

## Direct determination of liquid phase coexistence by Monte Carlo simulations

Henk J. A. Zweistra\* and N. A. M. Besseling

Laboratory of Physical Chemistry and Colloid Science, Dreijenplein 6, NL-6703 HB Wageningen, the Netherlands

(Received 3 January 2006; published 19 July 2006)

A formalism to determine coexistence points by means of Monte Carlo simulations is presented. The general idea of the method is to perform a simulation simultaneously in several unconnected boxes which can exchange particles. At equilibrium, most of the boxes will be occupied by a homogeneous phase. The compositions of these boxes yield coexisting points on the binodal. However, since the overall composition is fixed, at least one of the boxes will contain an interface. We show that this does not affect the results, provided that the interface has no net curvature. We coin the name “Helmholtz-ensemble method,” because the method is related to the well-known Gibbs-ensemble method, but the volume of the boxes is constant. Since the box volumes are constant, we expect that this method will be particularly useful for lattice models. The accuracy of the Helmholtz-ensemble method is benchmarked against known coexistence curves of the three-dimensional Ising model with excellent results.

DOI: [10.1103/PhysRevE.74.016111](https://doi.org/10.1103/PhysRevE.74.016111)

PACS number(s): 82.20.Wt, 05.50.+q, 05.70.Fh

### I. INTRODUCTION

Phase coexistence of fluids is an important subject from both a scientific and a technological viewpoint. For example, the complex phase behavior of oil, water, and surfactants is interesting in its own right. Phase separation is also an important purification mechanism in the process industry.

Since the advent of the Metropolis algorithm [1] in the 1950s, Monte Carlo methods have been used extensively to simulate equilibrium properties of fluids. The Metropolis technique lets us sample a representative part of configuration space, which enables us to calculate thermodynamic properties of the system.

An important goal of simulations of immiscible fluids is to find the compositions of the coexisting phases. To this end, Panagiotopoulos introduced the so-called Gibbs-ensemble method almost 20 years ago [2]. In his elegant scheme, the entire system is partitioned into two simulation boxes which can exchange both particles and volume [2,3]. This method depends on the property that the systems tend to avoid the formation of an interface. After equilibration, no interface is found in either box. When the overall composition is in the two-phase regime, each box assumes the same composition as one of the coexisting homogeneous phases. The results agree well with compositions that were calculated by earlier methods.

Elegant as this scheme may be, the Gibbs-ensemble technique breaks down when one of the phases becomes very dense, since then the exchange of monomers between the systems becomes a highly unlikely event [4]. Lattice models of monomeric species do not suffer from this drawback. Lattice models have been in use for a long time in statistical mechanics. They usually require less computational time and memory than their continuum counterparts, and structural analysis of such systems is usually much simpler. Paradoxically, the determination of phase coexistence points has proved to be more involved with lattice models than with continuous-space models.

For instance, the Gibbs-ensemble method can be applied to lattice models only with great difficulty. The principal problem that one has to solve is incorporating volume changes. In order to maintain periodic boundary conditions, only entire lattice layers can be transferred from one system to another. The probability that such an event occurs is very low due to the large number of contacts. Moreover, as the volumes can only be changed in relatively large discrete steps, the equilibrium volume ratio between the coexisting phases cannot generally be reached. The convergence speed is further deteriorated if polymers are present. However, Mackie *et al.* devised a scheme to improve the convergence behavior [5,6].

Indirect methods to determine phase coexistence points are more often used for lattice systems at the moment. Indirect methods, in contrast with direct methods, generally make use of a single simulation box. It is usually not possible to sample the concentrated and dilute phase directly from a single box because it is difficult to locate the phase boundaries. This is especially true near the critical point.

Instead, the free energy per unit volume of the system is calculated for a range of overall compositions. The coexistence points can then be calculated by means of a Maxwell construction (or variant thereof). Several authors reported quantitative results for coexistence curves calculated using the indirect determination. The development of the indirect method applied to water-oil-amphiphile systems is due to Larson *et al.* [7]. Their method has been modified recently to study amphiphile solubility and phase behavior in supercritical CO<sub>2</sub> [8,9]. Yan *et al.* used an indirect method to obtain an accurate coexistence curve for the three-dimensional (3D) Ising lattice, which is equivalent to a binary mixture with symmetric interaction potentials [10].

