Free-volume fraction in hard-sphere mixtures and the osmotic spinodal curve

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The sensitivity of the theoretical spinodal curve deduced from the osmotic equilibrium equation for asymmetric hard-sphere mixtures is examined by evaluating the free-volume fraction from three expressions of the excess chemical potential. The conditions for predicting a reduction of the stability domain with increasing asymmetry are discussed. The necessity of modifying this approach in the presence of attractions between the smaller species is underlined.

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The stability of highly asymmetric mixtures of particles with hard core interactions has recently been the subject of several theoretical [1–4] and experimental [5–7] investigations. Their theoretical study is however still a difficult problem because of the large difference in size between the various species. For instance, computer simulations are available only for limited diameter ratios or packing fractions [8]. Their phase behavior is thus presently discussed mostly from approximate analytical theories, including integral equations [1], density functionals [3] and other thermodynamical methods [2, 4]. In this last group, the approach recently presented by Lekkerkerker *et al.* [2] is much easier to implement than integral equations or density functional calculations for instance. In particular, it leads to a very simple equation for the spinodal curve. It might thus be very useful for a quick estimation of the stability domain of mixtures with hard core interactions. It is therefore important to test the reliability of its predictions. For a diameter ratio $\varepsilon=0.1$, these predictions [2(a)] are in qualitative agreement with Biben and Hansen [1] and Rosenfeld's [3] results. The first purpose of this note is then to examine—in the case of hard spheres mixtures—the sensitivity of the estimated spinodal to the diameter ratio ε and to the expression of the free volume fraction α. The latter plays indeed a central role in this approach (see, for instance, Ref. [2b]). The second purpose is to discuss it in the more general context of particles with attractive forces. The relevant equations from Ref. [2a] are thus briefly outlined here.

By considering the osmotic equilibrium of a mixture of small (diameter d_1, number density ρ_1, packing fraction η_1 and chemical potential μ_1) and large (d_2,ρ_2,η_2) particles, an approximate expression of the osmotic pressure was obtained as

$$\Pi=\Pi_2^0(\eta_2)+\Pi^r(\mu_1)\left[\alpha-\rho_2\frac{d\alpha}{d\rho_2}\right], \tag{1}$$

where Π^r and Π_2^0 are, respectively, the pressure in the reservoir of small particles and that of the pure fluid of large ones. The spinodal condition $(\partial\Pi/\partial\rho_2)_{\mu_1}=0$ then reads:

$$\frac{\partial\Pi_2^0}{\partial\rho_2}-\Pi^r(\mu_1)\frac{d^2\alpha}{d\rho_2^2}=0 . \tag{2}$$

In the derivation of Eqs. (1) and (2), the potential of mean force is approximated as $W(\mathbf{R}_N,\mu_1)=U(\mathbf{R}_N)-\Pi(\mu_1)V^{\text{free}}(\mathbf{R}_N)$ and the free volume $V^{\text{free}}(\mathbf{R}_N)$ available to the small spheres for a given configuration $\mathbf{R}_N$ of the N large ones is replaced by its mean field value $V^{\text{free}}=\alpha V$ on the pure fluid of large spheres (V being the volume of the system). For a practical application, Π^r and Π_2^0 can be evaluated from known expressions of the compressibility factor $Z=\beta\Pi/\rho$ of the one component fluid of hard spheres (ρ is the number density and $\beta=1/k_BT$). As suggested in Ref. [2], α can be obtained from Widom's particle insertion theorem [9] as $\alpha=\exp(-\beta\mu^{\text{ex}}(\eta_1=0))$, the small spheres excess (over the ideal gas value) chemical potential $\mu^{\text{ex}}(\eta_1=0)$ being evaluated from known expressions for hard spheres mixtures. It is convenient to express $\beta\mu^{\text{ex}}$ as $\beta\mu^{\text{ex}}(\eta_1=0,\eta_2,\varepsilon)=-\ln(1-\eta_2)+P(y,\varepsilon)$ where $y=\eta_2/(1-\eta_2)$ and where $P(y,\varepsilon)$ depends on the equation of state used. The free volume fraction is then given by $\alpha=(1-\eta_2)e^{-P(y,\varepsilon)}$, and the equation for the spinodal reads:

$$\frac{d(\eta_2 Z(\eta_2))}{d\eta_2}-\eta_2(1-\eta_2)^{-4}\eta_1 Z\left[\eta_1^r\right]\times\varepsilon^{-3}\left\{\left[\frac{dP}{dy}\right]^2+\frac{d^2P}{dy^2}\right\}=0 . \tag{3}$$

