Phase Behavior and Structure of Binary Hard-Sphere Mixtures

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By integrating out the degrees of freedom of the small spheres in a binary mixture of large and small hard spheres, we derive an explicit effective Hamiltonian for the large spheres. Using the two-body (depletion potential) contribution to this effective Hamiltonian in simulations, we find stable fluid-solid and both metastable fluid-fluid *and* solid-solid coexistence in a mixture with size ratio $q = 0.1$. For $q = 0.05$ the solid-solid coexistence becomes stable. [S0031-9007(98)07074-4]

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Understanding the structure and phase equilibria of binary hard-sphere mixtures is a long-standing problem in liquid state physics. These idealized systems provide a natural reference system for determining the properties of more realistic models of mixtures of simple (atomic) fluids, of colloids and polymers, and of other colloidal systems. A contentious issue, which attracts much attention, is whether fluid-fluid phase separation occurs in this model system. A classic study [1], based on the Percus-Yevick approximation, showed that hard spheres mix at all state points, for any ratio of diameters $q \equiv \sigma_s/\sigma_l$. In 1991, improved integral equation studies provided evidence for a spinodal instability when $q \leq 0.2$ [2]. The main reason for the subsequent interest resides in the fact that any mechanism for a demixing transition in hard-sphere systems must be purely entropic. In Ref. [2] the depletion effect was identified as the mechanism behind the possible instability. This effect, which was first invoked to explain phase separation in colloid-polymer mixtures [3], is based on the idea that clustering of the large spheres allows more free volume for the small ones which may lead to an increase of the entropy. A scaled particle theory for the free volume yielded a fluid-fluid spinodal [4]. The weakness of the integral equation and the free volume theories lies in the sensitivity of the existence and location of the spinodal instability to fine details of the theory [5]. Moreover, experimental work on colloidal systems indicates that any demixing is strongly coupled to the freezing transition [6,7], whereas both types of theories are not designed to deal with solid phases—see Ref. [8], however. One might suppose that the issue could be settled by computer simulations; however, direct simulations of a highly asymmetric binary mixture are prohibited by slow equilibration. It therefore remains an open question as to whether or not (meta)stable fluid-fluid phase separation does occur and, indeed, just what the phase diagram of the binary hard-sphere mixture is when the size ratio q is small.

In this Letter, we take advantage of the large size asymmetry, and integrate out the degrees of freedom of the small spheres to obtain an effective Hamiltonian for the large ones. The depletion effect is now described in terms of effective potentials between the large spheres, and for $q \leq 0.1$ we expect the pairwise contribution to dominate. The pairwise (depletion) potential is essentially attractive, and arises from an unbalanced osmotic pressure of the "sea" of small spheres when the surface-surface separation of two large spheres is $\leq \sigma_s$ [3]. Provided the attraction is sufficiently strong and of sufficient range, it might drive fluid-fluid phase separation—in keeping with the classical van der Waals picture of vapor-liquid separation in a simple fluid. On the other hand, when the range of the attraction is much smaller than that of the repulsion, it is known that the vapor-liquid transition becomes metastable with respect to (w.r.t.) the fluid-solid [9] and that for very short-ranged attraction an isostructural solid-solid transition can appear in the phase diagram of a simple model fluid [10]. Since the range of the attraction in the depletion potential is $\leq \sigma_s$, and that of the repulsion is σ_l, one might hope to find solid-solid, in addition to fluid-fluid and fluid-solid coexistence, in hard-sphere mixtures with $q \leq 0.1$. We investigate *all* of these possibilities using Monte Carlo simulations for the effective one-component fluid.

We consider N_l large and N_s small hard spheres with diameter ratio q in a macroscopic volume V at temperature T. The total Hamiltonian consists of (trivial) kinetic energy contributions and interaction terms $H = H_{ll} + H_{ls} + H_{ss}$. It is convenient to consider the system in the (N_l, z_s, V, T) ensemble, in which the fugacity z_s of the small spheres is fixed. The Helmholtz free energy F of this system can be written as $\exp[-\beta F] = \mathrm{Tr}_l \exp[-\beta H_{\mathrm{eff}}]$, where $H_{\mathrm{eff}} = H_{ll} + \Omega$ is the effective Hamiltonian of the large spheres and $\beta = 1/k_B T$. Here, Ω is the grand potential of the fluid of small spheres in the external field of a fixed configuration of N_l large spheres with coordinates $\{\mathbf{R}_i\}; i = 1, 2, \ldots, N_l$, and is given by $\exp[-\beta\Omega] = \sum_{N_s=0}^{\infty} z_s^{N_s} \mathrm{Tr}_s \exp[-\beta(H_{ls} + H_{ss})]$. The trace Tr_ν is short for $1/N_\nu! \Lambda_\nu^{3N_\nu}$ times the volume integral over the coordinates of the particles of species ν, where Λ_ν is the thermal wavelength.

