Phase behavior of nonadditive hard-sphere mixtures

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We show the existence of a fluid-fluid demixing transition in binary mixtures of nonadditive asymmetric hard-sphere mixtures by performing Gibbs ensemble Monte Carlo simulations for a size ratio of 0.1 and varying degrees of nonadditivity. We compare our results with the theoretical binodals obtained from the equation of state proposed by Barboy and Gelbart [J. Chem. Phys. **71**, 3053 (1979)] and we find reasonable agreement for sufficiently large values of the nonadditivity parameter. Upon decreasing the nonadditivity parameter, we find that the fluid-fluid demixing region shifts to higher pressures and becomes narrower. For sufficiently small nonadditivities, we do not find a fluid-fluid demixing transition for total packing fractions <0.5. [S1063-651X(98)02412-X]

PACS number(s): 64.70.$-$p, 61.20.Gy, 82.70.Dd

I. INTRODUCTION

During the past few years evidence has accumulated for the existence of entropy-driven fluid-fluid demixing transitions. One way in which phase separation can occur in an athermal mixture is if the hard-core interactions in the mixture are ''nonadditive,'' i.e., $\sigma_{AB}>(\sigma_{AA}+\sigma_{BB})/2$, where σ_{ij} denotes the distance of closest approach of particles of types i and j. Loosely speaking, this phase separation can be understood from the fact that the pure phases can fill the space more effectively than the mixture. An extreme case of nonadditivity was studied by Widom and Rowlinson, who considered $\sigma_{AA}=\sigma_{BB}=0$ and $\sigma_{AB}=\sigma>0$ [1]. For this system, they showed the existence of a demixing transition. Similarly, a demixing transition is found in the simplest model of colloid-polymer mixtures. In this model the colloids with diameter σ_B and the polymers with a radius of gyration R_g and a diameter $\sigma_A=2R_g$ are assumed to interact with hard-core potentials. As the polymers are interpenetrable, the range of the repulsion between two polymers is assumed to be $\sigma_{AA}=0$, while $\sigma_{AB}=\frac{1}{2}(\sigma_A+\sigma_B)$ and $\sigma_{BB}=\sigma_B$ [2]. A semiphenomenological theory for this model predicts a fluid-fluid demixing transition for $q=\sigma_A/\sigma_B\gtrsim0.35$ [3].

A special case is a mixture of *additive* hard spheres, for which $\sigma_{AB}=(\sigma_{AA}+\sigma_{BB})/2$. For these mixtures, using the Percus-Yevick closure in the Ornstein-Zernike equation [4], no spinodal instability is found in the fluid phase for any size ratio, while the Rogers-Young closure does give evidence for spinodal instability when the size ratio $q<0.2$ [5]. A fluid-fluid demixing transition was also found by Rosenfeld within a self-consistent density functional theory provided the size ratio $q<0.25$ [6]. However, the predictions depend heavily on the assumptions or details of the theories and it remains an open question whether a fluid-fluid demixing transition exists in a binary mixture of additive hard spheres.

As the mechanism of a demixing transition in hard-sphere systems must be purely entropic, the demixing transition cannot be explained by (un)favorable energetic interactions. The mechanism behind this instability is often explained by the *depletion* effect. This depletion effect is based on the gain of free volume of the small spheres due to clustering of the large spheres. The depletion effect can also be under-

stood as an unbalanced osmotic pressure, which arises when the large spheres are so close together that no small particle fits in between. In 1954, this depletion effect was already recognized to drive the phase separation in colloid-polymer mixtures [2]. However, the depletion effect in colloid-polymer mixtures is extremely enhanced by nonadditivity. An indication of this enhancement is that, for instance, in the case of colloid-polymer mixtures a fluid-fluid demixing transition is predicted for $q\gtrsim0.35$ [3], while no fluid-fluid demixing is found for *additive* hard-sphere mixtures with size ratios $q\gtrsim0.35$ [5,6]. Note also that in the case of additive hard-sphere mixtures an upper bound for the size ratio is found, while in the case of colloid-polymer mixtures a lower bound is found. The depletion effect in additive hard-sphere mixtures becomes stronger for smaller size ratios, while the depletion effect due to packing effects in nonadditive hard-sphere mixtures is enhanced when the spheres become more similar. It is therefore not clear to what extent this phase separation of colloid-polymer mixtures is caused by nonadditivity and whether the depletion effect can lead to a fluid-fluid phase separation in *additive* hard-sphere mixtures.