In the second term of this equation, Z depends on the ratio $\eta_1^r=\eta_1/\alpha$ because the pressure $\Pi^r(\mu_1)$ must be computed with the packing fraction of the small particles in the reservoir [2a].

In order to test the sensitivity of the predicted spinodal, we have compared three different expressions of $\beta\mu^{\text{ex}}$. The first one—used by Lekkerkeker *et al.*—is the scaled particle theory (SPT) expression [10]. $P(y,\varepsilon)$ can then be put in the form:

$$P_{\text{SPT}}(y,\varepsilon)=3y\varepsilon+\left[3y+\frac{9}{2}y^2\right]\varepsilon^2+(y+3y^2+3y^3)\varepsilon^3 . \tag{4}$$

The second one obtained from the Mansoori Carnahan Starling Leland (MCSL) equation of state [11(b)] gives:

$$P_{\rm MCSL}(y,\varepsilon)=(-3\varepsilon^2+2\varepsilon^3)\ln(1+y)+3y\varepsilon+(6y+3y^2)\varepsilon^2+(-y+4y^2+2y^3)\varepsilon^3 . \quad (5)$$

The last (and less familiar) one is obtained by following Andrews and Ellerby's prescriptions [12] for computing the volume available to the inserted particle. In this approach, the central quantity is the average volume ω effectively excluded to the inserted particle by the host particles. Simple physical arguments are given for estimating this volume [12]. ω is taken as a linear function of density with coefficients depending on the diameter ratio ε. The volumes ω_{iLk} and ω_{iHk} excluded at low and high density by a single host of type k to an inserted particle of type i are interpolated between the values for $\varepsilon=0$ (insertion of a point particle) and $\varepsilon\geq 1$ (inserted particle of same or larger size than the host particles). As discussed by Speedy [13], this approach amounts to parametrizing in the range $\sigma/2\leq r\leq\sigma$ the density $\rho G(r)$ of spheres (of diameter σ in the one component case) at the surface of a cavity of radius r. One can then write $P(y,\varepsilon)$ as:

$$P_{\rm AE}(y,\varepsilon)=(3\varepsilon+3\varepsilon^2+\varepsilon^3)(y+y^2)\{1+y(2-c_L)+y^2[c_0(c_L-c_H)+1-c_L]\}^{-1} \quad (6)$$

where $c_0=6/\pi\sqrt{2}$ and where the coefficients $c_L=1+\frac{15}{14}\varepsilon$ and $c_H=1+(c_0-1)\varepsilon$ arise from a linear interpolation of ω_{iLk} and ω_{iHk} with ε.

One finally needs to specify the compressibility factor Z. Though the results were found to be rather insensitive to the specific form used, each expression of $P(y,\varepsilon)$ was used with the corresponding Z, i.e., $Z_{\rm SPT}=(1+\eta+\eta^2)/(1-\eta)^3$ [10], $Z_{\rm CS}=(1+\eta+\eta^2-\eta^3)/(1-\eta)^3$ for Carnahan Starling's (CS) equation of state [11(a)] and for Andrews and Ellerby's one [12]:

$$Z_{\rm AE}=\frac{\beta z}{1-\gamma z+\Delta z^2}-\frac{1}{\eta}\ln(1-\eta)-\frac{\beta\gamma}{2\Delta(1-\Delta)z}\times\ln\left[\frac{1-\Delta z}{1-z}\right]-\frac{\beta}{2\Delta z}\ln(1-\gamma z+\Delta z^2)$$

$(z=c_0\eta,\beta=7c_0^{-1},\gamma=\frac{29}{14}c_0^{-1}=1+\Delta)$.

