Phase Separation of Asymmetric Binary Hard-Sphere Fluids

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On the basis of thermodynamically self-consistent integral equations for the pair structure it is shown that dense binary mixtures of hard spheres, of diameters σ_1 and σ_2, phase separate when the size ratio σ_1/σ_2 is less than 0.2, and the partial packing fractions of the two species are comparable.

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Phase separation of binary liquid or fluid mixtures is a very common thermodynamic phenomenon, even in simple atomic or molecular systems governed by excluded-volume and van der Waals interactions. Miscibility gaps in such simple mixtures are traditionally believed to be induced by the van der Waals attractions which, in certain cases, favor homocoordination over heterocoordination. It has, however, become clear from recent experimental and theoretical investigations of binary fluid mixtures at high temperatures and pressures, where attractive forces between molecules become negligible, that phase separation may be induced by purely repulsive interactions.[1,2] These findings naturally raise the question whether the simplest possible model for such mixtures, namely, a binary mixture of hard spheres of diameters $\sigma_1 \neq \sigma_2$, may exhibit phase separation in the fluid phase. Ever since Lebowitz and Rowlinson[3] showed that within the Percus-Yevick (PY) approximation, which may be solved analytically for fluid multicomponent hard-sphere systems,[4] such mixtures are completely miscible for all concentrations and size ratios, the generally accepted belief is that binary hard-sphere fluids never phase separate.

In this Letter we present strong evidence to the contrary, namely, that for highly asymmetric hard-sphere mixtures, such that the size ratio $y=\sigma_1/\sigma_2$ differs considerably from 1, phase separation sets in for packing fractions typical of liquids. We consider a binary system of N_1 spheres of diameter σ_1 and N_2 spheres of diameter $\sigma_2 > \sigma_1$ $(0<y<1)$ in a volume V. The partial packing fractions are $\eta_\alpha = \pi\rho_\alpha\sigma_\alpha^3/6$ $(\alpha=1,2)$, where $\rho_\alpha = N_\alpha/V$ is the number density of species α; $\rho=\rho_1+\rho_2$ and $\eta=\eta_1+\eta_2$ denote the total density and packing fraction. The pair structure of the mixture is described by three partial pair distribution functions $g_{\alpha\beta}(r)$ and their Fourier transforms, the partial structure factors $S_{\alpha\beta}(k)$. Let $\rho_{\mathbf{k}}^\alpha$ denote a Fourier component of the partial microscopic density of species α. Density and concentration fluctuations in binary mixtures are conveniently characterized by the three structure factors $S_{nn}(k)$, $S_{nc}(k)$, and $S_{cc}(k)$ correlating linear combinations of the partial densities,[5] namely, $\rho_{\mathbf{k}}^n = \rho_{\mathbf{k}}^1 + \rho_{\mathbf{k}}^2$ and $\rho_{\mathbf{k}}^c = x_2\rho_{\mathbf{k}}^1 - x_1\rho_{\mathbf{k}}^2$, where $x_\alpha = N_\alpha/N$. Phase separation is signaled by a strong enhancement of concentration fluctuations which lead to the divergence of the long-wavelength $(k\to 0)$ limits of the structure factors $S_{\alpha\beta}(k)$ [where $\alpha(\beta)=1,2$ or n,c], when the spinodal line, which marks the limit of thermodynamic stability, is approached. In particular, according to elementary fluctuation theory,[5]

$$\lim_{k\to 0} S_{cc}(k) = \lim_{k\to 0}\frac{1}{N}\langle \rho_{\mathbf{k}}^c \rho_{-\mathbf{k}}^c\rangle = \frac{Nk_BT}{(\partial^2 G/\partial x_1^2)_{N,P,T}}, \tag{1}$$

where G denotes the Gibbs free energy, which turns from a concave to a convex function of the concentration x_1 on the spinodal. The pair structure may, in principle, be computed "exactly" by numerical simulation (Monte Carlo or molecular dynamics).[6,7] For highly asymmetric size ratios $(y \ll 1)$, in which we are interested here, configuration sampling of mixtures where both species have comparable volume fractions $(\eta_1 \simeq \eta_2$ and hence $x_2 \ll x_1$ if $y \ll 1)$ runs into severe ergodicity problems, even for a ratio of $\frac{1}{3}$,[8] thus precluding the numerical exploration of more extreme size ratios.

