

Entropy and Fluid–Fluid Separation in Nonadditive Hard-Sphere Mixtures

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We study the equilibrium behavior of a two-component mixture of equal-sized, nonadditive hard spheres with an interspecies collision diameter that is larger than that of each component. We calculate the thermodynamic and structural properties by simulating a system of 4000 particles in a canonical ensemble through a standard Monte Carlo technique. The phase behavior of the model is analyzed through a multiparticle correlation expansion of the statistical entropy whose prediction on the existence of a fluid–fluid separation threshold compares favorably with independent results on the phase coexistence line.

1. Introduction

A two-component mixture composed of unequal hard spheres is the simplest but still nontrivial model for describing basic excluded-volume effects in real fluid mixtures.¹ The phase diagram of a hard-core mixture shows a variety of phase transitions that are driven by entropic effects only.² In past decades this model has been investigated extensively as a reference model for describing the structural properties of colloidal systems.³

The model is characterized by an inter-species collision diameter $\sigma_{12} = (1/2)(\sigma_{11} + \sigma_{22})(1 + \alpha)$, where σ_{11} and σ_{22} are the collision diameters of like particles and α is a dimensionless parameter which measures the deviation from additivity. If α is different from zero, the model explicitly accounts for nonadditive effects in the effective potentials of the two interacting species.

One of the most discussed features of the phase diagram of a liquid mixture is the phenomenon of demixing which appears to be driven by two distinct mechanisms.⁴

In the case of an additive hard-sphere (AHS) mixture, the possibility of phase separation in a regime of highly asymmetric sizes and concentrations can be explained in terms of the osmotic depletion of smaller particles in the contact region of two larger particles.³ However, the question has not yet received a conclusive answer.⁴

In a nonadditive hard-sphere (NAHS) mixture, the dominant mechanism which underlies phase separation is rather different.⁴ In fact, in this case the sign of the nonadditivity parameter is critical as to the type of thermodynamic behavior exhibited by the mixture. For $\alpha < 0$, the system shows a tendency toward hetero-coordination. Correspondingly, the model is able to

reproduce the large compositional fluctuations that are observed in some liquid and amorphous mixtures.^{5,6,7} On the other hand, when $\alpha > 0$, even a symmetric hard-sphere mixture ($\sigma_{11} = \sigma_{22}$), where size effects play no role, is expected to separate at high density into two phases, one richer in particles of species 1 and the other richer in particles of species 2, respectively. This phenomenon is caused primarily by the extra repulsion between unlike spheres, which overcomes the disordering effect of thermal motion. Such a behavior is typical of some real systems such as He–rare gas and He–H₂ mixtures which, in extreme thermodynamic conditions of pressure and temperature, undergo a fluid–fluid phase separation.^{8–10}

The simplest analytical model where positive nonadditivity is known to produce phase separation is the *penetrable-sphere* model, formerly proposed by Widom and Rowlinson,¹¹ where $\sigma_{11} = \sigma_{22} = 0$, and $\sigma_{12} > 0$.

Exact analytical results are known for the second and third virial coefficients of a NAHS mixture.^{12,13} Recently, the fourth virial coefficient has been computed as well for a symmetric NAHS mixture.¹⁴

The NAHS model has been investigated with a variety of theoretical methods, such as the generalized scaled-particle theory,^{15,16} the γ expansion theory,^{4,17,18} and integral-equation theories.^{19–22} A number of phenomenological equations of state (EOS) has been proposed as well.^{24–27}

Numerical simulation studies of NAHS mixtures have been performed for both negative and positive nonadditivity.^{20,28–31} Recently, the phase equilibria of symmetric^{32,33} and asymmetric³³ NAHS mixtures have been studied with the Gibbs ensemble Monte Carlo (GEMC) technique and with the so-called semi-grand canonical Monte Carlo (SGCMC) method.²² Hoheisel and co-workers performed Monte Carlo (MC) and molecular dynamics (MD) simulations to obtain the critical density of a mixture for $\alpha = 1$.^{34,35}

The aim of this work is to study phase separation of a symmetric NAHS mixture for some values of α in the framework of a multiparticle correlation expansion of the configurational entropy.³⁶ This approach, that is based on the knowledge of pair correlations only in the homogeneous phase,

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has proved particularly successful for a wide class of models in that it provides a clear-cut indication of the emergence of ordering processes in the system and, consequently, of the onset of phase transitions.³⁶⁻⁴⁷

The paper is organized as follows: in section 2 we describe the entropic approach. Section 3 is devoted to the presentation of the MC-performed simulation to evaluate the equilibrium properties of the mixture. The results are then discussed in section 4. Section 5 is finally devoted to concluding remarks.