Figure 1 shows the resulting spinodals for $\varepsilon=0.1$ and $\varepsilon=0.025$ (the SPT curve for $\varepsilon=0.1$ is the same as that of Ref. [2(a)]). Besides the quantitative differences for $\varepsilon=0.1$, the striking feature is that while the MCSL and AE calculations predict a reduction of the stability domain with decreasing ε, the SPT one gives just the opposite, that is a clearly unphysical trend. This anomalous behavior has also been pointed out recently in Ref. [3(b)]. The technical reason for this is the behavior of the quantity $G(\eta_2,\varepsilon)=\varepsilon^{-3}\{(dP/dy)^2+d^2P/dy^2\}$ whose logarithm is shown in Fig. 2 versus ε^{-1} for two packing fractions of the large spheres. As the asymmetry increases $G_{\rm SPT}(\eta_2,\varepsilon)$ decreases at constant η_2 and becomes nearly constant. In parallel, α increases towards its limiting value $\alpha^{\rm lim}=1-\eta_2$. Since $Z_{\rm SPT}(\eta_1/\alpha)$ would then decrease were η_1 fixed, η_1 must increase with ε^{-1} in order to keep constant the product $\eta_1 Z_{\rm SPT}(\eta_1/\alpha)G_{\rm SPT}(\eta_2,\varepsilon)$. A simple algebra shows that $G_{\rm SPT}(\eta_2,\varepsilon)$ actually behaves as $g_0+g_1\varepsilon+O(\varepsilon^2)$, with $g_0>0$ and $g_1>0$, because of the exact cancellation of the terms of order ε^2 in $(dP/dy)^2+d^2P/dy^2$. This peculiarity does not occur with the MCSL and AE calculations, the function $G(\eta_2,\varepsilon)$ behaving as $g'_{-1}\varepsilon^{-1}+g'_0+O(\varepsilon)$ with g'_0 and $g'_{-1}>0$. The behavior (at constant η_2) of η_1 with ε^{-1} results there from a competition between the increase of $G(\eta_2,\varepsilon)$ and the decrease of $Z(\eta_1/\alpha)$. At low asymmetry, the decrease of $Z(\eta_1/\alpha)$ dominates so that η_1 must again increase with ε^{-1}. At least when compared to the results of Refs. [1] and [3], the MCSL and AE spinodals then suffer from the same defect than the SPT one, though the limit is remarkably lower for the AE spinodal ($\varepsilon^{-1}\approx 4$) than for the MCSL one ($\varepsilon^{-1}\approx 10$) (the AE spinodal is however rather sensitive to the coefficients of the

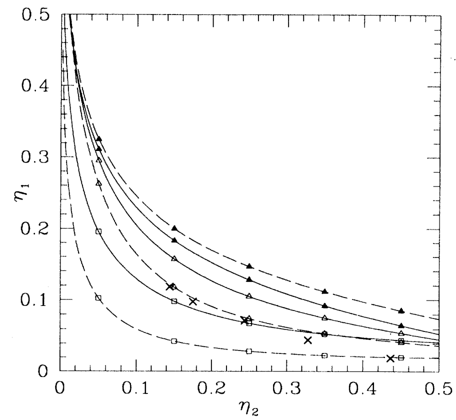

FIG. 1. Spinodal curve in the variables η_2 (large spheres) and η_1 (small spheres), at diameter ratios $\varepsilon=0.1$: full curves; $\varepsilon=0.025$: dashed curves. MCSL: empty triangles; SPT: full triangles, AE: empty squares; crosses: constant pressure results for $\varepsilon=0.1$ from Refs. [1(b),1(c)]