However, the problems associated with the indirect method are twofold. First, by comparison elaborate calculations are required in order to obtain accurate results, since the initial composition has to be varied over a broad range in order to obtain a single point on the coexistence curve. Second, in practice only systems that separate into two phases can be modeled. It is in principle possible to simulate phase behavior of a multiphase system, but this involves the calcu-

\*Electronic address: [henk.zweistra@wur.nl](mailto:henk.zweistra@wur.nl)

lation of a multidimensional Maxwell construction. The computational cost of such a calculation is astronomical as the concentration of each component would have to be varied independently.

Finally, we mention the Kofke method to trace the coexistence curve [11–13]. This method cannot be categorized as a direct or indirect method to calculate phase coexistence points. Rather, it depends on *a priori* methods to find a single point on the binodal. The other points are then found by integrating the Clausius-Clapeyron equation along the coexistence line. This method proved to be useful and it is extensively used. In its original form, it may be unstable [4] and numerical errors make that the result tends to grow away from the “true” coexistence line. Mehta and Kofke proposed a modification of the algorithm [14] that circumvents the numerical instability. Their modification works especially well for compositions that are not too close to the critical point. At any rate, this method still depends on *a priori* methods so the demand for fast and accurate direct and indirect methods will not diminish because of the development of the Kofke integration.

In this paper, we introduce a direct method to determine phase coexistence points by means of Monte Carlo simulations. This paper is organized as follows. In the next section (II), we will describe the method in general terms and provide justification for our method based on thermodynamic arguments. In Sec. III, we will benchmark the accuracy of the method against known results for the 3D Ising lattice.

## II. DESCRIPTION OF THE METHOD

The general idea of the method is to simulate phase coexistence in several unconnected boxes which can exchange particles. Most of the boxes will contain a homogeneous phase. The composition of those boxes is used to determine the phase coexistence points. In contrast with the Gibbs ensemble, volume changes are not needed, but we deliberately allow an interface to be formed in one of the boxes instead. Boxes that contain an interface are not used for the determination of coexistence points.

If monomeric, isotropic particles are involved, only one type of perturbation is needed: particle displacements. This is necessary and sufficient to reach the phase-separated state from any random configuration. If more complex particles are involved, also particle rotations, reorientations and possibly reconfigurations should be implemented. These perturbations are not specific for this method but have to be employed in any correct Monte Carlo sampling. We will restrict the discussion to monomeric, isotropic species, but without loss of generality. The principle of the method is not altered in any way if more elaborate perturbations of the particles have to be included in the Monte Carlo scheme.

The formalism can be justified on thermodynamic grounds. Consider a macroscopic, phase-separated system containing  $P$  coexisting phases, which are connected by  $I$  surfaces. At thermodynamic equilibrium, the chemical potential of any component and the pressure are constant throughout the system.

We are free to arbitrarily partition the macroscopic system into several unconnected simulation boxes which can ex-

change particles. Particle displacement is sufficient to induce phase separation in a macroscopic mixture. Hence phase separation will also occur in a collection of particle-interchanging boxes. However, this does not happen for each box individually, but rather for the ensemble of boxes as a whole. It is unlikely that a homogeneous phase will develop an interface because an interface contributes to the free energy of the system [4].

The important consequence of this is that as many boxes as possible will contain a homogeneous phase. One or several boxes will have to contain an interface, because the overall composition is conserved. The number of interface-containing boxes will not exceed  $I$ , the number of interfaces that were present in the macroscopic system, because the interface area is minimal at thermodynamic equilibrium. We conclude that we can find the compositions of the coexisting phases directly if we perform the simulation in at least  $P+I$  particle-interchanging boxes simultaneously. After equilibration, we identify boxes that contain a homogeneous phase as coexisting phases in the macroscopic system.

Note that the computational demands of this method scale much more favorably with the number of coexisting phases than indirect methods. In the present method, only a few boxes need to be added in a single computer experiment, while in the case of indirect methods, another *dimension* should be added to the Maxwell construction for each additional phase. However, we will restrict the discussion in this paper to two-phase systems.

Several features of the present method will be illustrated by means of an example: simulating phase coexistence of a binary liquid mixture. We will use lowercase letters  $a$  and  $b$  to refer to the components in the mixture. The composition of the system is determined by the overall volume fractions of the components:  $\phi_a$  and  $\phi_b$ .