2. Entropy and Correlations

The total excess entropy of an open system can be expanded as an infinite series:⁴⁸

$$s_{\text{(ex)}} = \sum_{n=2}^{\infty} s_n \quad (1)$$

where $s_{\text{(ex)}}$ is the excess entropy per particle in units of the Boltzmann constant and the partial entropies s_n are obtained from the integrated contributions of the spatial correlations between n -tuples of particles. In particular, in a multicomponent system the two-body term can be written as⁴⁹

$$s_2 = -\frac{1}{2}\rho \sum_{ij} x_i x_j \int \{g_{ij}(r) \ln[g_{ij}(r)] - g_{ij}(r) + 1\} \mathbf{dr} \quad (2)$$

where $\rho = \rho_1 + \rho_2$ is the total number density, x_i is the mole fraction of species i ($i = 1, 2$), and the quantities $g_{ij}(r)$ are the two-body partial distribution functions. The residual multiparticle entropy

$$\Delta s \equiv s_{\text{(ex)}} - s_2 \quad (3)$$

turns out to be a sensitive indicator of the structural changes which take place in the system. At variance with the pair entropy, Δs exhibits a non-monotonic behavior when plotted as a function of either the temperature or the number density. In particular, it has been shown that the zeros of this function do systematically correlate with the thresholds of thermodynamic stability of the homogeneous fluid phase.³⁶⁻⁴⁷

In a mixture composed of hard-core particles with diameters σ_{ij} , the excluded-volume contributions can be integrated out in eq 2 to give⁴⁴

$$s_2(\rho, x_1) = -B(x_1)\rho - 2\pi\rho \sum_{ij} x_i x_j \int_{\sigma_{ij}}^{\infty} \{g_{ij}(r) \ln[g_{ij}(r)] - g_{ij}(r) + 1\} r^2 \mathbf{dr} \quad (4)$$

where

$$B(x_1) = \frac{2}{3}\pi x_1^2 \sigma_1^3 + \frac{4}{3}\pi x_1(1 - x_1)\sigma_{12}^3 + \frac{2}{3}\pi(1 - x_1)^2 \sigma_2^3 \quad (5)$$

is the second virial coefficient. In a highly dilute mixture, the partial distribution functions can be explicitly calculated to first order in the number density.⁴⁴ Correspondingly, the residual multiparticle entropy can be evaluated analytically up to terms of order ρ^3 . This truncated low-density expansion turns out to be particularly useful for discussing the phase diagram of the mixture for values of the non-additivity parameter close to one.

3. Monte Carlo Simulation

In order to generate the pair distribution functions (PDF) we performed numerical simulations using the MC technique in a constant-temperature ensemble. We also implemented the

TABLE 1: Compressibility Factor of an Equimolar Symmetric NAHS Mixture for $\alpha = 0.1$

ρ	$\beta P/\rho$		
	present work	refs 23,24	ref 30
0.10	1.29	1.29	
0.20	1.68	1.68	1.68
0.30	2.20	2.20	
0.40	2.93	2.94	2.93
0.50	3.94	3.97	
0.55	4.55		
0.60	5.27		5.32

linked-cell method in order to manage large numbers of particles ($N = 4000$) not only to improve the overall statistics but also to extend the spatial range of the structural functions as much as possible. This condition is critical for obtaining a good estimate of the pair entropy since, in a strong-coupling regime, a few peaks of the pair correlation functions beyond the first give sizeable contributions to the integrals in eq 4. We calculated the partial PDFs of an equimolar mixture for $\alpha = 0.1$, and for $\alpha = 0.2$ at four different values of the mole fraction ($x_1 = 0.1, 0.2, 0.3, 0.5$). The compressibility factor was determined through the following expression:

$$\frac{\beta P}{\rho} = 1 + \frac{2}{3}\pi\rho \sum_{ij} x_i x_j \sigma_{ij}^3 g_{ij}(\sigma_{ij}) \quad (6)$$

Upon integration, one can then compute the excess entropy of the mixture as

$$s_{\text{(ex)}}(\rho) = - \int_0^\rho \left[\frac{\beta P}{\rho} - 1 \right] \frac{d\rho'}{\rho'} \quad (7)$$

We used a perfectly ordered face-centered cubic (FCC) lattice as a starting configuration of a system composed of 4000 spheres enclosed in a cubic box with periodic boundary conditions. The equilibration period was typically 1×10^9 to 2×10^9 MC steps, depending on the density, where a MC step consisted of an attempt to move one particle chosen at random. The maximum displacement for each particle was varied in order to keep the acceptance ratio of the MC moves between 0.2 and 0.5. Sampling data were obtained by generating chains consisting of 1.2×10^8 to 2.4×10^8 MC steps. Equilibrium averages and relative errors were computed by using one configuration every 80 000 along the chain so as to reduce the correlation between the data.