Attempts at direct confirmation of the fluid-fluid demixing transition for additive hard-sphere mixtures by computer simulations are hampered by slow equilibration. Evidence of a purely entropy-driven demixing transition between two fluid phases is found only for a binary mixture of large and small parallel cubes on a lattice and for a binary mixture of thin and thick spherocylinders [7,8]. However, in the case of the parallel cubes only fluid phases are considered and it is therefore not clear whether this transition is stable or metastable with respect to the freezing transition. For the systems of parallel cubes and the spherocylinders the depletion mechanism is enhanced by the shape of the individual species. Similarly, one might argue now that a demixing transition can be induced by introducing a small degree of nonadditivity. Indeed it has been shown recently that by using an equation of state for nonadditive binary hard-sphere mixtures, a small degree of nonadditivity $[2\sigma_{AB}/(\sigma_A+\sigma_B)\sim1.01]$ leads to a fluid-fluid demixing for $q<0.2$ [9]. In this article we investigate the effect of nonadditivity on the fluid-fluid demixing transition and in particular whether a

small amount of nonadditivity can indeed induce a fluid-fluid demixing transition.

II. SIMULATIONS

We consider a binary mixture of nonadditive hard spheres with diameters $\sigma_A = 1$ and $\sigma_B = 10$. The ranges of the repulsion between the particles, i.e., the distance of closest approach, are given by

$$\sigma_{AA} = \sigma_A,$$

$$\sigma_{BB} = \sigma_B, \tag{1}$$

$$\sigma_{AB} = \frac{1}{2}(\sigma_A + \sigma_B)(1 + \Delta),$$

where $\Delta > 0$ is the nonadditivity parameter. In order to determine the coexistence curve of the two fluid phases directly, we carry out Gibbs ensemble Monte Carlo simulations [10]. In this method the two coexisting phases are simulated in separate simulation boxes that may exchange volume and particles at a given temperature in order to fulfill the phase equilibrium requirements of equal pressure and chemical potentials. During the simulation ordinary Monte Carlo steps are performed in both phases in order to equilibrate both systems internally. However, the acceptance ratio for exchanging a large particle is small in a dense system of small particles, as a large particle will almost always overlap with one of the small particles. In order to speed up equilibration we use collective particle moves that employ a generalization of the configurational-bias Monte Carlo scheme of Ref. [8]. In this approach we first choose randomly a large sphere in one box and try to insert this particle at a random position in the other box. When the particle overlaps with another large sphere the trial move is immediately rejected. If no such overlap is found, the small spheres overlapping with the large sphere in its new position are removed and are then moved to the volume vacated by the large sphere in the first box using a generalization of the Rosenbluth sampling. The trial move is then accepted with a probability determined by the ratio of the Rosenbluth weights of the new and old configurations. For more technical details, we refer the reader to Ref. [8]. In our simulations we perform the following trial moves: (i) random displacement of a particle in one of the boxes, (ii) small particle exchange between the boxes, (iii) large particle exchange between the boxes using the configurational-bias Monte Carlo scheme, and (iv) volume exchange between the boxes.

In each simulation we measure the composition x of the large spheres in both boxes, given by $x = N_B/(N_B + N_A)$, where N_B and N_A are, respectively, the number of large and small spheres in that box. In addition, the numerical value of the pressure was determined by virtual volume changes. This method is based on the fact that the pressure is minus the volume derivative of the Helmholtz free energy, which can be related to the acceptance ratio of virtual volume changes as described in Ref. [11].

Most runs consist of 10^4–10^5 cycles per particle per thermodynamic state point. In each cycle we attempt a displacement of a particle in one of the boxes and we try to exchange

volume and a particle between the boxes. For the particle exchange we select with equal probability the box where a particle is removed and the species of the particle that will be transferred. The system size varies from about 100 to 200 large spheres with 400–1200 small spheres.