$a$  and  $b$  are only partially miscible, therefore the mixture will segregate into an  $a$ -rich and a  $b$ -rich phase. These phases are named here simply  $A$  and  $B$ , respectively. We are interested in the compositions of the coexisting phases:  $\phi_a^A$  (the volume fraction of component  $a$  in phase  $A$ ),  $\phi_b^B$  (the volume fraction of component  $b$  in phase  $B$ ), and so on.

Two phases and one interface exist, so we will use three simulation boxes and enforce full periodic boundary conditions. This is schematically depicted in Fig. 1. The system is initialized by filling the boxes at random for a given initial composition. During equilibration, particles are exchanged between boxes I, II, and III (indicated by bidirectional arrows). Particles can also be displaced within a single box. The boxes are therefore in thermodynamic equilibrium internally and with the other boxes.

It is usually not possible to predict which boxes will develop a homogeneous phase from the random configuration of particles. In this specific simulation, boxes I and III contain homogeneous phases  $B$  and  $A$  after equilibration. Therefore we use the composition of boxes I and III to find the coexistence points:  $\phi_a^B = \phi_a^I$ ,  $\phi_b^B = \phi_b^I$ ,  $\phi_a^A = \phi_a^{III}$ , and  $\phi_b^A = \phi_b^{III}$ .

Box II *must* contain an interface because the total composition is conserved. The initial (or overall) composition of the boxes determines the composition of box II, and thus the volume that is occupied by phase  $A$  in II. The *phase volume fraction* of phase  $A$  in box II is indicated by  $\varphi^A$ .  $\varphi^A$  deter-

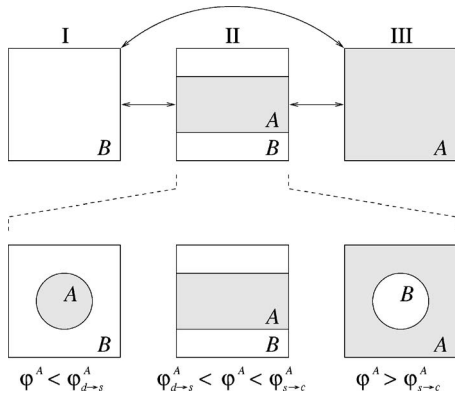


FIG. 1. Schematic illustration of the proposed method for a binary mixture. See text for details.

mines the shape of phase A in box II since the shape of the phase is adjusted in order to minimize the surface area (Fig. 1).

At low  $\varphi^A$ , phase A forms a droplet ( $d$ ) inside a continuous phase B (Fig. 1). If  $\varphi^A$  is increased above a certain droplet-to-slab transition volume fraction  $\varphi_{d \rightarrow s}^A$ , the formation of a “slab” of phase A becomes favorable since it has a smaller surface area than a droplet of the same volume. The system passes a second transition  $\varphi_{s \rightarrow c}^A$  at even higher values of  $\varphi^A$ . The situation is now reversed: phase A forms a continuous phase ( $c$ ) around phase B.

The shape of phase A in box II is of relevance because a pressure difference, known as the Laplace pressure, exists across a curved interface [15]. The Laplace pressure influences the chemical potentials of the box containing the interface, and also the chemical potentials of the collection of boxes as a whole. The composition of the homogeneous boxes is therefore affected by a nonzero average curvature of the interface. Box II should contain an interface with vanishing average curvature in order to obtain accurate results. Note that an interface with vanishing average curvature is formed when  $\varphi_{d \rightarrow s}^A < \varphi^A < \varphi_{s \rightarrow c}^A$ .

