{1}{2}+m_d}\right)+\left(\frac{1}{2}-m_i\right)\ln\left(\frac{\frac{1}{2}-m_i}{\frac{1}{2}-m_d}\right)\right\}+\frac{3}{2}\sum_{i=1}^{N}\left\{\left(\frac{1}{2}+m_i\right)\ln\left(\frac{\gamma_{Ai}}{\gamma_{Ad}}\right)+\left(\frac{1}{2}-m_i\right)\ln\left(\frac{\gamma_{Bi}}{\gamma_{Bd}}\right)\right\}$$

$$-\frac{3}{2}(N-N_d)\left\{\left(\frac{1}{2}+m_d\right)\rho_d\left.\frac{\partial\ln\gamma_{Ad}}{\partial\rho}\right|_{m_d,\rho_d}+\left(\frac{1}{2}-m_d\right)\rho_d\left.\frac{\partial\ln\gamma_{Bd}}{\partial\rho}\right|_{m_d,\rho_d}\right\}$$

$$-\frac{3}{2}N(m_{\mathrm{ave}}-m_d)\left\{\left(\frac{1}{2}+m_d\right)\left.\frac{\partial\ln\gamma_{Ad}}{\partial m}\right|_{m_d,\rho_d}+\left(\frac{1}{2}-m_d\right)\left.\frac{\partial\ln\gamma_{Bd}}{\partial m}\right|_{m_d,\rho_d}\right\}+N(\mathcal{G}_2(\rho)-\mathcal{G}_2(\rho_d))-(N-N_d)\rho_d\left.\frac{d\mathcal{G}_2}{d\rho}\right|_{\rho_d}$$

$$+Nm_{\mathrm{ave}}(\mathcal{G}_1(\rho)-\mathcal{G}_1(\rho_d))-(N-N_d)m_d\rho_d\left.\frac{d\mathcal{G}_1}{d\rho}\right|_{\rho_d}+\frac{1}{2}\sum_{i=1}^{N}\sum_{j}(m_i-m_d)(m_j-m_d)C_{ij}^{(2)}(\rho)$$

$$+N\left(m_{\mathrm{ave}}-\frac{1}{2}m_d\right)m_d(\mathcal{G}_3(\rho)-\mathcal{G}_3(\rho_d))-\frac{1}{2}(N-N_d)m_d^2\rho_d\left.\frac{d\mathcal{G}_3}{d\rho}\right|_{\rho_d}. \tag{35}$$

It should be emphasized that $\gamma_{\alpha i}$ in Eq. (35) is not an independent parameter, but is given by Eq. (15). The first term is the ideal mixing entropy for a pure Ising-like model. It is the same term that appears in the lattice gas formalism. More interesting is the second term (corrected by the next two terms, which cancel its linear parts) which also derives from the ideal part of the free energy. $(\gamma_{\alpha d}/\pi)^{-3/2}$ has units of volume, and represents the approximate volume over which the atom is likely to be. Writing this term as

$$\Delta\beta\Omega \approx \dots - \sum_i\left\{c_{Ai}\ln\left(\frac{\gamma_{Ai}^{-3/2}}{\gamma_{Ad}^{-3/2}}\right)+c_{Bi}\ln\left(\frac{\gamma_{Bi}^{-3/2}}{\gamma_{Bd}^{-3/2}}\right)\right\}+\cdots, \tag{36}$$

it can be thought of as representing the difference in an entropy term based on the average volume available to the atom to wander in. The assumption of Gaussian distributions approximates each atom as an independent oscillator from this point of view. We can therefore consider this expression as a lowest nonzero order approximation to the vibrational entropy difference. Note that this ''entropy'' term, which does not appear in the lattice gas formalism, does not directly depend on the density. Rather, it depends on γ, which is the variable describing the probability distribution for an atom about its site, in our very simple density ansatz. This makes sense. In the lattice gas model there is just an occupation variable at a site, with no idea of a fluctuation of an atom position about a site. The nonoverlapping Gaussian distributions we have adopted correspond to attaching an atom to each site with an independent harmonic spring. (Where the spring constant depends on both the overall density, and the state of chemical order.) In this picture it is not surprising that the entropy can be represented in terms of the mixing entropy plus an entropy term based purely on the effective volume an atom occupies about its site. Thus this term represents a lowest-order estimate of the vibrational entropy change on ordering. Even in this simple approximation, however, this term depends on both the overall density and the state of chemical order, as seen below.

