

Phase Separation of Binary Mixtures of Symmetric Non-Additive Hard Spheres *

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The behavior of a binary mixture of non-additive hard spheres with positive non-additivity parameter is investigated. The coexistence curves are calculated with a high accuracy for a few system sizes. The applicability of semigrand ensemble simulation method to calculation of the coexistence curve and the critical properties of mixtures is compared with other simulation method.

Key words: critical phenomena, Monte Carlo simulations, binary mixture

The calculation of the critical point parameters by computer simulation is a real challenge. The difficulties result from the fact that the correlation length diverges to infinity when the critical point is approached, whereas the size of the simulated systems is limited, due to computer resources. Thus, near the critical point, the correlation length is greater than the linear dimension of the simulation box. Additional problem is the effect of critical slowing down, which makes the simulation time-consuming. The knowledge of the critical point parameters and the shape of the coexistence curve close to the critical point is important, since it can be used to identification of the universality class of the system.

The model system for which the critical behavior is well established is the Ising model. The Ising model is equivalent to the lattice-gas model in which the positions of the particles are restricted to the lattice sites and also to an incompressible binary mixture. For the bulk critical phenomena the restriction of the positions of the particles to the lattice sites plays no role and the simple fluids near the gas-liquid critical point or binary fluid mixtures near the consolute point belong to the Ising universality class. However, when the fluid is confined in narrow pores, with the pore thickness equal to several lattice spacings (or molecular diameters), the restriction of the positions of the particles to the lattice sites may play an important role. It is therefore important to know the behavior of a simple model fluid with continuous degrees of freedom near the critical point. Such knowledge will enable the investigation of the differences in the critical behavior of fluids in porous materials from the bulk critical behavior. The question whether the fluid confined in a porous material belongs to a different univer-

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sality class remains open. Computer simulations of a simple model fluid in porous media are the best tool to answer such question. Moreover, the comparison of the simulation data with the theoretical results is a very useful check of the accuracy of the theory. Especially for a hard spheres fluid such accurate data are important, since the hard spheres fluid is often used as a reference system in perturbation theories.

Here, we present the results of computer simulations of coexistence for the model system of a non-additive hard spheres fluid, which is often called Widom-Rowlinson model [1].

The model: We study a mixture of symmetric non-additive hard spheres [1] with the interaction potential defined by:

$$U_{\alpha\gamma}(r) = \begin{cases} \infty & \text{if } r < \sigma_{\alpha\gamma} \\ 0 & \text{if } r > \sigma_{\alpha\gamma} \end{cases} \quad (1)$$

where indices $\alpha \in \{A, B\}$ and $\gamma \in \{A, B\}$ describe the species. The length scale is set by A component hard sphere diameter σ_{AA} . For symmetric non-additive mixtures

$$\sigma_{BB} = \sigma_{AA} \quad (2)$$

and

$$\sigma_{AB} = 1/2(\sigma_{AA} + \sigma_{BB})(1 + \Delta) \quad (3)$$

where Δ is a non-additivity parameter. In our case $\Delta = 0.2$ for all calculations. Above the critical density, the mixture separates into two phases: one phase rich in component A and the other rich in component B. The symmetry of interactions imposes for the two phases I and II in equilibrium the following conditions:

$$x_A^I = x_B^{II}, \quad x_B^I = x_A^{II} \quad (4)$$

and

$$\mu_A^I = \mu_A^{II} = \mu_B^I = \mu_B^{II} \quad (5)$$

where μ_α^i and x_α^i are the chemical potential and the composition of α component in the i -th phase respectively. The composition of the coexisting phases is symmetric. An interesting feature of the model is the fact that the internal energy is zero and the phase transitions are entropically driven.

