

Direct Simulation of the Phase Behavior of Binary Hard-Sphere Mixtures: Test of the Depletion Potential Description

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We study the phase behavior of additive binary hard-sphere mixtures by *direct* computer simulation, using a new technique which exploits an analog of the Gibbs adsorption equation. The resulting phase diagrams, for size ratios $q = 0.2, 0.1$, and 0.05 , are in remarkably good agreement with those obtained from an effective one-component Hamiltonian based on pairwise additive depletion potentials, even in regimes of high packing (solid phases) and for relatively large size ratios ($q = 0.2$) where one might expect the approximation of pairwise additivity to fail. Our results show that the depletion potential description accounts for the key features of the phase equilibria for $q \leq 0.2$. [S0031-9007(98)08128-9]

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Understanding the stability of colloidal mixtures is relevant for many industrial applications, e.g., paint, ink, etc., but is also interesting from a fundamental statistical physics point of view [1]. Surprisingly, the phase behavior of even the simplest model colloid mixture, i.e., large and small hard spheres, is still not established and remains a topic of much debate. For instance, it is still unclear whether a (stable) fluid-fluid demixing transition exists for any additive binary hard-sphere mixture. The celebrated Percus-Yevick approximation [2] predicts no fluid spinodal instability, while other integral equation approximations do [3,4], although at completely different statepoints. Experiments on colloidal hard-sphere mixtures suggest that the demixing transition is strongly coupled to the freezing transition, although sedimentation effects preclude definite conclusions [5]. Theoretical approaches that consider both the fluid and solid phase have also been inconclusive. First, a phenomenological free volume theory predicts a fluid-fluid demixing transition that is metastable with respect to a broad fluid-solid coexistence region [6]. Here “broad” refers to the width of this coexistence region in terms of the difference between the packing fractions of the larger species in the two coexisting phases. Another scenario is reported in Ref. [7] where a virial expansion is used for the fluid phase and a density functional approximation for the solid. This yields a narrow freezing transition for $q = 0.1$, a broad one for $q = 0.2$, and a fluid-fluid spinodal instability at such high pressures that it is argued to be metastable. Yet another theoretical treatment predicts a narrow fluid-solid coexistence for $q \rightarrow 0$ [8]. The calculated phase behavior is thus very sensitive to the details of the approximations involved in the above approaches.

An alternative approach to asymmetric binary hard-sphere mixtures stems from the analogy with colloid-polymer mixtures. The properties of such mixtures have been described successfully in terms of the so-called depletion potential ϕ_{dep} which arises between a pair of (large)

colloidal particles due to the presence of a “sea” of (small) polymers. This depletion potential is essentially attractive, and was derived by Asakura and Oosawa and independently by Vrij for the case of ideal polymers [9]. As it is generally accepted that the stability of binary mixtures is determined by these depletion potentials, several groups attempted to measure them directly in experiments [10]. Moreover, explicit theoretical expressions for ϕ_{dep} have been derived by several groups [11,12] and these have been tested against simulations [4,13]. In this Letter we show that phase diagrams calculated using an effective pairwise potential $\phi_{\text{eff}} = \phi_{\text{ll}} + \phi_{\text{dep}}$, where ϕ_{ll} is the hard-sphere potential, agree well with those determined by direct simulation of the true binary hard-sphere mixture for $q = 0.2, 0.1$, and 0.05 . Our results provide the first justification for the effective depletion potential description of phase equilibria.