It is therefore of interest to estimate  $\varphi_{d \rightarrow s}^A$  and  $\varphi_{s \rightarrow c}^A$ . For the moment, we will assume that surface roughness does not contribute to the total surface area in a significant way, and the composition of the different phases on both sides of the interface does not depend on the average curvature of the interface. Surface free energy is then the only quantity that needs to be minimized. For a given  $\varphi^A$ , phase A adjusts its shape to minimize the surface free energy.  $\varphi_{d \rightarrow s}^A$  then follows from simple geometric considerations, since it is the value of  $\varphi^A$  where the surface area of a droplet equals the surface area of a slab.  $\varphi_{s \rightarrow c}^A$  follows from equivalent arguments, and we obtain

$$\varphi_{d \rightarrow s}^A = \frac{1}{3} \sqrt{\frac{2}{\pi}} \approx 0.266, \quad (1)$$

$$\varphi_{s \rightarrow c}^A = 1 - \frac{1}{3} \sqrt{\frac{2}{\pi}} \approx 0.734. \quad (2)$$

To a first approximation, we expect to find an on average flat interface if the phase volume fractions of the box containing

the interface lie roughly in between these values.

The approximations used in this argument may prove to be quite severe. Larson *et al.* observed that the interface of a segregated system with symmetric interactions can exhibit a large degree of surface roughness [7]. Moreover,  $\phi_a^{II,A}$  and  $\phi_a^{II,B}$  are not completely independent of the curvature of the surface. Nonetheless, it gives some idea of how the system reacts to a mismatched phase volume fraction.

Direct assessment of  $\varphi^A$  is not straightforward, as it requires the determination of a dividing plane between the two phases. It is much more convenient to measure  $\phi_a^{II}$ , the volume fraction of component  $a$  in system II, instead. In certain special cases, it is possible to check that  $\varphi^A \approx 0.5$ , which is desirable in any situation. For example, when the phases are strongly segregated,  $\phi_a^{II,A} \approx 1 \gg \phi_a^{II,B}$  therefore  $\varphi^A$  and  $\phi_a^{II}$  are roughly equal in this case. Furthermore, if interactions between the particles are symmetric, the volume fractions of the phases must be equal if the volume fractions of the particles are equal, which is easy to check.

If one is interested in a complex model at high temperatures, no direct relation between  $\varphi^A$  and  $\phi_a^{II}$  is known. In such a case, one should check if a simulation with a slightly different initial composition leads to the same composition of the homogeneous phases. Alternatively, one could use for instance Widom’s test-particle method [16] to determine the chemical potentials of the equilibrated system, and check if they do not depend on  $\phi_a$ . If this is the case, it can be assumed that the interface is on average flat and that the chemical potential (and thus the compositions) are correct.

In the case that a curved interface is formed, one can simply adjust the overall composition and redo the simulation. It is therefore in principle always possible to find the compositions of two coexisting phases, even if the interaction potentials are highly asymmetric. The range of applicability is therefore not affected by the possible occurrence of a curved interface.

It would be worthwhile for future research to find expressions to improve the estimation of  $\varphi^A$  and the average curvature of the interface from  $\phi_a^{II}$ . Such an analysis should at least take the surface tension and roughness and the size of the droplet into account. If these expressions are available, it is possible to define explicit criteria which the composition of the interface box must satisfy in order to have a interface without net curvature.

If the interface has no average curvature, we can use the compositions of the boxes that contain homogeneous phase to obtain a direct determination of the phase coexistence points. In contrast to the original Gibbs-ensemble method [2], volume exchanges are unnecessary in this scheme. This methodology is therefore both easier to implement and much more suitable for lattice systems.

We propose the term “Helmholtz-ensemble method” for our method for several reasons. First, equilibration of the boxes is equivalent to minimization of the Helmholtz energy. The collection of boxes comprises a system within the canonical ensemble. Equilibrium is reached when the Helmholtz free energy of such a system is minimal [15]. Moreover, we would like to indicate the connection with the Gibbs-ensemble method. The most important difference between the present method and the Gibbs-ensemble method is

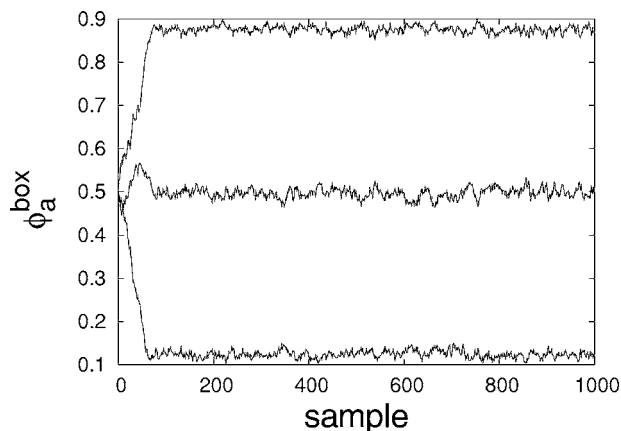


FIG. 2. Sample run for the 3D Ising model at  $T^* = 1.0$ . The volume fraction of component  $a$  is plotted against the sample ranking number for each box individually.  $10^5$  swaps were attempted between samples.

that the volumes of the boxes are constant in the present method, while it is variable in the Gibbs-ensemble method. The fact that the simulations are performed at constant volume also explains our choice for the term Helmholtz-ensemble method.

