Density-Functional Theory of Freezing of Hard-Sphere Mixtures into Substitutional Solid Solutions

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The density-functional theory of freezing is extended to investigate the crystallization of binary hard-sphere mixtures. As the ratio of diameters $\alpha = \sigma_1/\sigma_2$ is lowered, the fluid-solid phase diagram for disordered alloys evolves from a spindle shape ($1 > \alpha > 0.94$) into an azeotropic diagram ($0.94 > \alpha > 0.92$) and finally into a eutectic diagram ($0.92 > \alpha > 0.85$). Below $\alpha = 0.85$, nearly complete immiscibility is predicted, in agreement with the empirical Hume-Rothery rule for metallic alloys.

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In a binary substitutional solid solution, atoms of two chemical species are distributed on a common lattice. The empirical Hume-Rothery rule states that the formation of such disordered metallic alloys is very unlikely if the atomic sizes differ by more than 15%.[1] In this Letter we apply a recently developed density-functional theory of freezing[2] to the simplest possible model of a binary alloy, namely a mixture of hard spheres of diameters σ_1 and $\sigma_2 > \sigma_1$. Such binary hard-sphere systems are known to be completely miscible in the fluid phase for all ratios $\alpha = \sigma_1/\sigma_2$,[3] but from purely geometrical considerations we may expect incomplete miscibility in the solid phase below some critical value of α. The aim of our work is to investigate the dependence of the fluid-solid phase diagram on the ratio α, and to gain a first-principles understanding of the Hume-Rothery rule.

Our starting point is the following exact representation of the Helmholtz free energy density of the solid, $f[\rho]$, viewed as a functional of the local one-particle densities of species ν, $\rho_\nu(\mathbf{r})$:

$$\beta f[\rho] = \sum_\nu \int \frac{d^3r}{V} \rho_\nu(\mathbf{r}) \{ \ln[\Lambda_\nu^3 \rho_\nu(\mathbf{r})] - 1 \} - \sum_\nu \sum_\mu \int \frac{d^3r}{V} \int d^3r' \int_0^1 d\lambda (1-\lambda) C_{\nu\mu}(\mathbf{r}, \mathbf{r}'; [\lambda\rho]) \rho_\nu(\mathbf{r}) \rho_\mu(\mathbf{r}'), \qquad (1)$$

where $\beta = (k_B T)^{-1}$ denotes the inverse temperature, V the total volume, and Λ_ν the de Broglie thermal wavelength of particles of species ν. The first and second terms on the right-hand side of Eq. (1) are the ideal and interaction parts of the free energy, respectively. The latter term involves the partial direct correlation functions $C_{\nu\mu}$, integrated over a linear path in one-particle density space in the manner first introduced by Saam and Ebner[4] (see also Evans[5] for an exhaustive review of density-functional techniques) in their study of classical inhomogeneous systems, and subsequently applied to the freezing problem by Baus and Colot.[2] Freezing of a pure hard-sphere system ($\sigma_1 = \sigma_2$) has been considered by Haymet[6] who used a closely related approach.

In the first step we locate the minima of the free energy (1), corresponding to possible, mechanically stable alloys. This search is greatly simplified by parametrizing the local densities by a set of Gaussians centered around a given lattice $\{\mathbf{R}_j\}$:

$$\rho_\nu(\mathbf{r}) = x_\nu (\gamma_\nu/\pi)^{3/2} \sum_j \exp\{-\gamma_\nu (\mathbf{r} - \mathbf{R}_j)^2\}, \qquad (2)$$