We consider N_l large and N_s small hard spheres in a macroscopic volume V at temperature T . The total Hamiltonian consists of kinetic energy contributions and interaction terms $H = H_{\text{ll}} + H_{\text{ls}} + H_{\text{ss}}$. It is convenient to consider the system in the (N_l, V, z_s) ensemble, in which the fugacity z_s of the small spheres is fixed; the packing fraction of the corresponding reservoir is denoted η_s^r and we omit the explicit T dependence. The appropriate thermodynamic potential $F(N_l, V, z_s)$, from which the phase behavior can be deduced as in Ref. [14], is defined by

$$\exp[-\beta F] = \text{Tr}_l \sum_{N_s=0}^{\infty} z_s^{N_s} \text{Tr}_s \exp[-\beta H], \quad (1)$$

where 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 , and where Λ_ν is the thermal wavelength and $\beta = 1/k_B T$. F is the Helmholtz free energy of an effective one-component large-sphere system described by a z_s -dependent effective Hamiltonian H_{eff} , viz. $\exp[-\beta F] = \text{Tr}_l \exp[-\beta H_{\text{eff}}]$ with

$H_{\text{eff}} = H_{ll} + \Omega$. The physical meaning of Ω is the grand potential of the sea of small spheres in the presence of the N_l large spheres at fixed positions [14]. By neglecting three- and more body terms in H_{eff} and using accurate (but empirical) expressions for the depletion potential ϕ_{dep} , we determine F for fixed z_s and packing fraction $\eta_l = (\pi/6)\sigma_l^3 N_l/V$ by standard thermodynamic integration using Monte Carlo simulations [14]. The resulting phase diagrams, which follow from common tangent constructions, are shown by the solid lines in Fig. 1. These calculations predict the existence of a fluid-fluid demixing transition for $q = 0.1$ and 0.05 , although this is metastable with respect to the fluid-solid transition [14]. Perhaps more surprisingly, they also yield a stable isostructural solid-solid transition for $q = 0.05$, and a metastable one for $q = 0.1$. For $q = 0.2$ the effective one-component calculations predict only a fluid-solid transition that becomes broader for larger η_s^r . Note, however, that these results are not exact, since three- and higher body interactions are neglected. One might expect this approximation to break down at sufficiently high densities (e.g., in the solid phase) or for less extreme size ratios (e.g., $q > 0.154$, where three nonoverlapping large spheres can overlap with a small one [15]), thereby casting doubt on the specific predictions (in particular, those for the solid-solid transition). Moreover, even the potential ϕ_{dep} used in the simulations is approximated by an empirical form that does not take into account the longer-ranged oscillations [14]. To the best of our knowledge these approximations—and therefore the depletion picture as a whole—have never been tested directly by a comparison with results of a full treatment of true binary mixtures. Given the richness of the predicted phase diagrams and the experimental and computational effort that is being put into the determination of the depletion potential, it seems both important and timely to perform such a test. It has been argued by many authors (including the present) that direct simulations are not feasible for highly asymmetric binary hard-sphere mixtures because of ergodicity problems. However, results of Fig. 1 show such interesting phase behavior at (surprisingly) low η_s^r that we were motivated to perform direct simulations in this regime. Note that direct simulations have recently been performed in Ref. [16], but their new algorithm precludes a study of the state points of interest here ($\eta_l + \eta_s^r > 0.25$).

The scheme we use to calculate the “exact” phase diagrams of binary hard-sphere mixtures by direct simulation employs the identity

$$\beta F(N_l, V, z_s) = \beta F(N_l, V, z_s = 0) + \int_0^{z_s} dz_s' \left[\frac{\partial \beta F(N_l, V, z_s')}{\partial z_s'} \right]. \quad (2)$$

The system at $z_s = 0$ is the pure system of large hard spheres, and hence the first term of the right-hand side of