For that reason we have turned to the numerical solution of thermodynamically self-consistent integral equations to explore the regime $y \ll 1$ and $\eta_1 \simeq \eta_2$. Integral equations supplement the coupled Ornstein-Zernike equations, relating the total and direct correlation functions $h_{\alpha\beta}(r) = g_{\alpha\beta}(r) - 1$ and $c_{\alpha\beta}(r)$, by approximate closure relations.[9] The familiar PY closure reads, for hard spheres,

$$g_{\alpha\beta}(r) = \Theta(r-\sigma_{\alpha\beta})[1+\gamma_{\alpha\beta}(r)],$$

where $\Theta(x)$ denotes the Heaviside step function, $\sigma_{\alpha\beta} = (\sigma_\alpha + \sigma_\beta)/2$, and the function $\gamma_{\alpha\beta}(r) = h_{\alpha\beta}(r) - c_{\alpha\beta}(r)$ is continuous at contact $(r=\sigma_{\alpha\beta})$. The partial inverse compressibilities, calculated directly from the $k\to 0$ limits of the Fourier transforms of the direct correlation functions, according to

$$\left(\frac{\partial \beta P}{\partial \rho_\alpha}\right)_{\rho_\alpha} = 1 - \sum_\beta \rho_\beta \hat{c}_{\alpha\beta}(k=0), \tag{2}$$

differ from those obtained by numerical differentiation of the virial pressure

$$\frac{\beta P}{\rho} = 1 + \frac{2\pi\rho}{3}\sum_\alpha\sum_\beta x_\alpha x_\beta \sigma_{\alpha\beta}^3 g_{\alpha\beta}(\sigma_{\alpha\beta}) \tag{3}$$

with respect to the partial densities ρ_α. In order to overcome this deficiency, generalized closures incorporate one (or several) parameter that is adjusted in order to enforce thermodynamic consistency. One of these closures, due to Ballone *et al.*[10] (BPGG), assumes that

$$g_{\alpha\beta}(r) = \Theta(r - \sigma_{\alpha\beta})\exp\{[1 + s\gamma_{\alpha\beta}(r)]^{1/s} - 1\}\,,$$

where the single parameter s is varied until the two estimates of the *total* inverse compressibility, $(\partial\beta P/\partial\rho)_{x_1}$, based on Eqs. (2) and (3), coincide. Another self-consistent closure is due to Rogers and Young[11] (RY); in its simplest version, applicable to binary mixtures,[12] it reads

$$g_{\alpha\beta}(r) = \Theta(r - \sigma_{\alpha\beta})\left[1 + \frac{\exp\{\gamma_{\alpha\beta}(r) f_{\alpha\beta}(r)\} - 1}{f_{\alpha\beta}(r)}\right],$$

where the switching functions $f_{\alpha\beta}(r)$ are chosen to be of the form $1 - \exp(\xi_{\alpha\beta} r)$, with $\xi_{\alpha\beta}$ assumed to be of the simple scaling form $\xi_{\alpha\beta} = \xi/\sigma_{\alpha\beta}$; the RY closure depends thus on a single dimensionless parameter ξ which is adjusted as in the BPGG case. An improved version of the RY closure[13] (RY2) allows for two adjustable parameters, ξ_{11} and ξ_{22}, in order to satisfy the two thermodynamic consistency conditions associated with the partial (rather than the total) inverse compressibilities (2); ξ_{12}^{-1} is chosen equal to $(\xi_{11}^{-1} + \xi_{22}^{-1})/2$. These various closures have been extensively tested for a variety of fluid systems[10-13] and turn out to lead to very accurate structural and thermodynamic results, particularly in the case of purely repulsive pair potentials.