III. THEORY

Most studies of nonadditive binary hard-sphere mixtures are restricted to the symmetric case, i.e., $\sigma_A = \sigma_B$. In the case of equal diameters, a nonadditivity of $\Delta = 0.05$ is already sufficient to induce phase separation [12]. For the asymmetric case an equation of state was derived by Barboy and Gelbart. This expresses the pressure P in powers of $y_\alpha = n_\alpha/(1 - \eta)$, with $n_\alpha = N_\alpha/V$ the number density of species α, V the total volume of the system, and η the total packing fraction [1]. To third order in y_α this equation of state reads

$$\frac{P}{k_B T} = \sum_\alpha y_\alpha + \sum_{\alpha,\beta} A_{\alpha\beta} y_\alpha y_\beta + \sum_{\alpha,\beta,\gamma} A_{\alpha\beta\gamma} y_\alpha y_\beta y_\gamma. \tag{2}$$

The coefficients $A_{\alpha\beta}$ and $A_{\alpha\beta\gamma}$ are such that the low-density expansion of Eq. (2) coincides with the third-order virial expansion of nonadditive hard-sphere mixtures, given by

$$\frac{P}{k_B T} = n + \sum_{\alpha,\beta} B_{\alpha\beta} n_\alpha n_\beta + \sum_{\alpha,\beta,\gamma} B_{\alpha\beta\gamma} n_\alpha n_\beta n_\gamma,$$

$$B_{\alpha\beta} = \frac{2}{3} \pi \sigma_{\alpha\beta}^3, \tag{3}$$

$$B_{\alpha\alpha\gamma} = \frac{1}{9} \pi^2 \left[\frac{1}{6} \inf(\sigma_\alpha, 2\sigma_{\alpha\gamma})^6 - 3 \inf(\sigma_\alpha, 2\sigma_{\alpha\gamma})^4 \sigma_{\alpha\gamma}^2 \right.$$
$$\left. + \frac{16}{3} \inf(\sigma_\alpha, 2\sigma_{\alpha\gamma})^3 \sigma_{\alpha\gamma}^3 \right],$$

with

$$\inf(\sigma_\alpha, 2\sigma_{\alpha\gamma}) = \begin{cases} \sigma_\alpha & \text{for } \sigma_\alpha < 2\sigma_{\alpha\gamma} \\ 2\sigma_{\alpha\gamma} & \text{otherwise} \end{cases} \tag{4}$$

and $n = \Sigma_\alpha N_\alpha/V$. Comparing Eqs. (2) and (3) leads to

$$A_{\alpha\beta} = B_{\alpha\beta} - \frac{\pi}{6} \frac{\sigma_\alpha^3 + \sigma_\beta^3}{2}, \tag{5}$$

$$A_{\alpha\alpha\gamma} = B_{\alpha\alpha\gamma} - \frac{\pi}{9}(A_{\alpha\alpha}\sigma_\gamma^3 + 2A_{\alpha\gamma}\sigma_\alpha^3) - \frac{\pi^2}{36}\sigma_\alpha^3 \frac{\sigma_\gamma^3 + \sigma_\beta^3}{3}. \tag{6}$$

For $\Delta = 0$, the resulting equation of state reduces to the compressibility equation of state of the Percus-Yevick approximation for all q [13]. Integrating the equation of state with respect to $v = 1/n = V/(N_A + N_B)$ gives the Helmholtz free energy per particle $f(x,v)$ with $x = N_B/(N_A + N_B)$. However, in order to compute the phase equilibria, it is convenient to consider the Gibbs free energy per particle $g(x,P)$, which can easily be obtained by using a Legendre transformation
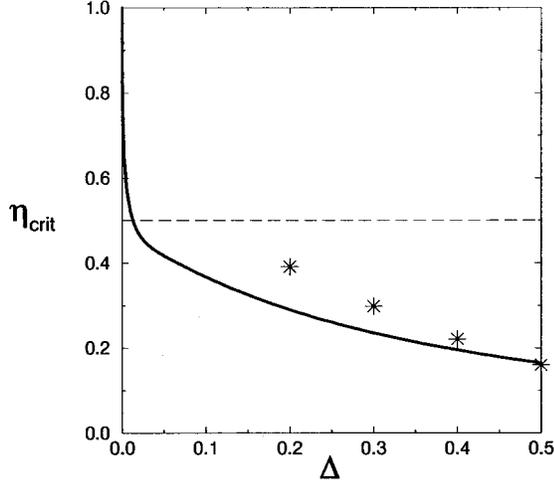
FIG. 1. Total packing fraction at the critical point $\eta_{crit} = \eta_A + \eta_B$ for a nonadditive hard-sphere mixture with size ratio $q = 0.1$ versus the nonadditivity parameter Δ. The simulations results are denoted by the crosses, while the solid line is the results of the theory.

$$g(x,P) = f(x,v) + Pv(x,P). \tag{7}$$

The spinodal can now be determined from the condition

$$\left(\frac{\partial^2 g}{\partial x^2} \right)_P = 0 \tag{8}$$

and the critical point is determined by Eq. (8) and

$$\left(\frac{\partial^3 g}{\partial x^3} \right)_P = 0. \tag{9}$$

The binodals can be obtained by equating the pressure and the chemical potentials of both species in the two coexisting phases.