Gibbs-ensemble and Helmholtz-ensemble calculations both yield coexistence points at constant pressure. The pressures are the same in each box, as this is one of the conditions of phase coexistence at thermodynamic equilibrium. This is in contrast with the method by Nelson *et al.* [17]. This method is based on performing a simulation in two boxes simultaneously. Particle exchanges between the boxes are allowed for all but one of the particle types. This method has been used to calculate partition coefficients of oil in water in the presence and absence of amphiphiles.

Although similar to the present method in the sense that the box volumes are constant and that only particle displacements are necessary to reach equilibrium, there are fundamental differences. In Nelson *et al.*'s method, an osmotic pressure difference arises between the boxes, because particle exchange between the boxes is disallowed for one of the species. Nelson *et al.*'s method is therefore not suitable to calculate phase coexistence points at arbitrary compositions.

### III. NUMERICAL RESULTS FOR THE 3D ISING MODEL

In this section, we will present results that validate our method. Up to this point, we did not make a distinction between continuous and lattice systems. The Helmholtz-ensemble method is equally applicable to both types of systems. We will discuss only lattice models in this section, because it is to be expected that the Helmholtz ensemble is superior to the Gibbs-ensemble method for lattice systems.

We chose the 3D Ising lattice to benchmark the method. The 3D Ising lattice is equivalent to phase separation of a binary mixture with symmetric interaction potentials. The Ising model is a convenient choice because the properties of this model are reasonably well known. Moreover, the Ising

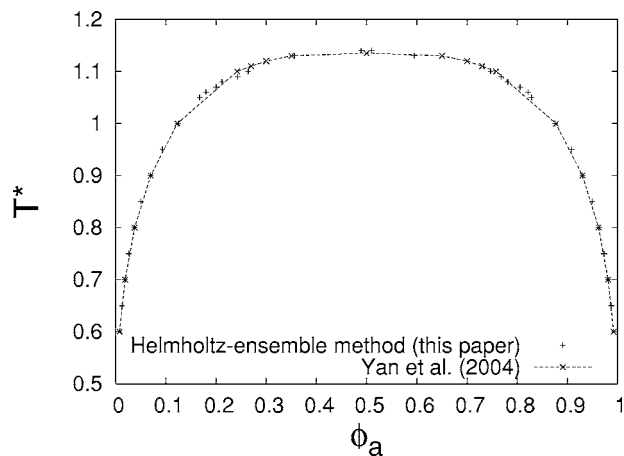


FIG. 3. Coexistence curves calculated by means of the Helmholtz-ensemble method benchmarked against accurate results by Yan *et al.* [10]. Used with permission from the authors.

model is symmetric with respect to the exchange of two species. As a result, the interface is guaranteed to be on average flat if  $\phi_a = \phi_b = \frac{1}{2}$ .

The Helmholtz ensemble is equally applicable to systems with asymmetric interactions. If we apply the Helmholtz-ensemble method to such a model, we have to explicitly check that the interface is on average flat. The overall composition should be adjusted accordingly if this is not the case.

In the 3D Ising lattice, space is discretized into cubic lattice sites, and only nearest neighbor interactions are taken into account. Boxes of  $20 \times 20 \times 20$  lattice sites and periodic boundary conditions were used. Each box had the same initial composition and the initial configuration of each box was random.

Only random particle exchanges were used to reach equilibrium. An internal energy change  $\Delta E$  was calculated for each perturbation. The change was accepted when  $\Delta E \leq 0$  or with probability  $\exp(-\beta\Delta E)$  when  $\Delta E > 0$ , where  $\beta = (kT)^{-1}$ ,  $T$  the temperature and  $k$  is Boltzmann's constant. This is simply the Metropolis scheme to traverse phase space [1]. Pseudorandom numbers were generated using the Mersenne twister algorithm [18] which has a very large period and a uniform distribution.