Using Gillan's hybrid algorithm,[14] we have solved the BPGG, RY, and RY2 integral equations numerically for size ratios $y = 0.5$, 0.2, 0.15, and 0.1; the PY equation was also solved with the same code and the results compared to the known exact solution,[4] to provide a stringent test of the accuracy of the numerical procedure. This test is particularly useful in view of the very rapid variation of $g_{22}(r)$ near contact, where this function takes on very large values.[15,16]

The phase behavior of fluid mixtures is normally studied at constant pressure, e.g., by calculating G as a function of concentration x_1, for fixed pressure and temperature. This procedure is very cumbersome when integral equations are used, since these yield the pressure as output, for given values of concentration and density. On the other hand, we expect a continuum limit to hold for $y \ll 1$, when the small spheres may be considered as forming a fluid occupying the volume $V' < V$ left by the large spheres; the total pressure should then be essentially equal to that of a one-component hard-sphere fluid of packing fraction $\eta_1' = \pi N_1 \sigma_1^3/6V'$, the contribution of the large spheres being negligible, since $N_2 \ll N_1$. Consequently, we have solved the integral equations for fixed η_1' and increasing η_2, a situation typically achieved by adding colloidal particles to a concentrated suspension in an incompressible solvent.

There remains to relate the effective η_1' to the input packing fractions η_1 and η_2. Clearly, $V - N_2\pi(\sigma_1 + \sigma_2)^3/6 < V' < V - N_2\pi\sigma_2^3/6$, and hence $\eta_1/(1-\eta_2) < \eta_1' < \eta_1/(1 - \alpha\eta_2)$, where $\alpha = (1+y)^3$; the two bounds coincide in the continuum limit $y \to 0$. For small, but finite values of y, V' may be calculated from the exact relation $V' = V\exp[\beta\mu_1^{\mathrm{ex}}(\eta_1 = 0)]$ (Ref. 17) and from the scaled particle[18] estimate of the chemical potential of species 1 in an infinitely dilute ($\eta_1 = 0$) solution of these spheres in a fluid of large spheres of packing fraction η_2. An elementary calculation leads to the following desired result:

$$\eta_1' = \frac{\eta_1}{1-\eta_2}\exp\left(\frac{3\eta_2}{1-\eta_2}y + \frac{3\eta_2}{(1-\eta_2)^2}\left[1 + \frac{\eta_2}{2}\right]y^2 + \frac{\eta_2 + \eta_2^2 + \eta_2^3}{(1-\eta_2)^3}y^3\right). \tag{4}$$

When $y \ll 1$ (i.e., $\alpha \simeq 1$) and/or η_2 is not too large, the value of η_1' calculated from (4) is very close to the upper bound, $\eta_1' \sim \eta_1/(1 - \alpha\eta_2)$.

Figure 1 shows the reduced pressure $P^* = P\sigma_1^3/k_B T$ vs η_2 for η_1', calculated from (4), fixed at the value $\eta_1' = 0.4$; the results from the PY, RY, and BPGG integral equations are shown for size ratios $y = 0.5$, 0.2, and 0.1. The pressure is seen to drop in all cases, but more and more slowly as y decreases; in the continuum limit $y = 0$, P^* would be constant. Thus working at constant η_1' is practically equivalent to maintaining a constant pressure, for sufficiently small y. For $y = 0.5$, the RY and BPGG results are indistinguishable, and go through a minimum for $\eta_2 \simeq 0.36$. For $y = 0.2$ and 0.1, P^* varies almost linearly with η_2; the BPGG and RY results coincide within 1%. In all cases the PY virial pressures lie below the previous results, whereas the pressures calculated from the compressibility (2) (not shown) would lie above.

However, a more detailed analysis of the PY predictions reveals some severe discrepancies compared to the results of the self-consistent integral equations. As already mentioned, the contact value $g_{22}(\sigma_2)$ [which does not affect the pressure much, due to the x_2^2 factor in Eq. (3)] increases rapidly as $y \to 0$. This increase is strongly underestimated by PY theory, which predicts a slow $1/y$ divergence;[16] for example, the PY, BPGG, RY, and RY2 closures predict $g_{22}(\sigma_2) = 18.73$, 97.38, 126.20, and 247.53, respectively, for $y = 0.1$, $\eta_1' = 0.4$, $\eta_2 = 0.04$. This means that the effective "stickiness" of the large spheres, an osmotic depletion effect,[15,16] is enhanced by the thermodynamically self-consistent closures.