The remaining terms can be rewritten as

$$\Delta\beta\Omega \approx \cdots + \frac{1}{2}\sum_{i=1}^{N}\sum_{j}(m_i-m_d)(m_j-m_d)C_{ij}^{(2)}(\rho)$$

$$+N(m_{\mathrm{ave}}-m_d)(\mathcal{G}^{**}(\rho)-\mathcal{G}^{**}(\rho_d))$$

$$+\frac{1}{2}N(\mathcal{G}^*(\rho)-\mathcal{G}^*(\rho_d))-\frac{1}{2}(N-N_d)\rho_d\left.\frac{\partial\mathcal{G}^*}{\partial\rho}\right|_{\rho_d}, \tag{37}$$

where

$$\mathcal{G}^*(\rho)\equiv 2\mathcal{G}_2(\rho)+2m_d\mathcal{G}_1(\rho)+m_d^2\mathcal{G}_3(\rho)$$

$$=c_{Ad}^2\mathcal{G}_{AA}(\rho)+2c_{Ad}c_{Bd}\mathcal{G}_{AB}(\rho)+c_{Bd}^2\mathcal{G}_{BB}(\rho),$$

$$\mathcal{G}^{**}(\rho)\equiv\mathcal{G}_1(\rho)+m_d\mathcal{G}_3(\rho)$$

$$=c_{Ad}\mathcal{G}_{AA}(\rho)+(c_{Bd}-c_{Ad})\mathcal{G}_{AB}(\rho)-c_{Bd}\mathcal{G}_{BB}(\rho). \tag{38}$$

The first term is the second order term that appears in the lattice gas formulation, and $C^{(2)}$ are available for many systems from experiment or first principles calculations. Note that it is most conveniently written in terms of the direct correlation function at the trial lattice constant. The last term is $O((\rho-\rho_d)^2)$ [the $O(\rho-\rho_d)$ portions of the two subterms cancel on expanding $\mathcal{G}^*(\rho)$ about ρ_d], and can be estimated from the bulk modulus of the reference state. The middle term is $O((m_{\mathrm{ave}}-m_d)(\rho-\rho_d))$, and can be estimated from the concentration dependence of the density of the disordered alloy.

Equation (35) is the primary result. It is expressed in terms of the desired variables ρ and $\{m_i\}$. Except for the ''vibrational entropy'' terms the coefficients can be estimated using available information. It is used to predict the transition from the disordered to the ordered state in the same way as the lattice gas analog of classical density func-

tional theory is. Given $\{\rho_d, m_d\}$, the disordered state always minimizes the free energy, by construction. As the temperature is lowered, there may be another minimum of the free energy. The highest temperature where there is an ordered state which minimizes the free energy, and for which the free energy difference is zero, is the predicted transition [15]. If the ordered state at the transition differs from the disordered state by a finite amount the transition is predicted to be first order. For a second order transition the ordered state will be equal to the disordered state at the transition, but can be determined by the fact that there will be ordered states different from the disordered states that minimize the free energy, and have free energies lower than the disordered state, for any temperature strictly less than the transition temperature.

One difficulty exists. The vibrational entropy term is still expressed in terms of the liquid partial direct correlation functions. These are unlikely to be available and suitable for many systems. It would be even more appropriate to use the partial correlation functions of the solid, but these are also unlikely to be available.