Interactions between unlike particles are described by the parameter  $\epsilon$ :

$$\epsilon = 2\epsilon_{12} - \epsilon_{11} - \epsilon_{22} \quad (3)$$

in which the  $\epsilon_{\alpha\beta}$  represents the energy of a contact between a particle of type  $\alpha$  and a particle of type  $\beta$ . The reduced temperature of the Ising system is defined as

$$T^* = \frac{kT}{\epsilon}. \quad (4)$$

$\phi_a$  was 0.50 to ensure that the interface is flat on average after equilibration. A sample run is shown in Fig. 2. The entire coexistence curve, together with the accurate Monte Carlo results of Yan *et al.* from Ref. [10], is depicted in Fig. 3. The two plots coincide over the entire concentration range. Our method works surprisingly well near the critical point

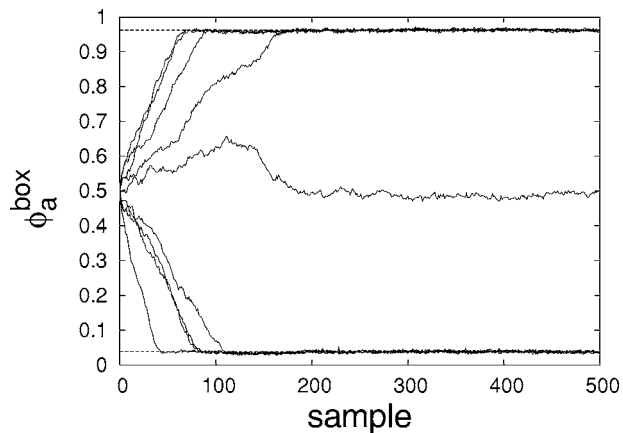


FIG. 4. Evolutions of volume fractions of component  $a$  in the 3D Ising system at  $T^*=0.8$  for a run containing nine boxes. The volume fraction of component  $a$  in the boxes is plotted against the sample ranking number for each box individually.  $5 \times 10^5$  particle swaps were attempted between samples. The compositions published in Ref. [10] are shown with a dashed line.

and the results are indistinguishable from Yan *et al.*'s Monte Carlo data at lower  $T^*$ .

A rerun of the Ising lattice at  $T^*=0.8$ , but now for nine boxes, yielded eight homogeneous boxes and only one box containing an interface (Fig. 4). This clearly corroborates our prediction that as many boxes as possible will develop a homogeneous phase due to the free energy contribution of an interface.

The effect of  $\phi_a$  on the equilibrium composition of the homogeneous phases is shown in Fig. 5. Apparently,  $\phi_a^B$  depends significantly on the initial composition. This plot exhibits a clear plateau at the correct composition around  $\phi_a = 0.5$ , which is the region where we expect to find a surface with vanishing average curvature. Significant errors are found outside that plateau region, which is most likely due to the formation of a curved interface. The errors continue to grow if we move away from the plateau, since the further away from the plateau, the smaller the phase droplets are, and the Laplace pressure scales with the inverse radius of the droplet.

The results shown in Fig. 5 indicate that the regime of flat interfaces is narrower than predicted by our first-order estimation. Still, it shows that a substantial volume fraction regime exists where very accurate results can be obtained. Finally, it is noted that the possibility of the formation of a curved interface does not limit the applicability of the Helmholtz-ensemble method. If it is found that the interface has a finite average curvature, then the overall composition