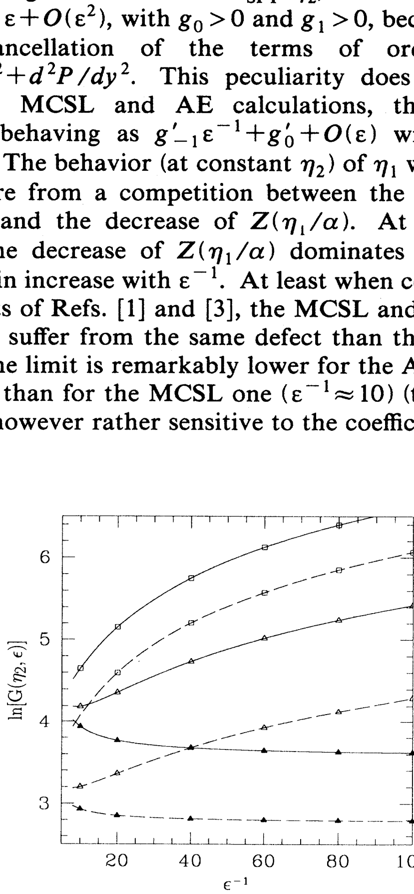

FIG. 2. Logarithm of the function $G(\eta_2,\varepsilon)$ versus ε^{-1}. Dashed curves: $\eta_2=0.1$, full curves: $\eta_2=0.4$. Meaning of symbols as in Fig. 1.

interpolation with ε for low asymmetry). In some ways, an incorrect behavior for ε close to unity is not surprising since the approximation for the potential of mean force and the replacement of the free volume by its average [2] should worsen then. At sufficiently large ε^{-1}, the increase of $G(\eta_2,\varepsilon)$ dominates so that η_1 decreases. Then the MCSL and AE spinodals both obey the expected trend with increasing asymmetry. However, in contrast with the larger stability domain predicted by the MCSL calculation, the AE calculation is close to quantitative agreement with the results of Ref. [1] (crosses in Fig. 1 for $\varepsilon^{-1}=10$).

Since the numerical values of α computed with the three expressions are very close (for $\varepsilon=1$ de Souza *et al.* [14] found both $\alpha_{\rm SPT}$ and $\alpha_{\rm MCSL}$ in good agreement with Monte Carlo data), the qualitative difference between the SPT and the MCSL or the AE spinodals illustrates well the importance of having the correct variation of $d^2\alpha/d\rho_2^2$ with ε^{-1} and the corresponding increase of $Z(\eta_1/\alpha)G(\eta_2,\varepsilon)$ (at constant η_1). However, while these contrasted behaviors with ε originate from differences in the expressions of $\mu^{\rm ex}$, the physical meaning of the latter is not immediate. Yet, the possibility of significant improvement on the SPT spinodal by using two approaches which are all but closely related suggests that the SPT results are an exception and not the rule (we mention in passing that we found the SPT and the MCSL equation of state consistent with Smith and Labik's criterion [15] $Z=1+\frac{1}{3}\{\partial\beta\mu_1^{\rm ex}(\eta_1=0)/\partial\varepsilon\}_{\varepsilon=1}$, in contrast with the AE equation. In the latter case, the discrepancy depends on the way one interpolates ω_{iLk} and ω_{iHk} with ε).

It is finally instructive to consider the phase diagram in the variables $\Pi^*=\beta\Pi d_1^3$ and $x_2^{1/3}$ where x_2 is the concentration of the large spheres (Fig. 3), as in Ref. [1(c)]. At fixed diameter ratio and with x_2 increasing at constant pressure, the AE spinodal can be reached well before the MCSL or SPT ones, in agreement with a predicted smaller stability domain in the variables η_2,η_1. Figure 3 also well illustrates an important feature related to the higher SPT and MCSL η_1 values on the spinodal. At low x_2, these values go together with an important contribution to the pressure from the fluid of small hard spheres and hence with much higher pressures than the AE and the integral equations pressures [1].