The Monte Carlo method: We use the semigrand Monte Carlo simulation method [2,3] to model an open system in contact with a reservoir. In this method the system is simulated under constant total number of particles N , total volume V , temperature T , and the difference of the chemical potential of one species with respect to an arbitrarily chosen species. Thus, the number of molecules of each species fluctuates, while the total density remains constant. The distribution of microstates Γ in the semigrand ensemble at constant volume for n -component mixture is given by:

$$P(N, V, T, \{\Delta_\gamma\}; \Gamma) \propto \prod_{\alpha=1}^n \frac{1}{N_\alpha!} \exp(\beta N_\alpha \Delta_\alpha^0 + N \ln V - \beta U(\Gamma)) \quad (6)$$

where $\Delta_\alpha^0 = \mu_\alpha^0 - \mu_\gamma^0$ and $\mu_\alpha^0 = \mu_\alpha - \ln(\Lambda_\alpha^3)$, $\Lambda_\alpha = \sqrt{h^2/(2\pi m_\alpha k_B T)}$ is the thermal de Broglie wavelength of particles of type α and $\beta = 1/k_B T$ is the inverse temperature. For two component systems:

$$P(N, V, T, \Delta\mu^0, \Gamma) \propto \sum_{N_B=1}^N \frac{1}{(N_B)!(N - N_B)!} \exp(\beta N_B \Delta\mu^0 + N \ln V - \beta U(\Gamma)) \quad (7)$$

where $\Delta\mu^0 = \mu_A^0 - \mu_B^0$, N_α is the number of particles of the component α , $\alpha \in \{A, B\}$. The realization of the semigrand ensemble Monte Carlo simulation for symmetric non-additive hard spheres requires two kinds of moves: translation and identity change. For a symmetric binary hard spheres mixture, the internal energy and the chemical potential difference are both zero. Thus, the probability of identity change is given by $\mathcal{R} = \min\{1, Q_{\alpha \rightarrow \gamma}\}$, where

$$Q_{A \rightarrow B} = \frac{P_{new}}{P_{old}} = \frac{N_A}{N_B + 1} \quad (8)$$

if a molecule A is converted into a molecule B ($A \rightarrow B$) and

$$Q_{B \rightarrow A} = \frac{P_{new}}{P_{old}} = \frac{N_B}{N_A + 1} \quad (9)$$

if a molecule B is converted into a molecule A ($B \rightarrow A$). For this choice of acceptance criteria, the identity change moves are performed in the following way: First a species A or B is chosen with equal probability, next a molecule of this species is chosen randomly and converted into a molecule of the other species with acceptance probability given by (8) or (9). For translation moves the maximum displacement is chosen to ob-

tain 50% acceptance ratio. The identity change and translation move are chosen randomly with the ratio of one exchange move per ten translation moves. The equilibrium values of the mole fraction and errors are calculated from the histograms of the mole fraction taken during the simulation. The accuracy of the histogram is determined by the total number of particles in the simulation box N . The histogram near the equilibrium values is approximated by the Gaussian. The mean value of the Gaussian is taken for the equilibrium value of the concentration. The errors are determined from the width of the Gaussian.

We have also performed the simulation with a variant of Gibbs ensemble Monte Carlo method [4], where the particle transfer moves between boxes are omitted. Therefore, the number of molecules in each simulation box is the same ($N^I = N^{II}$) and the volume of the boxes is the same ($V^I = V^{II}$) during the simulation, while the composition changes. The equilibration of the chemical potential of both components is obtained by mutual identity change of two randomly chosen molecules of different species in two simulation boxes. That is when a molecule A is converted into a molecule B in box one, at the same time a molecule B is converted into a molecule A. The acceptance probability for the identity change move is given by $\mathcal{R} = \min\{1, \mathcal{Q}\}$, where

$$\mathcal{Q} = \frac{P_{new}}{P_{old}} = \frac{N_A^I}{N_B^I + 1} \frac{N_B^{II}}{N_A^{II} + 1} \quad (10)$$