where γ_ν determines the width of the peaks and $x_\nu = \rho_\nu/\rho$ ($\rho = \sum_\mu \rho_\mu$) is the concentration of species ν of mean number density ρ_ν. The Gaussian shape (2) is a reasonable representation of the one-particle density,[7] even for the hightly anharmonic hard-sphere solid, as shown by molecular-dynamics simulations.[8] The lattice sites $\{\mathbf{R}_j\}$ in Eq. (2) are chosen to be those of an fcc lattice, since the density-functional theory predicts the equilibrium structure of the pure ($\alpha = 1$) hard-sphere crystal to be a compact structure.[2,9] The lattice constant a is fixed by the condition that $4/a^3$ equals the total number density ρ of the solid while the width parameters γ_ν will be determined by minimizing of the free energy of the solid at a given temperature T and given mean density ρ_ν. Choice of the one-particle local densities (2) eliminates any consideration of ordered solid alloys with atoms occupying well-defined sublattices, and hence any possible long-range compositional order. However, this does not mean that we are considering completely random alloys; the local densities (2) specify only the mean distribution of atoms of both species on the fcc lattice sites, while short-range order is explicitly taken into account through the direct correlation functions $C_{\nu\mu}$ appearing in Eq. (1). Since at present little is known about these functions in the solid phase, we follow the usual procedure of approximating them by their isotropic fluid counterparts,[10] evaluated at an effective density chosen such that the position of the main peak in the total static structure factor of the fluid mixture at the density coincides with the smallest reciprocal lattice vector of the fcc lattice, $2\pi\sqrt{3}/a$, at the density of the solid, the effective fluid and the solid having the same composition. This prescription has been shown to yield freezing data for the one-component hard-sphere system which are in good agreement with the results of computer simulations.[2,9] Explicit analytic expressions for the $C_{\nu\mu}$ and for the static structure factor of the fluid are obtained from the solution of the Percus-Yevick (PY) equations for hard-sphere mixtures.[11] The PY approximation states that the partial direct (pair) correlation functions vanish outside (inside) the corresponding excluded-volume radii $(\sigma_\nu+\sigma_\mu)/2$; it is known to yield a good description of hard-sphere tures in the fluid phase when compared to computer simulations.[3] With the help of these three approximations, the free energy of the solid relative to that of the fluid can be worked out explicitly and the minimization program can be carried out easily.

Since the temperature scales out for hard spheres, the excess free energy of the mixture depends only on the number concentration of, say, the largest species $(x=x_2)$ and of the total packing fraction $\eta = \pi\rho[(1-x)\sigma_1^3+x\sigma_2^3]/6$. For fixed values of $\alpha = \sigma_1/\sigma_2$ $(1>\alpha>0)$, of x, and of η, the free energy is then minimized with respect to the widths, γ_1 and γ_2. At low densities $(\eta<0.50)$, the free energy exhibits a single minimum corresponding to the fluid phase $(\gamma_1=\gamma_2=0)$. Above a bifurcation value of $\eta\sim 0.50$, the mixture becomes bistable, with one minimum corresponding to the fluid phase and a second minimum associated with a mechanically stable solid phase $(\gamma_1,\gamma_2\neq 0)$. The latter minimum disappears at densities sufficiently high for two spheres to touch (i.e., when $\sigma_{12}=a/\sqrt{2}$). This scenario occurs for all ratios in the range $1>\alpha>0.85$, while for still lower values of α, it becomes increasingly difficult to find a mechanically stable solid phase. In the range $0.9>\alpha>0.85$, the free energy exhibits eventually two minima for nonzero values of γ_1 and γ_2 at high densities; one of the corresponding solid phases is always metastable. The emergence of a critical size ratio for the stability of the solid $(\alpha\simeq 0.85)$ yields the clue for the empirical Hume-Rothery rule.

Once the stable solid phases have been located, we can take the final step and inquire for possible fluid (F)-solid (S) coexistence. At a given temperature we look for solutions of the equilibrium conditions $p^{(S)}=p^{(F)}$ (equal pressures) and $\mu_\nu^{(S)}=\mu_\nu^{(F)}$ (equal chemical potentials for both species, $\nu=1,2$). These equilibrium conditions can be expressed explicitly through relations similar to (1) and are then solved to yield phase diagrams at constant pressure. In practice we switch from the free energy density, f, to the free enthalpy per particle, $g=(f+p)/\rho$, eliminate ρ in favor of the variables p, T, and x by using the equation-of-state $p=p(\rho,T,x)$ for each phase, and determine the compositions $x^{(S)}$ and $x^{(F)}$ of the coexisting phases by a double tangent construction on $g=g(T,p,x)$. The essential results are summarized in the following, and are illustrated by the phase diagrams under atmospheric pressure in Figs. 1–3.

In the range of size ratios $1>\alpha>0.94$ we find a *spindle* phase diagram (see Fig. 1): The spheres are miscible in all proportions in both phases, but the concentration x of large spheres is always slightly higher in the solid. The total packing fraction η remains practically constant along the liquidus and the solidus. Since α differs little from 1, this is an illustration of Vegard's empirical rule stating that the lattice constant a is a linear function of the concentration.[12]

For $0.94>\alpha>0.92$ we find an *azeotropic* phase diagram (Fig. 2). There now exists a range of concentrations where the fluid mixture remains the stable phase for temperatures below the crystallization point of the pure phases. Along the liquidus, $\eta(x)$ exhibits now a pronounced maximum at the azeotrope.