IV. RESULTS

One way to plot the coexisting curves is a representation in the $\beta P \sigma_B^3$-x plane, where $\beta = 1/k_B T$. At low pressures (below the critical point), we find no demixing, while for pressures higher than the critical point, the fluid can phase separate into two phases with different composition x but equal pressure. We first compute the critical point of the fluid-fluid demixing transition for a nonadditive hard-sphere mixture with size ratio $q = 0.1$ from Eqs. (2), (8), and (9). In Fig. 1 we plot the resulting total packing fraction $\eta_{crit} = \eta_A + \eta_B$ at the critical point as a function of the nonadditivity parameter Δ. As pure hard spheres freeze at a packing fraction of 0.495, we expect that the fluid range in binary hard-sphere mixtures corresponds to $\eta < 0.5$ and this value is indicated by the dashed line in Fig. 1. We find that η_{crit} increases upon decreasing Δ. For $\Delta < 0.0032$, η_{crit} becomes larger than 0.5 and we do not expect fluid-fluid demixing for hard-sphere mixtures with Δ in this range and with a size ratio of $q = 0.1$. In the limit $\Delta \to 0$, η_{crit} approaches rapidly
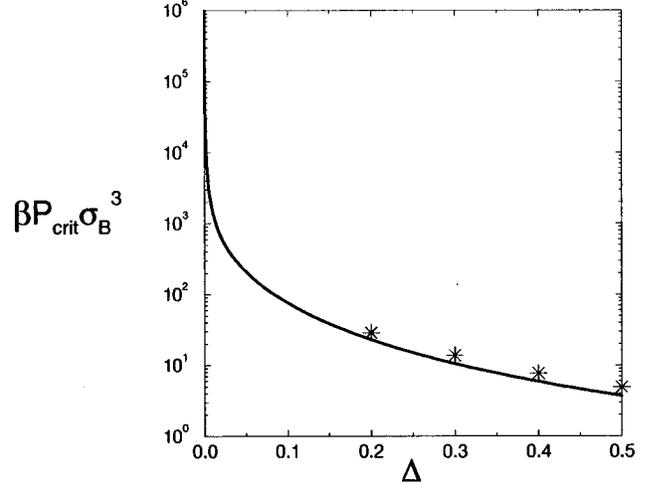
FIG. 2. Reduced pressure at the critical point $\beta P_{crit} \sigma_B^3$ for a nonadditive hard-sphere mixture with size ratio $q = 0.1$ versus the nonadditivity parameter Δ. The simulations results are denoted by the crosses, while the solid line is the result of the theory.

1. Recall that for $\Delta = 0$, the theory reduces to the compressibility equation of state of the Percus-Yevick approximation for which there is no demixing [4]. We plot our critical points, which are estimated by using a fit of the coexistence curves from Gibbs ensemble simulations, in the same figure. For $\Delta > 0.4$ we find good agreement between theory and simulation, but for lower values of Δ the simulations yield systematically higher values for η_{crit}. For $\Delta < 0.2$ we do not find a demixing transition for $\eta_{crit} < 0.5$, while the theory predicts that a small amount of nonadditivity ($\Delta > 0.013$) can induce a fluid-fluid demixing transition for $\eta_{crit} < 0.5$.

In Fig. 2 we plot the pressure $\beta P_{crit} \sigma_B^3$ at the critical point versus Δ for a nonadditive hard-sphere mixture with size ratio $q = 0.1$. We find that $\beta P_{crit} \sigma_B^3$ increases rapidly with decreasing Δ. The reduced pressure at the critical point obtained from simulations is also plotted and we find higher values for $\beta P_{crit} \sigma_B^3$ than those predicted by theory. In the limit $\Delta = 0$ the pressure diverges.