Here, we also take the advantage of the symmetry of the mixture. One may expect that the simulations in the Gibbs ensemble would give lower fluctuations of the composition in each phase, due to the fact that identity change moves are dependent, because they are performed simultaneously in two simulation boxes. Thus, the acceptance ratio for the identity change moves should be lower than in the semigrand ensemble and the fluctuations of composition should be smaller. Such property of the Gibbs ensemble allow for more precise calculations near the critical point, where the fluctuations become significant. The fluctuations of the composition in the Gibbs ensemble are in fact smaller, but only a little. This is reflected in the error bars, which are smaller for the Gibbs ensemble calculations than that for the semigrand ensemble. Fig. 1 shows the coexistence curves calculated in NVT semigrand and NVT Gibbs ensemble for the total number of particles $N = 256$ and $N = 256 + 256$ respectively. The composition of the coexisting phases, $x = N_A/(N_A + N_B)$, is plotted as a function of packing fraction, $\eta = \eta_A + \eta_B = \pi/6(N_A\sigma_{AA}/V) + \pi/6(N_B\sigma_{BB}/V)$. Only half of the phase diagram is presented, since the phase diagram is symmetric due to the symmetry of the mixture. Therefore, the critical concentration is always $x_A = 0.5$ and the composition of coexisting phases fulfill the relation $x_A = 1 - x_B$. The results obtained by the Gibbs and semigrand ensemble are identical. The same agreement between the Gibbs and semigrand ensemble was obtained in simulations of symmetric square well mixtures

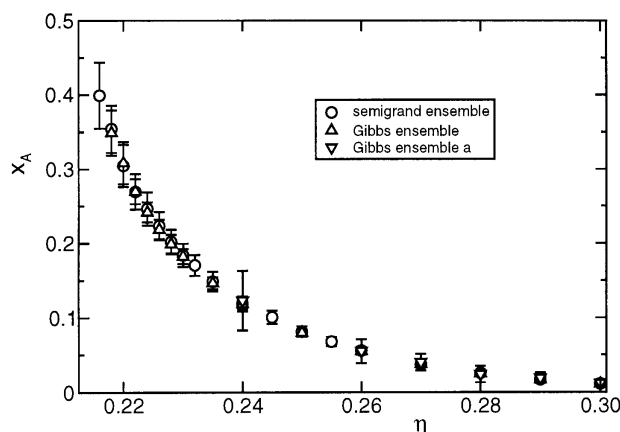


Figure 1. Comparison of coexistence curves for $N=256$ particles in the semigrand ensemble and $N=256 + 256$ particles in the Gibbs ensemble. Circles, triangles up – this work, triangles down – [5].

[3]. It is interesting to note that the system size effects are exactly the same for simulations in the semigrand ensemble and the Gibbs ensemble. We have observed that the values of the mole fraction near the critical point are the same for the same number of particles in the simulation box. In the Gibbs ensemble simulations, the number of molecules present in each simulation box is half of the total number of molecules taking part in the simulation. Thus, in the Gibbs ensemble simulation, it is necessary to simulate two times more molecules than in the semigrand ensemble simulation, to obtain the same accuracy.

For a symmetric mixture the Gibbs ensemble Monte Carlo method is less advantageous than the semigrand ensemble method. The former requires simulation of two times more molecules to achieve the same accuracy, as obtained in the semigrand Monte Carlo simulations.

We have also compared the results of NVT semigrand ensemble with NPT semigrand ensemble calculation from [6] for two different system sizes. In both cases the agreement between NPT and NVT semigrand calculation for higher packing fraction is good, but near the critical point the two-phase region obtained by the NPT method is smaller, see Fig. 2 and 3. However, the results agree within the rather large error bars in Fig. 3. Another feature, present in the NVT and absent in the NPT semigrand simulations, is the strong system size dependence of the coexistence curve near the critical point. Similar behavior was observed in [3] for symmetric square well mixture. It has to be noted that the results obtained with the NVT semigrand ensemble for $N = 864$ are in very good agreement with the results obtained in the NVT Gibbs ensemble from [5] for $N = 864 + 864$ particles, where particles transfer moves were employed.