Once Ω, and thus H_{eff}, are known for all values of z_s, the thermodynamics and the phase behavior of the mixture can be determined. To this end, we expand

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$\exp[-\beta\Omega]$ in terms of the Mayer functions associated with the pair-potentials ϕ_{ls} and ϕ_{ss}. After taking the logarithm, and using standard diagrammatic techniques [11,12], the resulting terms of the diagrammatic expansion of $-\beta\Omega$ can be classified according to the number $n = 0, 1, 2, \ldots, N_l$ of large hard spheres that interact simultaneously with the sea of small spheres, so that $\beta\Omega = \sum_{n=0}^{N_l} \beta\Omega_n$. We give expressions for $\beta\Omega_n$ for $n = 0, 1$, and 2, and argue that higher order (3-body, 4-body, etc.) terms should not be important for highly asymmetric binary hard-sphere mixtures.

$\Omega_0 = -p(z_s)V$ is the grand potential of a pure system of small spheres at fugacity z_s in a volume V, where $p(z_s)$ is the pressure of that system. We can also show that Ω_1/N_l is the grand-potential difference between a system in a volume V at fugacity z_s with and without a large sphere at the origin. An accurate approximation for Ω_1 is given in [13]. This consists of a volume, a surface, and a term K which is independent of σ_l: $\Omega_1/N_l = p(z_s)\pi\sigma_l^3/6 + \gamma(z_s)\pi\sigma_l^2 + K(z_s)$, where $\gamma(z_s)$ is the surface tension of the small hard-sphere fluid at a hard spherical wall of diameter σ_l. Explicit scaled particle results are given for p, γ, and K in Ref. [13]. Within the same formalism, Ω_2 can be written as a sum of pair-potentials $\Omega_2 = \sum_{i<j}^{N_l} \phi_{\rm dep}(R_{ij}; z_s)$, where we can show that $\phi_{\rm dep}$ is the grand potential difference between a sea of small spheres at fugacity z_s containing *two* large spheres separated by a distance $R_{ij} \equiv |\mathbf{R}_i - \mathbf{R}_j|$ and by infinite distance. It follows that $\phi_{\rm dep}$ can be identified with the standard definition of the depletion potential [14,15]. Several theories and approximations exist for $\phi_{\rm dep}$ and these are summarized in Ref. [16]. Recently, Mao *et al.* [17] used a virial expansion to calculate $\phi_{\rm dep}$, within the Derjaguin approximation. For $q = 0.1$ and for values of η_s^r as high as 0.37 their results at third order in η_s^r were in remarkable agreement with those of a simulation [15] for separations in the important depletion range: $\sigma_l < R_{ij} < \sigma_l + \sigma_s$. Here η_s^r is the packing fraction of a reservoir of small hard spheres at fugacity z_s. We use a simpler third order expression, derived in [16], which provides an equally accurate account of the simulation data:

$$\beta\phi_{\rm dep}(R_{ij}) = -\frac{1+q}{2q}\left[3\lambda^2\eta_s^r + (9\lambda + 12\lambda^2)(\eta_s^r)^2 + (36\lambda + 30\lambda^2)(\eta_s^r)^3\right] \quad \text{for } -1 < \lambda < 0, \qquad (1)$$

where $\lambda = R_{ij}/\sigma_s - 1/q - 1$. This form describes a deep and very narrow potential well close to the surface of the large sphere, whose depth increases with increasing η_s^r, followed by a small repulsive barrier. We set $\phi_{\rm dep} = 0$ for $R_{ij} > \sigma_l + \sigma_s$, neglecting any weak oscillations in this range [15,17]; we expect these to be unimportant for the phase behavior of the mixture. Note that the first term in (1) corresponds to the Asakura-Oosawa approximation to $\phi_{\rm dep}$.