What is γ like in this theory? From Eq. (15), we have

$$
\gamma_{Ai} = \frac{1}{6} \sum_j \{ c_j \nabla_{\vec{r}}^2 |_{\vec{r}=\vec{R}_{ij}(\rho)} C_{AA}^{(2)}(\vec{r})
$$
$$
+ (1-c_j) \nabla_{\vec{r}}^2 |_{\vec{r}=\vec{R}_{ij}(\rho)} C_{AB}^{(2)}(\vec{r}) \}. \qquad (39)
$$

This talks about the curvature of the liquid partial direct correlation functions. Note that

$$
\nabla_{\vec{r}}^2 |_{\vec{r}=\vec{R}_{ij}(\rho)} C_{\alpha\beta}^{(2)}(\vec{r}) = C_{\alpha\beta}^{(2)\prime\prime}(|\vec{R}_{ij}(\rho)|)
$$
$$
+ \frac{2}{|\vec{R}_{ij}(\rho)|} C_{\alpha\beta}^{(2)\prime}(|\vec{R}_{ij}(\rho)|). \quad (40)
$$

At constant density this approximation is linear in concentration for a disordered state. The density dependence will be complicated, however. Considering nearest neighbors only, we expect to be near the minimum of $C_{\alpha\beta ij}^{(2)}(\rho)$, subject to the competition between three different terms, and the contributions of the further neighbors, etc. Over a small range the curvature might have a simple form, but it eventually must go to zero in each direction. Because of the sum over the neighbor shells, $\gamma_{\alpha i}$ depends on the state of chemical order as well.

In what limit does this reduce to the lattice gas expansion? For large bulk modulus the density change will be small. However even for fixed density, the dependence of $\gamma_{\alpha i}$ on

the ordering will appear. Thus to regain the lattice gas formula, an additional assumption that $\gamma_{\alpha i} = \gamma_{\alpha d}$ as well as $\rho = \rho_d$ must be made.

V. CONCLUSIONS

The above computation demonstrates how a truncated binary density functional expansion has a form like the terms appearing in the equivalent lattice gas expansion, plus additional terms. These additional terms are the expected ''interaction'' terms from the added density variable, and an additional ideal gas entropy term involving $\ln(\gamma)$. This computation is easily extended, under the same assumptions, to a global strain tensor variable in place of the density variable. The results are the same, except that a particular tensorial form for the ''interaction'' terms involving the traceless portion of the strain tensor is chosen from the possible forms, because $C^{(2)}$ depends on distance only and has no angular part. (This will not be the case if the expansion is extended to $C^{(3)}$.)

In order to use this formalism in situations where the liquid correlation functions are unavailable, some assumption will need to be made in regard to the $\ln(\gamma)$ terms. One way to proceed is to ignore Eq. (15) and make an *ad hoc* assumption for the γ's. In a ''purely harmonic'' approximation we could assume γ to be a constant, independent of density, concentration, and order. In this case it drops out of Eq. (35) entirely. A slightly more ambitious assumption would be to assume that for the ''volume'' of the distribution scales as the volume per atom. In this case the density dependence of the $\ln(\gamma)$ term is numerically very small compared to the other terms, so that in numerical solutions it would be negligible.

This application of this formalism, including a general global elastic strain tensor rather than just the density as considered here, to nickel-rich nickel-vanadium alloys is in progress, under the assumption that the $\ln(\gamma)$ terms are small [5,14]. Work is also planned to apply the formalism to the simpler case of a volume change only in Cu_3Au, where estimates of the change in $\ln(\gamma)$ can be made from embedded atom simulations.

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[14] Truncating the functional expansion at second order in the densities leads to Eq. (35) being second order in δm_i. As in the case of freezing (see Y. Singh [15] for a review of the application of density functional theory to freezing and references), it is desirable to include higher order terms in some way. In the studies of freezing of hard spheres using density functional theory, this has been accomplished either through the inclusion of explicit partial third-order terms [10,11], or through the use of an effective density [8,9], or a weighted density functional theory [13] or effective liquid free energy model approach [12]. In applications of the lattice gas analog of density functional theory, a mean spherical approximation to the third order term [3], or partial third order terms based on the variation of the two point direct correlation function with the disordered concentration [4], have been used. In applying the current formalism, involving both the lattice gas and elastic variables, similar approaches will be needed.

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