Figure 3 shows the theoretical critical composition $x_{crit} = N_B/(N_A + N_B)$ versus Δ for a size ratio $q = 0.1$. We find that x_{crit} decreases approximately linearly upon decreasing Δ until small values of Δ. As it is difficult to get an accurate estimate of x_{crit} in the present simulations for nonadditive mixtures, we did not compare these with the theoretical results. It is now interesting to consider the limiting behavior of x_{crit} for $\Delta \to 0$ in more detail. It turns out that x_{crit} has a well-defined value as $\Delta \to 0$, viz., $x_{crit} = 0.0010$, even though $\eta_{crit} \to 1$ in this limit. Other theories for hard-sphere mixtures predict the values $x_{crit} \simeq 0.0056$ [3], 0.02 [5], and 0.002 [6] for this size ratio and $\Delta = 0$, while a recent simulation study predicts a critical point at $\eta_B = 0.27$ and $\eta_A = 0.22$, which corresponds to a composition of $x_{crit} = 0.0012$ [14]. Note that the total packing fraction at this critical point is smaller than 0.5. However, in the same simulation study it was also shown that the fluid-fluid transition was metastable with respect to a broad fluid-solid transition.

We calculate from $f(x,v)$ or, equivalently, $g(x,P)$ the
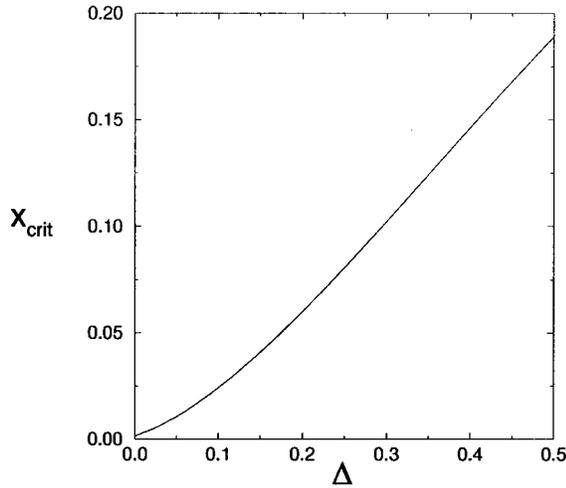
FIG. 3. Composition at the critical point $x_{crit} = \sigma_B / (\sigma_A + \sigma_B)$ for a nonadditive hard-sphere mixture with size ratio $q = 0.1$ versus the nonadditivity parameter Δ.

phase equilibria and compare the results with those of our computer simulations for a size ratio $q = 0.1$ and nonadditivities $\Delta = 0.5$, 0.4, 0.3, and 0.2. In Fig. 4 we show the resulting dimensionless pressure $\beta P \sigma_B^3$ of the coexisting phases as a function of the composition x. The theoretical binodals are shown in the same plot. For large Δ we find reasonable agreement. However, the simulation pressures are consistently higher than the pressures predicted by theory. By decreasing the nonadditivity parameter Δ, we observe the following features: (i) The binodals shift to higher pressures, (ii) the coexistence regions become narrower, and (iii) the binodals shift to lower values of $x = N_B / (N_A + N_B)$. For $\Delta < 0.2$, we do not find a demixing transition below a total
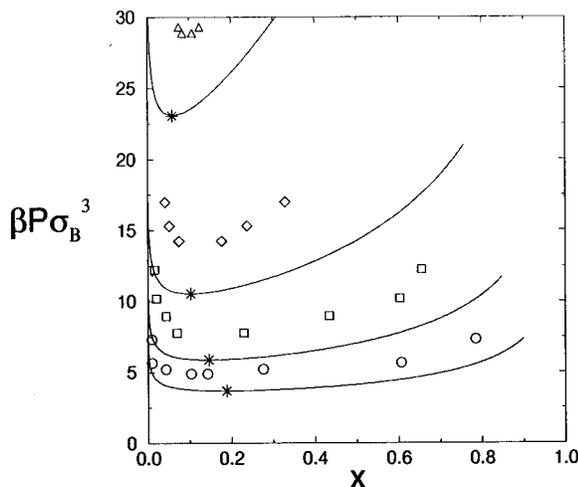
FIG. 4. Simulation results for the fluid-fluid coexistence in the pressure-composition plane of a nonadditive hard-sphere mixture of size ratio $q = 0.1$ with a nonadditivity parameter $\Delta = 0.5$ (circles), 0.4 (squares), 0.3 (diamonds), and 0.2 (triangles). The full lines denote the binodals obtained by using the theoretical equation of state 2 and the corresponding critical points are denoted by the asterisks.