When $0.92>\alpha$ we find a *eutectic* phase diagram (Fig. 3). The free enthalpy of the solid becomes concave for intermediate concentrations, signaling a phase separation in the solid phase. The azeotrope is re-

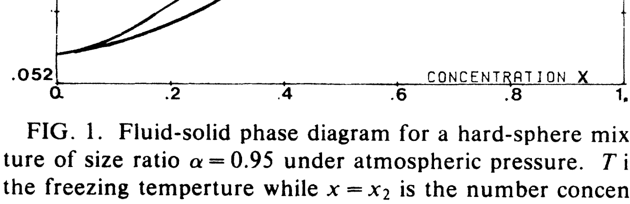

FIG. 1. Fluid-solid phase diagram for a hard-sphere mixture of size ratio $\alpha=0.95$ under atmospheric pressure. T is the freezing temperture while $x=x_2$ is the number concentration of large spheres. Inset: schematic representation of the concentration dependence of the solid and fluid free enthalpies at a given pressure and temperature.

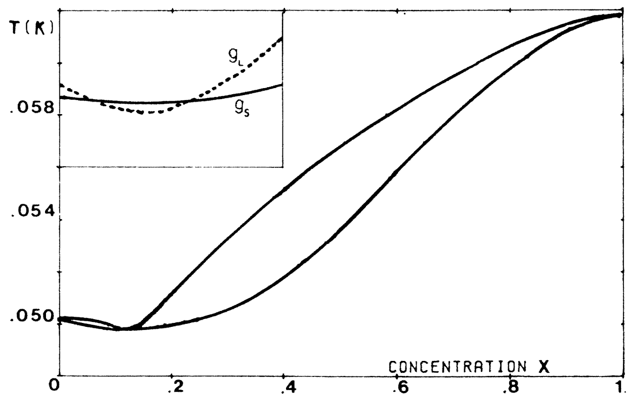

FIG. 2. Same as Fig. 1, but for $\alpha = 0.93$.

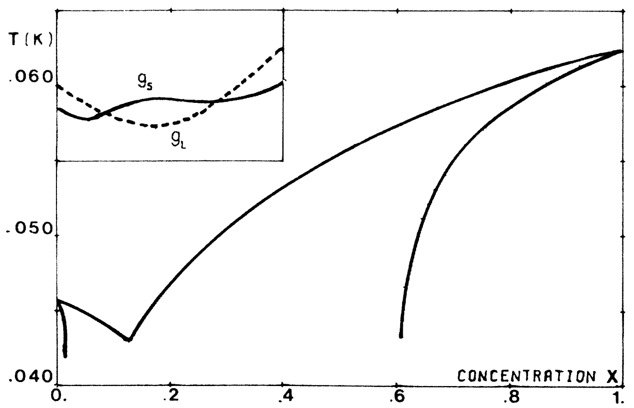

FIG. 3. Same as Fig. 1, but for $\alpha = 0.90$.

placed by a eutectic point. While the solubility of the small spheres in the crystal of large spheres remains quite substantial (about 40%), the solubility of the large in the small spheres is very low (below 5%). When the size ratio is lowered towards $\alpha \simeq 0.85$, it becomes impossible to obtain a mechanically stable solid for a gradually increasing range of intermediate concentrations. The solubility of large spheres in the crystal of small ones shrinks to zero, so that the solid phase separates into a pure crystal of small spheres and a solid rich in large spheres still containing an appreciable fraction (up to about 25%) of small spheres.

Except for this last circumstance, showing that even for $\alpha = 0.85$ the small spheres can still be accommodated in the lattice of larger spheres, with the effect of reducing the freezing temperature, the whole scenario is very reminiscent of the experience one has with real metallic alloys.[12] The departure from the Hume-Rothery rule near $x = 1$ can easily be understood by remembering that the hard-sphere model can only account for the geometric packing aspects of the solubility problem and does not take into account the modification of the electronic band structure in the alloying process. The hard-sphere model is, in that respect, better suited for the study of rare-gas mixtures. Unfortunately only few experimental data on the solid phases of rare-gas mixtures are as yet available. It is nevertheless encouraging that the experimental study of the Ar-Ne mixture ($\alpha = 0.84$) reported by Longuet-Higgins and Widom[13] shows the existence of an Ar-rich solid phase for Ne concentrations up to 20%, which is compatible with the hard-sphere results reported here.

A final remark is in order concerning the temperature scale of the results shown in Figs. 1–3. Since the hard-sphere model does not include the cohesive effect of interatomic attractions, the coexistence temperatures calculated for $p = 1$ atm are unphysically low. This defect is easily remedied by inclusion of a mean-field-type van der Waals contribution to the equation of state of the mixture, as has been successfully done to calculate the melting curve of one-component rare-gas systems.[14] This term leads to physically reasonable values of the freezing temperature and to richer phase diagrams which depend sensitively on the pressure and on the assumed mixing rules for the attractive part of the interatomic potentials. Detailed results of such a calculation are in progress and will be published elsewhere.

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