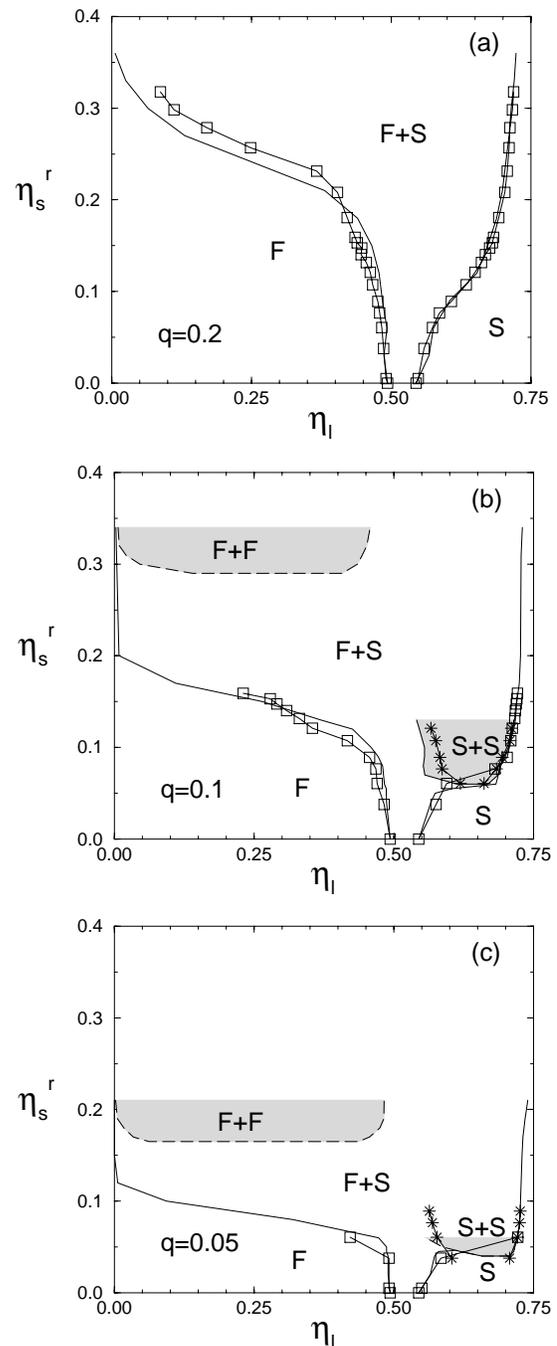


FIG. 1. Phase diagram of binary hard-sphere mixtures with size ratios (a) $q = 0.2$, (b) $q = 0.1$ and (c) $q = 0.05$ as a function of the large-sphere packing fraction η_l and the small sphere reservoir packing fraction η_s^r . F and S denote the stable fluid and solid (FCC) phase. $F + S$, $F + F$, and $S + S$ denote, respectively, the stable fluid-solid, the metastable fluid-fluid, and the (meta)stable solid-solid coexistence region. The solid and dashed lines are the effective one-component results, the squares and the asterisks (joined by lines to guide the eye) denote, respectively, the fluid-solid and the solid-solid transition obtained from direct simulations of the true binary mixture with $N_l = 32$ large spheres.

Eq. (2) is given accurately by Carnahan-Starling [17] in

the fluid phase and by Hall [18] in the solid phase. In the latter case, an integration constant was chosen such that the known fluid-solid coexistence of the pure hard-sphere system is recovered [19]. The integrand in the second term can be rewritten using Eq. (1) as

$$\left[\frac{\partial \beta F(N_l, V, z_s)}{\partial z_s} \right] = - \frac{\langle N_s \rangle_{z_s}}{z_s}, \quad (3)$$

where $\langle N_s \rangle_{z_s}$ denotes the average number of small particles in the (N_l, V, z_s) ensemble. This quantity can be measured directly in a grand-canonical simulation of the ‘‘adsorption’’ of small spheres from a reservoir at fugacity z_s onto a system of N_l large spheres in a volume V .