packing fraction of $\eta \sim 0.50$. This might be an indication that the fluid-fluid demixing transition becomes metastable with respect to the freezing transition or it may not exist at all for densities below $\eta < 0.50$ and for $\Delta < 0.2$. A possible reason for the apparent absence of a spinodal instability is the narrowing of coexistence region with decreasing Δ. Unfortunately, equilibration problems prevented us from increasing the packing fraction further, so that we could not investigate whether a metastable fluid-fluid demixing transition exists above the freezing transition. Moreover, slow equilibration prevented us from decreasing Δ further, so that the additive hard-sphere mixture ($\Delta = 0$) could not be studied directly, as expected from the outset of our study.

V. DISCUSSION

We present the results of a computer simulation study of binary mixtures of nonadditive hard spheres with a size ratio of $q = 0.10$. Fluid-fluid demixing transitions are found in mixtures with nonadditivity $\Delta = 0.5$, 0.4, 0.3, and 0.2. Reasonable overall agreement is found for $0.2 \leq \Delta \leq 0.5$ with the binodals calculated from a theoretical equation of state for nonadditive binary hard-sphere mixtures. We find that the critical point shifts to higher pressures and that the coexistence region becomes smaller upon decreasing the nonadditivity parameter Δ from 0.5 to 0.2.

For $\Delta < 0.2$, we do not find a demixing transition below a total packing fraction of $\eta \sim 0.50$ and we expect that the demixing transition disappears into the solid at $\Delta \sim 0.2$. If we assume the same monotonic behavior for smaller Δ, we expect no stable demixing transition in the fluid phase and expect that the critical point, if there is any, shifts deeper into the solid phase upon decreasing Δ. However, we also find that the fluid-fluid demixing region becomes narrower upon decreasing Δ from 0.5 to 0.2. From the assumption that the same monotonic behavior holds for smaller Δ, it could be possible that the fluid-fluid demixing region disappears completely.

It is interesting to compare our results of the nonadditive hard-sphere mixtures with previously obtained results of the binary mixture of thick and thin spherocylinders with diameters $\sigma_B = 10$ and $\sigma_A = 1$ and equal length L [8]. In the latter system, a clear isotropic fluid-isotropic fluid demixing transition was found. In Fig. 5 the phase diagram resulting from Gibbs ensemble Monte Carlo simulations are shown for $L / \sigma_B = 15$, 10, 8, 5, and 3 in the pressure-composition plane. Upon decreasing L (and hence upon approaching the binary hard-sphere mixture with $q = 0.1$) the demixing region shifts to higher pressures and becomes narrower. A similar behavior was found in mixtures of nonadditive hard spheres, in which the nonadditivity parameter Δ was decreased (see above). For length $L = 2\sigma_B$, no demixing transition is found below a total packing fraction of $\eta = 0.581$, which is above the packing fraction of the freezing transition of a pure fluid of thick rods. In this case it was not possible to investigate whether a metastable demixing region occurs above the freezing transition for length $L < 2\sigma_B$ and, once again, the binary additive hard-sphere mixture ($L = 0$) could not be investigated directly. If we assume the same monotonic behavior for smaller L, we expect no stable demixing transition in the fluid phase and expect that the critical point, if there is
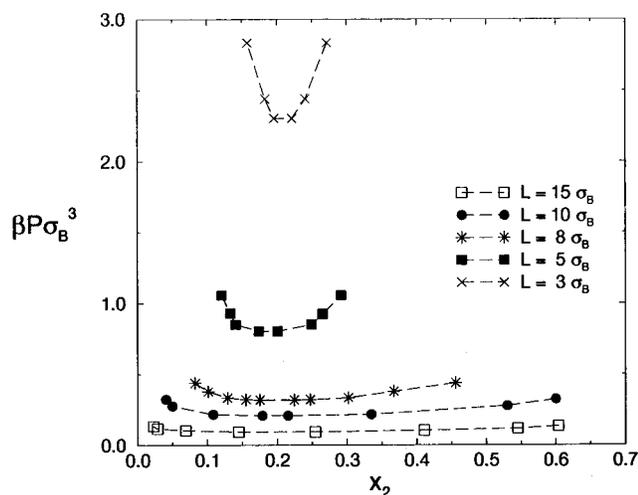
FIG. 5. Simulation results of the isotropic-fluid–isotropic-fluid coexistence in the pressure-composition plane of a mixture of hard spherocylinders with diameters $\sigma_B = 10$ and $\sigma_A = 1$ and equal length $L = 15\sigma_B$ (open squares), $10\sigma_B$ (closed circles), σ_B (stars), $5\sigma_B$ (closed squares), and $3\sigma_B$ (crosses).

any, shifts again deeper into the solid phase upon decreasing L.