This enhanced stickiness may be the physical origin of the key result of our calculations, namely, the unexpected phase separation predicted by the RY and BPGG clo-

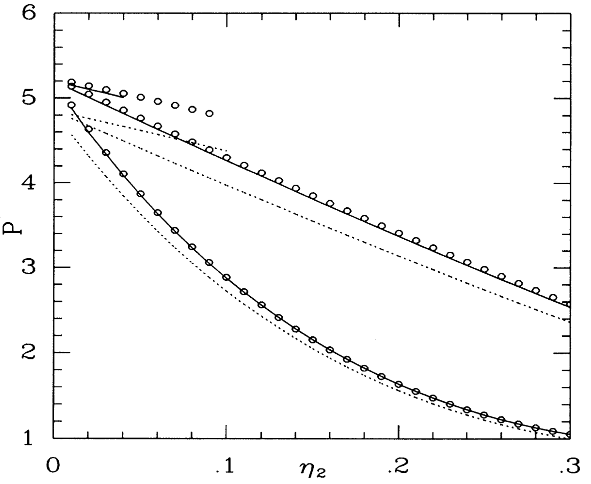

FIG. 1. Reduced pressure, $P^* = P\sigma_1^3/k_BT$, vs η_2 for $\eta_1' = 0.4$. The solid curves, dashed curves, and circles are for the RY, PY, and BPGG closures, respectively. Lower curves, $y = 0.5$; middle curves, $y = 0.2$; upper curves, $y = 0.1$.

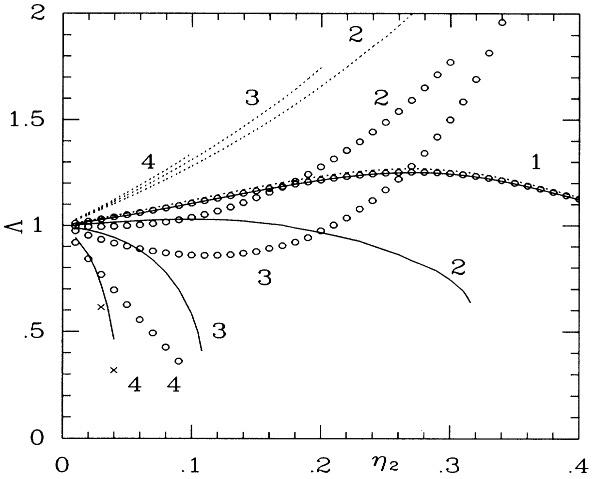

FIG. 2. Ratio $\Lambda = x_1x_2/S_{cc}(0)$ vs η_2 for $\eta_1' = 0.4$. Solid curves, dashed curves, and circles are for the RY, PY, and BPGG results, respectively. Curves labeled from 1 to 4 are for size ratios $y = 0.5$, 0.2, 0.15, and 0.1. The crosses correspond to the RY2 closure for $y = 0.1$.

sures for sufficiently small values of y. The situation is summarized in Fig. 2, where we have plotted the results of the various closures for the ratio $\Lambda = x_1x_2/S_{cc}(k=0)$ [cf. Eq. (1)] as a function of η_2 for fixed η_1'. In an ideal mixture Λ would equal 1, the limiting value when $\eta_2 \to 0$. On the contrary, Λ goes to 0 on the spinodal line of a phase separation. The mixture with the size ratio $y = 0.5$ still behaves almost ideally, and the predictions of the PY, RY, and BPGG equations are rather close for all η_2. The situation changes dramatically for smaller y. While the PY closure always yields an increase of Λ with η_2, i.e., a reduction of concentration fluctuations, the RY closure exhibits the opposite tendency, i.e., an increasingly rapid drop of Λ with η_2 as the size ratio is reduced. For $y = 0.15$, and even more so for $y = 0.1$, concentration fluctuations become very strong, leading to a sharp peak in $S_{cc}(k)$ at $k = 0$, the amplitude of which appears to diverge as η_2 increases. This divergence causes severe numerical problems, and no convergence of the iterative procedure could be achieved beyond some critical value of η_2. However, any reasonable extrapolation of the data shown in Fig. 2 shows that Λ will go to 0 (i.e., the spinodal is reached) at $\eta_2 \simeq 0.12$ when $y = 0.15$ and $\eta_2 \simeq 0.05$ when $y = 0.1$. The RY results for $y = 0.1$ are confirmed by the improved RY2 closure.