In what follows, we set $\Omega_n = 0$ for $n \geq 3$. The neglect of 3-body and higher potentials can be supported by geometric arguments for $q < 0.154$, since then three or more nonoverlapping large spheres cannot simultaneously overlap with a small one [15,18]. Moreover, analysis of simulation data [15] implies that pairwise additivity should be an excellent approximation for $q \leq 0.1$, even for high packing fractions η_l of the large spheres. We thus arrive at the effective one-component Hamiltonian $H_{\rm eff} = H_0 + \sum_{i<j}^{N_l} \phi_{\rm eff}(R_{ij})$, where $H_0 = -p(z_s)(1 - \eta_l)V + \gamma(z_s)\pi\sigma_l^2 N_l + KN_l$ is irrelevant for the phase equilibria, although it does contribute to the pressure of the mixture. The effective pair-potential is $\phi_{\rm eff} = \phi_{ll} + \phi_{\rm dep}$. Note that the formalism of mapping the two-component system onto an effective one-component system is not restricted to hard spheres.

At first sight, one might think that the phase behavior of this effective one-component system can be determined by standard perturbation theory based on the pure hard-sphere reference system. Indeed this was the approach adopted in earlier studies [3,18] of colloid-polymer mixtures based on the Asakura-Oosawa results for $\phi_{\rm dep}$. Using first order theory for $q = 0.1$, we do not find any indication for a fluid-fluid spinodal (see also [16]). However, when simulations are performed using $\phi_{\rm dep}$, we find that the radial distribution function $g(r)$ differs enormously from that of the reference hard-sphere fluid. This is illustrated in Fig. 1, where we plot $g(r)$ for $\eta_l = 0.35$ and $\eta_s^r = 0.25$ [19]. We find that $g(\sigma_l) \sim 42$, which should be compared with the much lower contact value, ~ 3, for the hard-sphere reference system at the same η_l. Similar large contact values, or strong tendencies for clustering, have been observed in previous simulation and integral equation studies [15,20], as well as in experiments on colloidal hard-sphere mixtures [21]. The vast

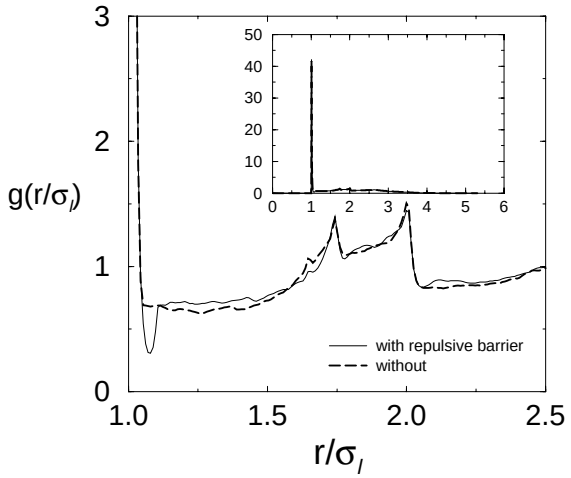

FIG. 1. The radial distribution function $g(r/\sigma_l)$ for the effective one-component system with packing fractions $\eta_l = 0.35$, $\eta_s^r = 0.25$, and size ratio $q = 0.1$ using $\phi_{\rm dep}$ (1), with and without the small repulsive barrier.

difference between $g(r)$ of the reference hard-sphere system and that of the effective system signals the breakdown of perturbation theory, and we thus resort to full numerical simulations for the free energy F of the effective system. Before describing the results, we compare $g(r)$ for a depletion potential with and without the repulsive barrier. Figure 1 shows that the contact value and most other features are not sensitive to the barrier. The small well near $r = 1.07\sigma_l$ does reflect the presence of the barrier, but the free energies calculated from the two potentials differ only slightly. We conclude that small differences in the choice of depletion potential should not have a drastic effect on the resulting phase equilibria.

