Critical behavior of simple fluids confined by microporous materials

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We have performed Monte Carlo simulations of a three-dimensional quenched-annealed system on a cubic lattice with nearest-neighbor interactions. A small fraction of the lattices sites are blocked, thereby creating a quenched matrix. Histogram reweighting techniques are applied to investigate the critical behavior of the system. We have studied lattice sizes ranging from $L = 10$ to $L = 18$. For each size, we have evaluated the number of matrix replicas necessary to obtain statistically meaningful results. This number, determined by analyzing the convergence of the histograms, ranged from 50 for the smallest system sizes to 200 for the largest sizes. We have evaluated the critical temperature, the fourth cumulant of Binder *et al.* [K. K. Kaski, K. Binder, and J. D. Gunton, *Phys. Rev. B* **29**, 3996 (1984)], and the critical exponents $1/\nu$ and β/ν . The estimated critical temperature is only slightly lower than that of the three-dimensional Ising model. The simulated critical exponents, however, differ significantly from those for Ising-class three- and two-dimensional systems.

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I. INTRODUCTION

The study of the structure and phase behavior of fluids confined by disordered porous adsorbents has been the subject of a number of recent investigations. One major goal of these studies has been to understand the role played by the matrix in inducing or altering phase transitions in such systems. Several experiments, see e.g., Refs. 1–7, have shown that the phase diagrams of fluids confined in disordered porous materials are substantially different from those of bulk systems under the same thermodynamic conditions, even in cases where the porous material occupies only a small fraction of the total volume (e.g., system porosities on the order of 95%).

Most theoretical approaches aimed at gaining insights into the behavior of fluids in disordered porous materials are based on a model in which a disordered matrix is obtained by the rapid quench of an equilibrium configuration of matrix particles created in the absence of fluid particles.^{8–10} Models of this sort are commonly referred to as “quenched-annealed fluid” models. Several studies have shown that the structural and thermodynamic properties of quenched-annealed fluids can be obtained from integral equations using the so-called “replica Ornstein–Zernike” formalism.^{8–13} The replica Ornstein–Zernike equations have also been generalized to the case of nonuniformly quenched matrices.¹⁴

The replica method for quenched-annealed systems is

also well suited for computer simulations; several Monte Carlo simulations of phase equilibria in quenched-annealed systems have been reported in the literature.^{15–19} However, to the best of our knowledge, all simulations to date have been carried out using a small number of replicas. Furthermore, none of these simulation studies has provided a systematic analysis of the fluctuations that arise when one goes from one replica to another. In order to lend credence to such studies, it is crucial to determine what is the appropriate number of replicas necessary to assure *quantitatively* correct estimates of the critical properties of such systems. Our previous simulations of two-dimensional quenched-annealed systems on a hexagonal lattice have indicated that the phase diagrams corresponding to distinct replicas may be significantly different. Consequently, one can observe significant differences in the values of the critical temperature corresponding to particular replicas of the system, cf. Fig. 1 of Ref. 19. Our simulations of Lennard-Jones fluids in quenched networks have also highlighted the sensitivity of the thermodynamic behavior to the particular structure of a replica.²⁰

In this work we report the results of studies of critical behavior of a fluid confined by a microporous material. Our investigations have been carried out using lattice Monte Carlo simulations supplemented by analysis using histogram reweighting and finite-size scaling techniques.^{21–23} Because of their simplicity, lattice models are well suited to carry out extensive simulations. Also, the introduction of histogram techniques^{21,24,25} to extract the information from Monte Carlo simulation data at a single temperature enhances the

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FIG. 1. Parts (a) and (b) present the density distributions $P(\rho^*)$ for a selection of temperatures along the line of liquid-vapor coexistence for the system having linear extent $L=10$ (a) and $L=18$ (b), respectively. Parts (c) and (d) show the corresponding energy density distribution $P(u)$. The curves with circles, squares, diamonds, and triangles correspond to $T^*=0.98, 0.99, 1.0$, and 1.01 , respectively.

potential resolution of Monte Carlo methods substantially. The use of histograms therefore makes possible a precise determination of the values of the critical temperature and critical exponents. The aim of this study is to determine the critical behavior (i.e., the critical temperature, the value of the chemical potential at the critical point, the critical exponents, and the value of the fourth cumulant of Binder^{22,23}) for a well-defined quenched-annealed system with high accuracy. The necessary number of replicas has been determined through the convergence of the histograms and their moments.