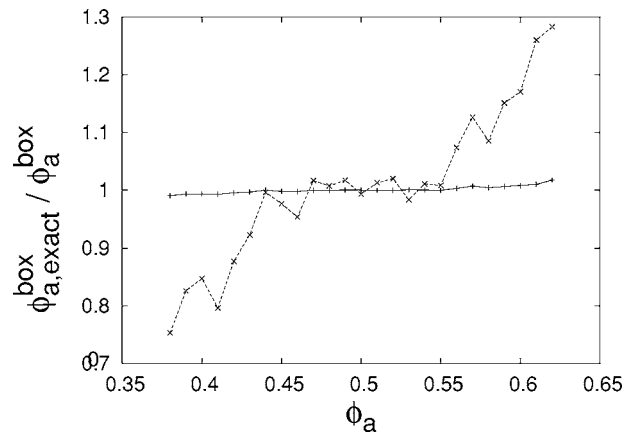


FIG. 5. 3D Ising model at  $T^*=0.8$ . This plot shows the accuracy of the Helmholtz-ensemble method relative to the “exact” volume fractions from Yan *et al.* [10]. The superscript “box” refers to the homogeneous box which was used to determine the compositions of phases  $A$  and  $B$ .  $\phi_{a,exact}^A / \phi_a^A$  (solid line) and  $\phi_{a,exact}^B / \phi_a^B$  (dotted line) are plotted against the initial volume fraction  $\phi_a$ . Note the plateau region where  $\phi_{a,exact}^B / \phi_a^B = 1$ ; this indicates the region where an on average flat interface is present.

should be adjusted accordingly and the simulation should be repeated. The Helmholtz-ensemble method is therefore capable of calculating phase coexistence for systems with symmetric interactions and for systems with asymmetric interactions.

#### IV. CONCLUSIONS AND RECOMMENDATIONS

In this paper, we introduce the Helmholtz-ensemble method: a formalism to determine the composition of coexisting phases by a single Monte Carlo experiment. In contrast with the Gibbs-ensemble method by Panagiotopoulos, volume changes are unnecessary. The present method is therefore especially useful for lattice models. Moreover, the Helmholtz-ensemble method is both faster and more flexible than current methods for lattice systems, which are usually based on free energy calculations.

The phase coexistence points for a 3D Ising model that were obtained with the Helmholtz-ensemble method are in very close agreement with accurate results from existing literature. Although we benchmarked the method against a simple lattice model system involving monomeric, isotropic particles, the work presented here is easily extended to continuous and/or more complex models. We therefore expect that the method presented here will be very useful to elucidate the phase behavior of, for instance, polymers and surfactants.

- [1] N. Metropolis, A. W. Rosenbluth, M. N. Rosenbluth, A. H. Teller, and E. Teller, *J. Chem. Phys.* **21**, 1087 (1953).  
 [2] A. Z. Panagiotopoulos, *Mol. Phys.* **61**, 813 (1987).  
 [3] A. Z. Panagiotopoulos, *Mol. Simul.* **9**, 1 (1992).  
 [4] D. Frenkel and B. Smit, *Understanding Molecular Simulation*

(Academic Press, London, 2002).

- [5] A. D. Mackie, A. Z. Panagiotopoulos, D. Frenkel, and S. K. Kumar, *Europhys. Lett.* **27**, 549 (1994).  
 [6] A. D. Mackie, A. Z. Panagiotopoulos, and S. K. Kumar, *J. Chem. Phys.* **102**, 1014 (1995).

- [7] R. G. Larson, L. Scriven, and H. T. Davis, *J. Chem. Phys.* **83**, 2411 (1985).
- [8] M. Lísal, C. K. Hall, K. E. Gubbins, and A. Panagiotopoulos, *J. Chem. Phys.* **116**, 1171 (2002).
- [9] L. F. Scanu, K. E. Gubbins, and C. K. Hall, *Langmuir* **20**, 514 (2004).
- [10] Q. Yan, H. Liu, and Y. Hu, *Fluid Phase Equilib.* **218**, 157 (2004).
- [11] D. A. Kofke, *Mol. Phys.* **78**, 1331 (1993).
- [12] D. A. Kofke, *J. Chem. Phys.* **98**, 4149 (1993).
- [13] D. A. Kofke, *Adv. Chem. Phys.* **105**, 405 (1999).
- [14] M. Mehta and D. A. Kofke, *Chem. Eng. Sci.* **49**, 2633 (1994).
- [15] P. Atkins and J. de Paula, *Physical Chemistry*, 7th ed. (Oxford University Press, Oxford, 2002).
- [16] B. Widom, *J. Chem. Phys.* **39**, 2802 (1963).
- [17] P. H. Nelson, T. A. Hatton, and G. C. Rutledge, *J. Chem. Phys.* **110**, 9673 (1999).
- [18] M. Matsumoto and T. Nishimura, *ACM Trans. Model. Comput. Simul.* **8**, 3 (1998).