Before discussing the results of these direct simulations (Fig. 1), a few remarks are in order. First, the scheme proposed in Eqs. (2) and (3) is merely a bulk analog of using the Gibbs adsorption equation to determine the surface tension, where $\langle N_s \rangle_{z_s}$ plays the role of the adsorption, F that of the surface tension, and where N_l , V , and q characterize the ‘‘substrate.’’ Second, it is important to realize that $\langle N_s \rangle_{z_s}$ is *not* identical to the unweighted average adsorption from the reservoir onto a system of *static* large hard spheres, since not all configurations of large spheres carry the same statistical weight. In fact, this weight is proportional to $\exp[-\beta H_{\text{eff}}]$, a quantity that is not known exactly as it involves empirical pair potentials and unknown higher-order interactions, as we have seen above. Consequently, the grand-canonical simulations that measure $\langle N_s \rangle_{z_s}$ must be combined with a *simultaneous* canonical average over the large-sphere configurations. This requirement still leads to ergodicity problems at high η_s^r , although the upperbound, which depends on N_l , V , and q , is high enough to permit us to study interesting regimes. Third, the requirement to perform a simultaneous canonical average over the large spheres in the calculation of $\langle N_s \rangle_{z_s}$ also points to a shortcoming in the free volume approach to asymmetric binary mixtures. The key quantity in this approach is $\alpha \equiv \eta_s / \eta_s^r$, where the packing fraction of the small spheres is defined by $\eta_s = (\pi/6) \sigma_s^3 \langle N_s \rangle_{z_s} / V$. If it is assumed that α (< 1) depends on η_l and q but is independent of z_s , and we employ the scaled particle expression for this quantity, we recover the free volume approach [6] from Eqs. (2) and (3). However, this scaled particle expression identifies α with the probability to insert a small sphere in the pure large-sphere system, and thus assigns an equal statistical weight to all (nonoverlapping) large-sphere configurations. This shortcoming can (formally) be remedied by realizing that the ‘‘free volume fraction’’ α is not an intrinsic property of the pure large-sphere system, as assumed in, e.g., Ref. [6], but also depends on the thermodynamic state of the reservoir of small ones, i.e., $\alpha = \alpha(\eta_l, q, z_s)$. Actually, the z_s dependence of α is a manifestation of the fact that not all large-sphere configurations carry the same statistical weight,

and this is crucial for a proper description of the depletion mechanism.

We now return to the calculation of F from Eqs. (2) and (3). Typical data are presented in Fig. 2, where we plot η_s as a function of η_s^r as measured in a simulation with $N_l = 32$ and $q = 0.1$ for several η_l . Here we converted z_s into η_s^r using the Carnahan-Starling expression $z_s(\sigma_s/\Lambda_s)^3 = (6\eta_s^r/\pi) \exp[(8\eta_s^r - 9\eta_s^{r2} + 3\eta_s^{r3})(1 - \eta_s^r)^{-3}]$, which is essentially exact in the regime of interest. Although $N_l = 32$ may seem too small a number to perform reliable simulations, one should recognize that (i) the pure large-sphere free energy (at $z_s = 0$) is taken from accurate independent sources, and (ii) the maximum value of $\langle N_s \rangle_{z_s}$ is about 5×10^4 due to the small size ratio. For comparison we also plot η_s as predicted by the free volume approach of Ref. [6]; these are straight lines. As expected, agreement with results of direct simulations becomes worse with increasing η_s^r for every value of η_l . Moreover, the differences between simulation and theory begin at lower η_s^r when η_l is higher. In particular, the difference for $\eta_l = 0.1$ increases dramatically at $\eta_s^r \approx 0.15$, which is close to the fluid-solid transition. This is a direct manifestation of the depletion mechanism, that allows more free volume (and hence a higher η_s) because of clustering of the large ones. This part of the depletion effect is not contained in the free volume approach.

Using the simulation data for η_s , we calculate $F(N_l, V, z_s)$ from Eq. (2) by numerical integration. Once F is known we employ common tangent constructions at fixed z_s to obtain the phase boundaries shown by the symbols in Fig. 1 [14]. The main observation is the strikingly good overall agreement with the effective one-component