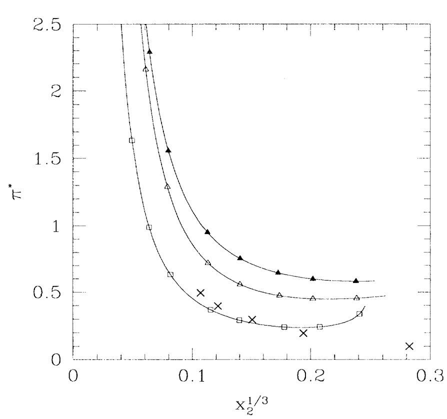

FIG. 3. Reduced total pressure $\Pi^*=(1/k_BT)\Pi d_1^3$ versus $x_2^{1/3}$ for $\varepsilon=0.1$. $x_2=\rho_2/(\rho_1+\rho_2)$: concentration of the large spheres; Crosses: constant pressure results from Refs. [1(b),1(c)]. The last cross on the right hand side corresponds to $\eta_2=0.59$ (also end points of the curves). Meaning of symbols as in Fig. 1.

Figure 3 clearly illustrates the crucial role of the pressure of the small hard spheres fluid. One may then wonder whether these features would remain in the presence of *attractive forces* between the small particles as in ordinary colloidal suspensions. Indeed these forces would considerably reduce the pressure of the fluid of small particles and accordingly the pressure imbalance when two large spheres approach at a distance smaller than the diameter of the small ones. This might have a significant influence on the stability of the mixture. The calculations of Jamnik *et al.* [16] on sticky hard spheres show for instance that adhesion among the small particles lowers the force between two approaching large spheres, a result coherent with simple expressions of the depletion force such as that proposed by Vrij [17]. The spinodal equation [Eq. (3)] also shows that if the free volume fraction were unchanged by this adhesion, a reduced pressure of the small particles fluid would imply larger values of η_1 at constant η_2, that is a greater stability than for pure hard spheres. We have checked that replacing the hard spheres compressibility factor Z in Eq. (3) by that of sticky-hard spheres [18] can suppress the spinodal instability even for a moderate stickiness (for instance this already happens for a Baxter stickiness parameter $\tau\approx 0.1$ for which an ordinary solvent would be above the critical point). However, calculations in the Percus Yevick approximation (PYA) for mixtures of sticky hard spheres show that small sticky spheres reduce the stability domain [19, 20]. This suggests that at least in this idealized model of attractive forces, the instability is not governed by a strong pressure imbalance. With pure hard core interactions, the latter indeed favors an increase of the free space available to the small spheres and hence an increase of their entropy when the large ones begin to cluster [21] (the large particles entropy decreases then, but they are much less numerous). Although a lower pressure imbalance would imply less available space and hence a lower increase of the small particles entropy, the instability associated with such attractions seems to be dictated by the associated lowering of the internal energy. This lowering could be strong enough to make the free energy of the inhomogeneous suspension lower than that of the homogeneous one. Besides its possible relevance to the interpretation of instability in some colloidal suspensions usually discussed mostly in terms of steric effects [5–7], this discussion suggests that important modifications in the spinodal equation would be required in the presence of attractions. In particular, they may significantly modify the free volume fraction compared with that relative to hard spheres mixture (a modification of the free volume by the attractions was suggested in Ref. [22] for mixtures of spheres and rod-like polymers). Since equations of state for mixtures with attractive forces are rather scarce, one still has to rely on simple theories such as the PYA. However, one then faces the difficulty that—at least for hard sphere mixtures—the PYA works poorly when the diameter ratio significantly differs from unity. In particular, it does not predict a spinodal instability. As suggested in our previous work [20], an *ad hoc* correction for this may be obtained by introducing an artificial stickiness between the large spheres. The associated stickiness parameter might thus be determined by imposing that the divergence of the PY structure factors occurs precisely for the packing fraction on the spinodal line. A simple route for the *hard spheres* spinodal as that proposed by Lekkerkerker *et al.* for example is then required, and this was the initial motivation for this study. In this respect obtaining reliable expressions of the derivatives of the free volume fraction would be a necessary first step. On the other hand, attempts to modify the expression of the free volume fraction in the presence of attractive forces while preserving the simplicity of the osmotic equilibrium approach should still remain useful.

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