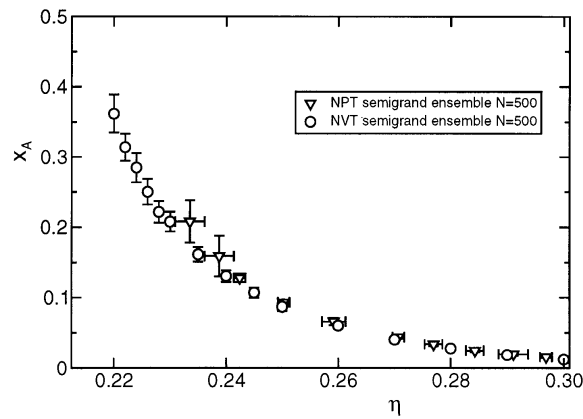


Figure 2. Comparison of coexistence curves for $N=500$ particles in NPT and NVT semigrand ensemble. Circles – this work, triangles – [6].

Critical packing fraction: The critical packing fraction of symmetric non-additive hard spheres mixture with positive non-additivity parameter $\Delta = 0.2$ was previously estimated in a few simulation studies: in [7] by molecular dynamics simulations, in [5] by Gibbs ensemble simulation method and in [6] by NPT semigrand ensemble. In [5] the implemented Gibbs Ensemble method used particle transfer moves, which are inefficient for dense fluids. Different simulation methods as well as different system sizes were used in these studies. The critical density η_c is strongly size dependent. Therefore, comparison between different results should be done carefully, with indication of the system size. We use the scaling relation to estimate the critical packing fraction (12) for a given system size, similar to the one used in estima-

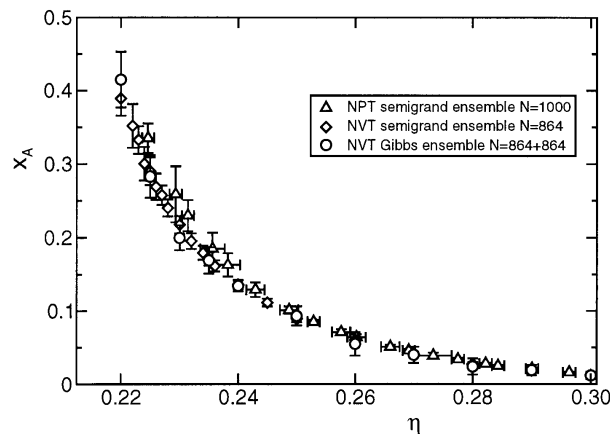


Figure 3. Comparison of coexistence curves for $N=864$ particles in the NVT semigrand ensemble and NVT Gibbs ensemble with particle transfer and for $N=864$ NPT semigrand ensemble. Diamonds – this work, circles – [5], triangles – [6].

tion of the critical temperature (11) fraction. It is assumed that the mixture of non-additive hard spheres belongs to the Ising universality class.

In general one can write that the order parameter near the critical point behaves as

$$\left| \frac{\zeta_a - \zeta_c}{\zeta_c} \right| \propto \left| 1 - \frac{t}{t_c} \right|^\beta \quad (11)$$

where ζ is the order parameter (for example density, composition, magnetization) and t is some intensive thermodynamic parameter (for example temperature, chemical potential). The subscript c indicates the value of the parameter at the critical point. The β is the critical exponent associated with the order parameter and assumes the same value for substances belonging to the same universality class. For the Ising universality class in 2D, β is known exactly and equals $\beta = 1/8$. In 3D only an approximate value of β is known from computer simulations [8], $\beta = 0.3258$. In analogy to (11) one can write for an athermal fluid mixture:

$$\left| \frac{x_A(\eta) - x_c}{x_c} \right| \propto \left| \frac{\eta}{\eta_c} - 1 \right|^\beta \quad (12)$$

where $x_A(\eta)$ is the composition of the coexisting phases at the packing fraction η , x_c is the composition at the critical point (for symmetric mixture $x_c = 0.5$ by definition), and η_c is the critical packing fraction. (12) is used to estimate the critical packing fraction from the simulation data. The data near the critical point are fitted to (12) with the exponent $\beta = 0.3258$. It is assumed that the non-additive hard spheres mixture belongs to the Ising universality class. Very good agreement between the fit and the data is obtained.