We calculate F from Monte Carlo simulations using the thermodynamic integration technique [9]. For a given z_s, i.e., a given η_s^r, the integration path starts at a hard-sphere fluid or solid (fcc) at the required η_l, proceeds by gradually switching on the depletion potential (1), and finishes at the full effective one-component system. For the free energy of the hard-sphere reference system, we use the Carnahan-Starling expression for the fluid, and the equation of state proposed by Hall [9] for the solid phase. In the latter case, an integration constant was determined such that the known fluid-solid coexistence of the pure hard-sphere system is recovered [22]. Simulations were performed in a similar fashion to those in Ref. [9]. In Fig. 2, we plot F as a function of η_l at several η_s^r for $q = 0.1$. For $\eta_s^r > 0.06$ we find that the solid branch of F becomes nonconvex, indicative of a spinodal instability. For $\eta_s^r > 0.29$ *another* spinodal instability is found on the fluid branch. This instability can be seen clearly in the inset of Fig. 2, where $\eta_s^r = 0.31$. Note that subtracting a linear function of η_l does not affect the common tangent construction. This simultaneous existence of a fluid-fluid *and* a solid-solid spinodal instability has not been observed before for binary hard-sphere mixtures. We fitted polynomials to F and computed the pressure and chemical potential at each η_l. The densities of two coexisting phases can then be determined by equating the pressures and chemical potentials in the two phases. In Fig. 3, we show the resulting phase diagram. At $\eta_s^r = 0$, we find the usual freezing transition of the pure hard-sphere system. As η_s^r increases, a widening of the fluid-solid transition occurs, implying that a fluid with a low packing fraction of large spheres coexists with a dense crystal. This observation is consistent with results of a perturbation theory [18] and with experiments on colloids, where adding small amounts of small spheres induces a rapid decrease in the lattice constant of the crystal [7]. The results of free energy calculations reveal that both the isostructural solid-solid and the fluid-fluid transitions are metastable with respect to the wide fluid-solid coexistence, although the critical point of the solid-solid spinodal near $\eta_l = 0.63$, $\eta_s^r = 0.06$ is close to the stable fluid-solid phase boundary. In Fig. 3, we also plot experimental state points for a colloidal hard-sphere system with $q \sim 0.1075$ [7]. In order to convert the experimental packing fraction

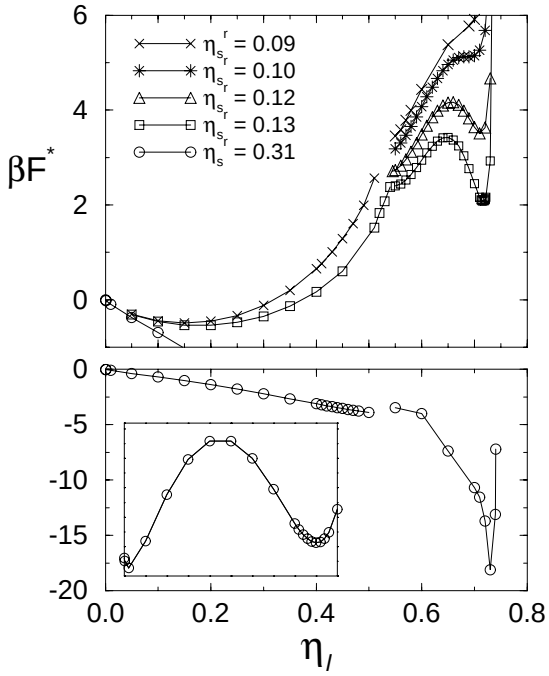

FIG. 2. Reduced free energy $\beta F^* = \beta[F - (\Omega_0 + \Omega_1)]\sigma_l^3/V$ versus η_l for $q = 0.1$ at several η_s^r. The curves for $\eta_l \geq 0.54$ are the solid branches, while the curves for lower η_l are the fluid branches. Note the difference in scale for $\eta_s^r = 0.31$. For clarity, we subtracted a linear fit in η_l to the data for $\eta_s^r = 0.31$ (see inset).

of small spheres to η_s^r, we used $N_s = -\partial\beta F/\partial \log z_s \sim -\partial\beta(\Omega_0 + \Omega_1)/\partial \log z_s$, and scaled particle expressions for $p(z_s)$ and $\gamma(z_s)$ [13]. (The details and accuracy of this procedure will be discussed elsewhere.) The following correlations are striking: (i) The crosses [denoting a (meta)stable fluid state] and the dashed line (the experimental estimate of the binodal) are, for $\eta_s^r < 0.12$, close to our stable fluid phase boundary. At higher η_s^r, there is a substantial deviation. Further details and a discussion of the origin of this deviation will be given elsewhere [12]; (ii) the open squares, denoting state points that correspond to fluid-solid coexistence, are well inside our fluid-solid coexistence region, and these appear to extend to large values of η_l provided there is no intervening metastable fluid-fluid or solid-solid binodal; (iii) the triangles, denoting the glassy states, are all within or close to the metastable fluid-fluid or solid-solid binodal. A similar correlation between the formation of nonequilibrium phases and the presence of metastable phase coexistence has been observed in experiments on colloid-polymer mixtures [23]. We also note that the state point ($\eta_l = 0.1$, $\eta_s^r \sim 0.367$) investigated in the effective one-component simulations of Ref. [15] lies well inside our metastable fluid-fluid binodal, which might explain the observed two-stage demixing dynamics. It is tempting to argue that the rapid clustering at the first stage reflects the fluid-fluid binodal, while the subsequent slow relaxation of clusters reflects the ultimate crystallization process.