Thus, extrapolating the results of both the nonadditive hard-sphere mixtures and the spherocylinder mixtures to the additive hard-sphere mixtures ($\Delta \rightarrow 0$ and $L \rightarrow 0$) and assuming that the same monotonic behavior holds for all Δ and L yields the conclusion that the demixing transition in the fluid phase is either metastable with respect to the freezing transition or disappears completely. A possible reason for the absence of the spinodal instability might be the narrowing of the coexistence region when one approaches the additive hard-sphere mixture.

However, more and more evidence becomes available in favor of the existence of a spinodal instability in the fluid phase for additive hard-sphere mixtures with size ratio $q = 0.10$ at a total packing fraction $\eta < 0.50$ [4,6,7,14]. It thus appears that a monotonic extrapolation from the spherocylinder mixture ($L \rightarrow 0$) or the nonadditive hard-sphere mixture ($\Delta \rightarrow 0$) to the additive hard-sphere mixture is not justified and that the critical point should turn over to lower pressures and packing fractions upon decreasing Δ and L even further. It would therefore be interesting to understand this turnover or change of trend of the critical points in more detail. This issue will be addressed in future work.

One way to study this turnover of the critical points is to map the two-component system onto an effective one-component system by integrating out the degrees of freedom of the smaller species. To lowest order the resulting effective

Hamiltonian of the bigger species can be written in terms of an effective pair potential (depletion potential) for the larger particles. For hard particles these effective pair potentials show an attractive well when the large particles are in contact and the range of the attraction is determined by the size of the smaller species. Recent studies show that a minimum range of attraction ($\sim 1/6$ times the diameter of the particle) is needed for the existence of a stable fluid-fluid (liquid-vapor) transition [15,16]. For shorter-ranged attractions the liquid-vapor transition becomes metastable with respect to the freezing transition. In the case of additive hard-sphere mixtures with size ratio $q = \sigma_A / \sigma_B = 0.10$, the range of the depletion attraction is about $0.10\sigma_B$ and no stable fluid-fluid transition is expected. For hard spherocylinders the range of attraction is increased upon increasing the length of the spherocylinders and one can expect that the fluid-fluid de-mixing transition becomes stable with respect to the freezing transition for sufficiently long rods. However, changing the spheres into spherocylinders results in an orientational de-pendence of the pair potential between the particles. This orientational dependence might be the reason for the change of trend of the critical points as a function of L. In the case of nonadditivity, the range of attraction is also increased upon increasing the nonadditivity parameter Δ and one can again expect that the fluid-fluid demixing transition becomes stable with respect to the freezing transition for sufficiently large Δ. Moreover, it is clear that as the size ratio q increases the physical behavior of additive and nonadditive hard-sphere mixtures becomes increasingly different, which ex-plains why a lower bound is found for the size ratio q for the simple, nonadditive model of colloid-polymer mixtures ($q > 0.35$) and an upper bound in the case of additive hard-sphere mixtures ($q < 0.20 - 0.25$).

In conclusion, by extrapolating the results for asymmetric nonadditive hard-sphere mixtures with finite nonadditivity parameter Δ towards $\Delta \rightarrow 0$, one might conclude that the de-mixing transition of the additive hard-sphere mixtures ($\Delta = 0$, $q = 0.10$) becomes metastable with respect to freezing or does not exist at all. A similar conclusion could be drawn from mixtures of spherocylinders as described in Fig. 5 and Ref. [9], where the length L of the spherocylinders plays a role equivalent to Δ here. However, given the mounting evi-dence for the existence of fluid-fluid demixing in the binary hard-sphere mixture, these extrapolations are probably not valid and a change of trend of the critical point as a function of Δ and L is to be expected.

ACKNOWLEDGMENTS

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