The data based on the BPGG closure show a much more gradual tendency towards phase separation as y decreases. In fact, the curvatures of the $\Lambda(\eta_2)$ curves based on the two closures are opposite, but for $y = 0.1$ the slope of the BPGG curve appears to be sufficient to ensure that Λ will go to 0 for $\eta_2 \lesssim 0.2$.

All results discussed so far are based on the value of η_1' estimated from Eq. (4), which leads to a drop in pressure with increasing η_2 (cf. Fig. 1). If η_1' is taken to be equal to the continuum limit $\eta_1/(1-\eta_2)$, even for finite values of y, the resulting pressure increases slowly with η_2; the corresponding results for $\Lambda(\eta_2)$ are shown in Fig. 3. In this case the RY and BPGG results are seen to be qualitatively and quantitatively much closer than in Fig. 2. This improved agreement reinforces our belief that the predicted phase separation indeed occurs for size ratios $y \lesssim 0.2$. Finally, calculations carried out for a higher effective packing fraction ($\eta_1' = 0.45$) show the same general behavior, but with an enhanced tendency towards phase separation. It is worth noting that, although the critical η_2 appears to go to zero with the size ratio y, a

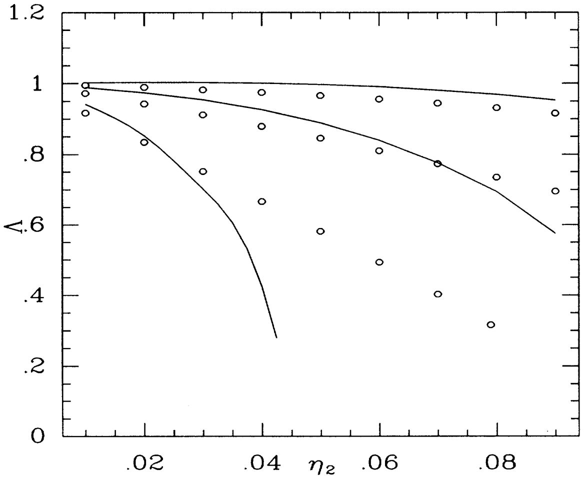

FIG. 3. Same as in Fig. 2 (without PY results), but for η_1' calculated from the continuum limit $\eta_1/(1-\eta_2)$ [rather than from Eq. (4)], and fixed at the value 0.4. Upper curves, $y = 0.2$; middle curves, $y = 0.15$; lower curves, $y = 0.1$.

simple perturbational analysis (e.g., in powers of η_2) is precluded by the strong divergence of the contact value $g(\sigma_2)$ in that limit.

We have presented strong evidence that when large spheres are dissolved in a fluid of small spheres a miscibility limit is reached for sufficiently small values of the size ratio. The question naturally arises of the nature of the conjugate phase, coexisting with the saturated solution of large spheres. In the numerical search for solutions of the integral equations at higher concentrations of large spheres (presumably beyond the miscibility gap), we were unable to detect a second fluid phase. Our conjecture is that the saturated mixture coexists with two crystal phases, of very different compositions.

To conclude, we would like to point out a fundamental difference between the present results and earlier observations of phase separation in less asymmetric "soft"-sphere mixtures.[1,2] In the latter case, the free energy has an internal energy contribution, which means that the underlying effective hard-sphere mixture must be characterized by nonadditive diameters. A positive nonadditivity [i.e., $\sigma_{12} > (\sigma_1 + \sigma_2)/2$] is known to drive phase separation, for obvious steric reasons. The miscibility gap discussed in the present work is perhaps more unexpected, since it is of purely entropic nature, with strictly additive hard-sphere diameters. Its physical origin may be ascribed to the effective attraction (stickiness) between the large spheres induced by the osmotic depletion effect. This attraction, of entropic origin, then leads to the clustering of the large spheres which thus will form a concentrated suspension (within the "solvent" of small spheres), in equilibrium with the dilute phase, the thermodynamic stability limit of which has been explored by the present integral-equation results.

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