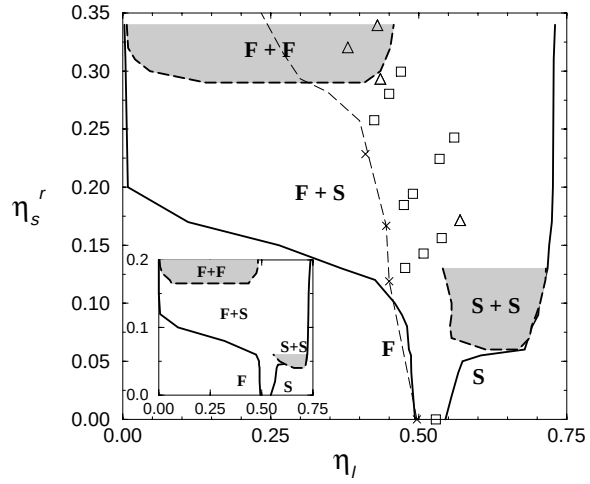

FIG. 3. Phase diagram for $q = 0.1$ and $q = 0.05$ (inset) in the $\eta_s^r - \eta_l$ plane. F and S denote the stable fluid and solid (fcc) phase. $F + S$, $F + F$, and $S + S$ denote, respectively, the stable fluid-solid, the metastable fluid-fluid, and (meta)stable solid-solid coexistence regions. The triangles, open squares, and crosses are experimental state points taken from Ref. [7], representing glassy states, fluid-solid demixing, and (meta)stable fluid, respectively. The thin dashed line denotes the fluid branch of the experimental binodal [7].

We used the same procedures to compute the phase diagram for $q = 0.05$, which is also shown in Fig. 3. The most striking feature is the downward shift of the solid-solid binodal compared to that of the fluid-solid. This gives rise to a stable solid-solid coexistence in a small regime, where $\eta_s^r \sim 0.05$, whose critical point is shifted towards close packing. Such a trend is consistent with studies [10] for a square-well fluid in which the width of the well is reduced. Note that decreasing q is equivalent to decreasing the range of the attraction. Because the fluid-solid coexistence also shifts down as q is decreased, fluid-fluid coexistence remains metastable at $q = 0.05$, and we find that for $\eta_s^r \geq 0.11$ coexistence occurs between an extremely dilute fluid and a solid whose density approaches that of close packing ($\eta_l^{\mathrm{cp}} = 0.7405$). Note that for $q \to 0$ the phase diagram should approach that of the sticky-sphere model [15]. This model shows for finite T, equivalent to $\eta_s^r > 0$, coexistence of an infinitely dilute gas and a close-packed solid, and a metastable solid-solid transition at close packing [10].

Finally, we note that recent simulations for the actual two-component system have been carried out [20] for several q for the single state point $\eta_l = \eta_s = 0.1215$, which we convert to $\eta_s^r \sim 0.136$. The results revealed no, weak, and strong tendencies to demix for $q = 0.1$, 0.05, and 0.033, respectively. According to Fig. 3 for $q = 0.05$, the clustering observed in [20] should be associated with crystallization rather than with fluid-fluid demixing, since the state point falls outside the fluid-fluid but inside the fluid-solid binodal.

In conclusion, we have shown that our effective one-component treatment predicts that a binary hard-sphere mixture with size ratio $q = 0.10$ exhibits a stable fluid-solid, a metastable fluid-fluid, and a metastable solid-solid coexistence. For $q = 0.05$, the solid-solid coexistence becomes stable w.r.t. fluid-solid near $\eta_s^r = 0.05$, while the fluid-fluid coexistence remains metastable.

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