There exist a few simulation studies, where the critical packing fraction is calculated for the symmetric non-additive hard spheres binary mixture with non-additivity parameter $\Delta = 0.2$. The chronologically first estimates are based on molecular dynamics simulations of [7]. 256 particles were used and the critical packing fraction was estimated to $\eta_c(N = 256) = 0.22 \pm 0.02$. This value is higher than that calculated from our semigrand and Gibbs ensemble simulations for the same system size. We obtained $\eta_c(N = 256) = 0.2166 \pm 0.0005$ with the higher accuracy calculations. This discrepancy may be attributed to the difficulties in estimation of the values of composition for coexisting phases in molecular dynamics simulation near critical temperature. In molecular dynamics simulation the composition of coexisting phases is obtained indirectly, while in the Monte Carlo methods, employed in our study, we get the composition directly from the simulations.

In [5] the critical packing fraction was estimated with a much higher precision by the Gibbs ensemble simulation method. For much larger system size the critical packing fraction was calculated as $\eta_c(N = 864 + 864) = 0.2175^{+0.0025}_{-0.0075}$. It agrees within the error bars with our estimates $\eta_c(N = 864) = 0.2205 \pm 0.0006$ from the semigrand ensemble simulations.

In [6] the critical packing fraction was estimated for the system size $N = 1000$ to $\eta_c(N = 1000) = 0.2225 \pm 0.0003$ by using simulations in constant pressure semigrand ensemble. This is in disagreement with our results for the system size closest to $N = 1000$. This discrepancy comes from the different way of calculating the mole fraction of the coexisting phases. In our simulations we take for the equilibrium mole fraction the value of the mole fraction at the maximum of the mole fraction histogram taken during the simulation. Thus, we do not count the configurations, where the fluid becomes mixed. Such configurations are the result of the small system size of the simulated fluid. If one takes these configurations to calculate the mole fraction, the value of the equilibrium mole fraction becomes smaller and the critical packing fraction estimated from such data near the critical point is higher. It is intriguing that the critical density estimated in [6] is very close to the critical density for the large system size we have simulated, $N = 2048$, which is $\eta_c(N = 2048) = 0.2216 \pm 0.0006$. We attribute this fact to pure coincidence.

We have observed a strong system size dependence near the critical point. Fig. 4 shows the difference between the coexistence curves for two system sizes $N = 256$ and $N = 2048$. The critical packing fraction η_c significantly depends on the number of molecules used in the simulation. Such behavior should be expected, based on the finite size scaling hypothesis [9]. From the calculations performed for $N \in \{256, 500, 864, 2048\}$ we see that the system size effects for $N > 256$ become negligible at the packing fraction $\eta = 0.3$, for which the mole fraction of coexisting phases is $x_A =$

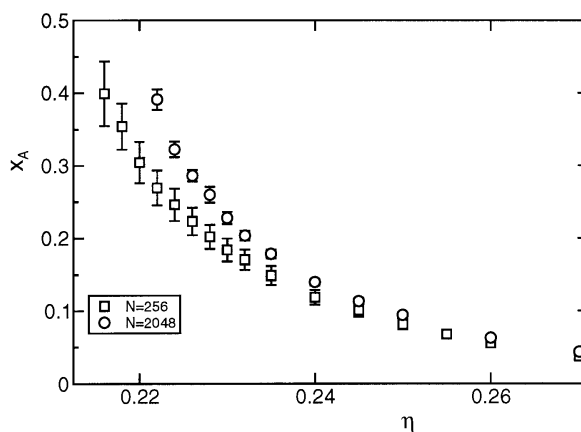


Figure 4. Coexistence curves for the systems with $N \in \{256, 2048\}$ molecules.

0.012. This is much above the critical packing fraction η_c . Thus, the critical packing fraction must be calculated with extreme care.

In [10] the crossover from the Ising to the mean field behavior near the critical point was observed for the two-dimensional Ising model. It was argued that near the critical point the correlation length diverges and the finite size of the simulation box influences the behavior of the fluid in such a way that it behaves as in the mean field. We have not seen the crossover from the mean field limit to the Ising limit, as it was seen in the studies of the two-dimensional Ising [10] and the square well fluid [11]. Our calculations definitely support the hypothesis that non-additive hard spheres mixtures belong to the Ising universality class.

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