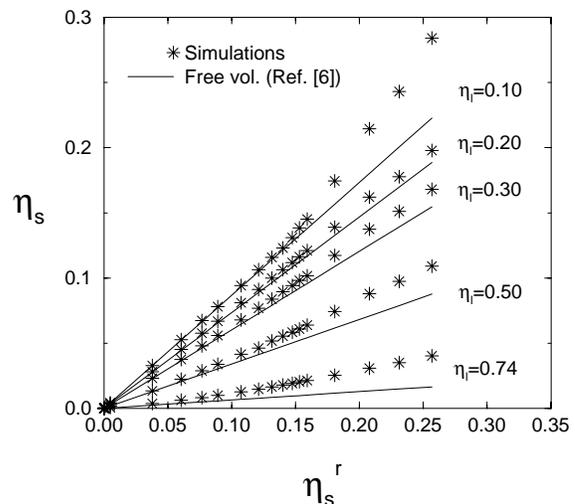


FIG. 2. The small sphere packing fraction η_s , of a hard-sphere mixture with size ratio $q = 0.10$ versus that of the reservoir η_s^r for several large sphere packing fractions η_l . The asterisks denote simulation data while the full lines denote the results of the free volume approach [6].

results for all three values of the size-ratio q . Such good agreement throughout the fluid-solid coexistence curve for $q = 0.2$ and at high η_l for $q = 0.1$ and 0.05 is rather unexpected, as one might expect the depletion picture to break down in these regimes. The only significant difference is that the isostructural solid-solid transition for $q = 0.1$ at $\eta_s^r \sim 0.06$ turns out to be stable with respect to fluid-solid coexistence, in contrast to the effective one-component prediction. The present results provide further evidence for a fluid-solid coexistence broadening with increasing η_s^r for all q , and do not support the narrowing predicted by some theoretical approaches [7,8]. Unfortunately, the ergodicity problems prevented us from reaching the fluid-fluid demixing regime by direct simulation, so that this feature of the effective one-component results could not be tested. Nevertheless, the quantitative agreement at the accessible values of η_s^r does not give any indication that breakdown of the depletion potential picture will occur at higher η_s^r .

In conclusion, we have studied the free energy of asymmetric binary hard-sphere mixtures by direct simulation, and compared the resulting phase diagrams with those obtained from an approximate effective one-component Hamiltonian. These two approaches can be seen as complementary, in the sense that the latter is based on the free energy cost H_{eff} to “insert” large spheres at fixed positions into a sea of small ones, while the former can be described in terms of the adsorption of the small spheres onto a system of freely moving large ones. These two approaches yield results in surprisingly good agreement for size ratios $q = 0.2, 0.1,$ and 0.05 , even at high packing fractions η_l corresponding to the solid phase. Our results provide strong support for the pairwise depletion potential description of phase equilibria given in our earlier paper [14]. In particular, we confirm our earlier prediction of an isostructural solid-solid transition for $q = 0.1$ and 0.05 , which is now found to be stable for both $q = 0.1$ and 0.05 . We also give evidence for a broadening of the fluid-solid coexistence as η_s^r increases. Our present approach should be relevant for studies of other asymmetric mixtures (e.g., nonspherical, charged, polydisperse, or flexible particles) for the following reasons: (i) The scheme, which is reliable and efficient, is based on an analog of the Gibbs adsorption equation that can be generalized to study the phase behavior of other asymmetric mixtures; (ii) the good agreement between the results of direct simulations and the depletion potential approach indicates that the three- and more body terms, which are generally difficult to obtain, are relatively unimportant for small values of q . This justifies, *a posteriori*, the experimental, numerical, and theoretical effort spent on the determination of the effective pair potential for various systems. Note that the depletion potential approach not only provides physical insight into the phase behavior of the mixture and the nature of the pair correlation function $g_{ll}(r)$ [14], but is also computationally more tractable than a treatment of the

true mixture. A word of caution is appropriate here, since the importance of the effective pair potential implies the need for an accurate one. In the present hard-sphere case the theoretical expressions employed in Ref. [14] for the depletion potential agree well, but probably fortuitously well at high η_s^r , with simulations [12]. Before embarking upon generalizations, it is necessary to understand better this fortuitous agreement.

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