The thermodynamic integration appearing in eq 1 was performed by numerical integration of a spline approximant of the data collected in Tables 1 and 2.

As is usual with computer simulations close to phase boundaries, one has to monitor with special care the nature of the phase present in the simulation box. Indeed, in some thermodynamic states the system starts to phase separate. Since the interdiffusion process is usually slow, it may be difficult to recognize the onset of a two-phase coexistence in the simulation box in a timely manner.

In our study, we monitored the possible appearance of systematic variations of the local coordination numbers well after the topological equilibration of the sample. We evaluated the residual multiparticle entropy for clearly homogeneous states only or for a few states marginally inside the two-phase region. In the last case the estimate of the residual entropy should be considered some kind of *transient* estimate. As we shall discuss in the next section, these cases actually correspond to the states characterized by positive values of Δs .

TABLE 2: Compressibility Factor of an Equimolar Symmetric NAHS Mixture for $\alpha = 0.2$ at Three Different Concentrations

x_1	ρ	$\beta P/\rho$	
		present work	ref 24
0.1	0.10	1.28	1.28
	0.20	1.65	1.64
	0.30	2.15	2.16
	0.40	2.83	2.85
	0.45	3.27	
	0.50	3.70	
	0.51	3.78	
	0.52	3.88	
0.2	0.10	1.30	
	0.20	1.72	
	0.30	2.29	
	0.35	2.63	
	0.40	3.03	
	0.45	3.47	
	0.46	3.54	
	0.47	3.61	
0.3	0.10	1.32	
	0.20	1.77	
	0.30	2.38	
	0.35	2.75	
	0.40	3.15	
	0.42	3.33	
	0.43	3.40	

4. Results

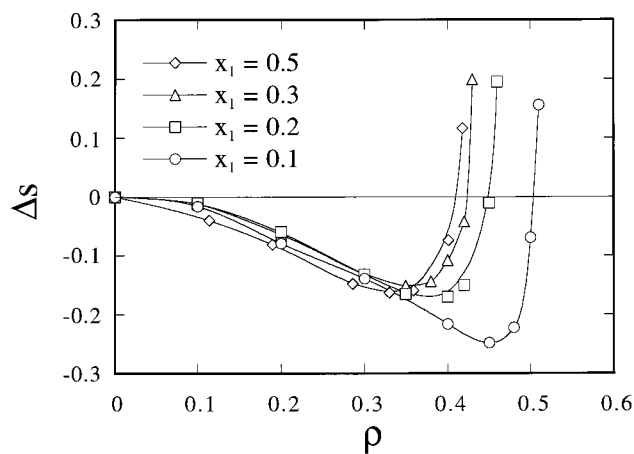
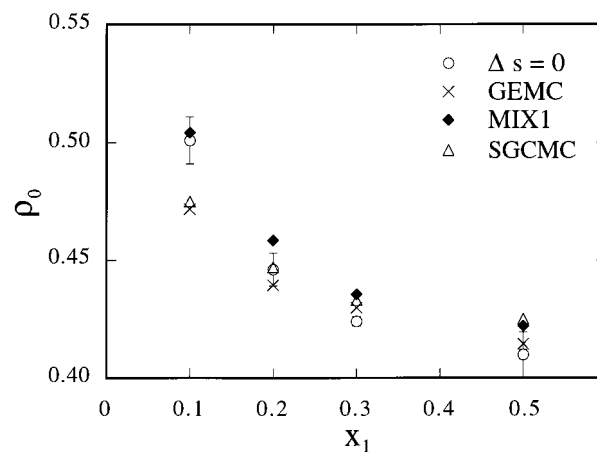
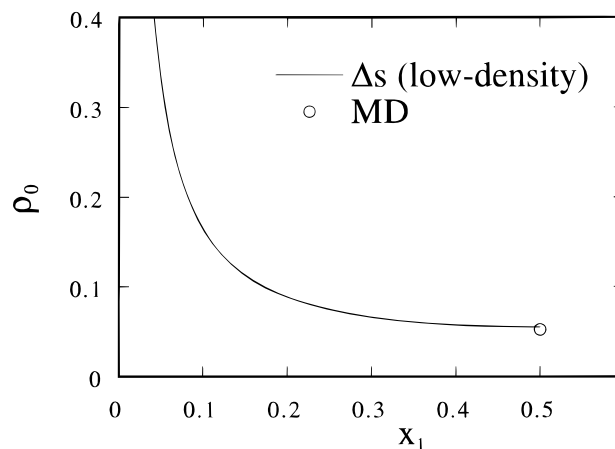
Tables 1 and 2 show the compressibility factor of a NAHS mixture with positive nonadditivity. Our results are in excellent agreement with previous MC data, where available.^{23,24,30}

The residual multiparticle entropy, plotted as a function of the number density, is shown in Figure 1 for $\alpha = 0.2$ and for $x_1 = 0.1, 0.2, 0.3, 0.5$. We note that, upon decreasing the fraction of larger particles, the value of the density ρ_0 , where the residual multiparticle entropy changes sign, increases. This behavior is consistent with the trend observed in the fluid–fluid transition threshold through both numerical simulation and approximate theories as reported in Figure 2.

The error bar on the simulation data corresponds to the bare statistical error. Possible systematic errors due to the potential onset of demixing in some thermodynamic states where simulation should exhibit phase separation are expected to be small due to the extreme slowness of the process at the investigated points.

The comparison with the numerical simulation results is very good all over the explored range of mole fractions. It is only at very small values of x_1 that the estimate obtained through the zero of the residual multiparticle entropy happens to slightly overestimate the simulation data. On the other hand, it systematically improves over the prediction of a widely used first-order perturbation theory (MIX1).²⁸

Figure 3 shows the locus of points where Δs vanishes for $\alpha = 1$ in an equimolar NAHS mixture. This locus was traced through a low-density expansion of Δs truncated at order ρ^3 . It appears that the present prediction of the critical-point density ρ_c is in excellent agreement with the MD results.^{34,35} Table 3 shows the comparison between different estimates of ρ_c . We remark that, even if the predictions offered for $\alpha = 1$ by the virial estimate of the free energy and by the low-density expansion of the residual multiparticle entropy both rely on the knowledge of the first four virial coefficients only, the latter estimate turns out to be largely more precise than the former one.

**Figure 1.** Residual multiparticle entropy plotted as a function of the number density for $\alpha = 0.2$ and mole fractions $x_1 = 0.1, 0.2, 0.3, 0.5$.**Figure 2.** Phase coexistence points of a NAHS mixture for $\alpha = 0.2$ and mole fractions $x_1 = 0.1, 0.2, 0.3, 0.5$. Open circles: locus of points where $\Delta s = 0$; full diamonds: results of a first-order perturbation theory;²⁸ crosses: GEMC estimates;³² open triangles: SGCMC estimates.²² The estimated uncertainties of the present results are reported as well whenever they can be resolved with respect to the size of the marker ($x_1 = 0.1, 0.2$). The error bar at the critical point refers to the GEMC data.³²**Figure 3.** The locus of points where $\Delta s = 0$ for a NAHS mixture plotted as a function of x_1 for $\alpha = 1$. The open circle represents an MD estimate of the critical density.³⁴

5. Concluding Remarks

We have presented a study of the demixing phase boundary in symmetric mixtures of nonadditive hard spheres based on the condition of vanishing multiparticle entropy. For the present

TABLE 3: The Critical Density ρ_c of Symmetric Mixtures for Different Values of the Nonadditivity Parameter α^a

α	simulation	$\Delta s = 0$	virial	MIX1	EOS1N	PY	MS	vdW1f
0.1	0.610	0.584	0.623	0.604	0.608	0.744	0.663	0.532
0.2	0.415	0.409	0.388	0.423	0.422	0.514	0.465	0.332
1.0	0.052	0.055	0.070	0.133	0.062	0.109	0.091	0.050

^a The simulation data are taken from ref 33 for $\alpha = 0.1$, from ref 32 for $\alpha = 0.2$, and from ref 34 for $\alpha = 1$. The virial values refer to ref 14, while the predictions of MIX1 (first-order perturbation theory), EOS1N (ref 25), PY (Percus–Yevick), MS (Martynov–Sarkisov), and vdW1f (van der Waals one-fluid model) are taken from ref 25.

cases, the criterion favorably compares with the best computer simulation estimates. Present experience with the liquid–vapor phase boundary suggests that the quantitative accuracy may decrease for binary systems interacting with soft repulsive potentials. We expect a similar good quality of the results for asymmetric mixtures.

The method has all the pros and cons of one-phase methods. On one hand, it does not need direct information on the two coexisting phases and, since it only requires thermodynamic quantities and pair correlation functions, it is suitable for more approximate but faster evaluations which may resort to high-quality integral equation results instead of computer simulation data. On the other hand, we can observe an intrinsic limit of the method due to the difficulties associated with the exact characterization of the phase transition as signaled by the vanishing of the residual multiparticle entropy. Indeed, for small or moderate positive nonadditivity, the liquid–liquid-phase separation should join the liquid–solid-phase transition, at least at high densities. There is no way, in the present empirical formulation of the multiparticle entropy criterion, to distinguish which of the two transitions takes place. We hope that the present results may motivate further elaboration toward a better understanding of the practical limits of the method and of the underlying theory.

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