II. A MODEL AND PROCEDURE

We consider a simple cubic lattice in three dimensions, consisting of L^3 sites, where L is the size of the system along each axis. The distance between nearest-neighbor sites defines the unit length. Periodic boundary conditions are applied along the three directions.

In the spirit of the replica method, we first generate samples of the quenched component, i.e., the matrix. The

matrix consists of species “ m ” at density, $\rho_m = N_m/L^3$, where N_m is the number “of blocked” lattice sites (i.e., sites occupied by species “ m ”). The microporosity of the system, $p = 1 - \rho_m$, is a measure of the space available for other fluid species. In this study we assume that the interaction between species “ m ” is of the hard-sphere type; blocked sites cannot be occupied by fluid particles, and there are no nearest-neighbor attractions between the fluid and the blocked sites.

We report results for one matrix density, namely $\rho_m = 0.05$. Consecutive matrix replicas have been prepared by simulations in the canonical ensemble. To that end, N_m randomly distributed matrix particles are evolved through the system by a series of conventional canonical-ensemble Monte Carlo steps. Having prepared distinct configurations of the matrix (i.e., distinct replicas), matrix particles are frozen in space, thereby giving rise to the “blocked” sites alluded to above. Confined fluid particles of species “1” are subsequently simulated in a given matrix replica at constant temperature, T , and at constant chemical potential μ . The Hamiltonian for species “1” is of the form

FIG. 2. Coexistence chemical potential μ^* vs $1/T^*$, for the systems having linear sizes: circle— $L=18$; squares— $L=16$; diamonds— $L=14$; and triangles— $L=12$.

$$H = -\left(\frac{\varepsilon}{2}\right) \sum n(i,j,k) \left\{ \sum n(i',j',k') \right\}, \quad (1)$$

where $n(i,j,k)$ equals 0 or 1 for empty or occupied lattice sites, and the summation in curly brackets is taken only over nearest neighbors, which attract each other with energy ε .

All results are reported in reduced units, $T^* = kT/\varepsilon$ and $\mu^* = \mu/kT$. We have introduced a normalized fluid density, $\rho^* = \rho/p$. Here $\rho = \langle \langle n(i,j,k) \rangle \rangle$, where $\langle \langle \dots \rangle \rangle$ denotes thermal averaging over the entire lattice in each Monte Carlo run for a given matrix configuration and subsequent averaging over all matrix realizations (replicas).

A Monte Carlo step consists^{23,24,26} of an attempt to insert a particle into the system, or an attempt to destroy an existing fluid particle. Five system sizes have been considered: $L=10, 12, 14, 16$, and 18 . Many replicas were employed for each system size. Note, however, that our calculations have been carried out by constructing a single histogram for all replicas, $P(\rho^*, u)$. Here u is potential energy in units of ε , per vertex available to fluid particles, i.e., the energy normalized by $L^3 p \varepsilon$. That is, for given values of the chemical

FIG. 3. Cumulant intersection plot for Monte Carlo simulation for the systems with linear dimensions: solid line— $L=18$, long dashed line— $L=16$, dotted line— $L=14$, dashed line— $L=12$ and long dashed-dashed line— $L=10$.

potential and of the temperature we have cumulated the energy-density histogram for all matrix realizations. The detailed description of the simulational procedure has been given in the review article by de Pablo *et al.*²⁷ The single-histogram technique is obviously a simplification, but following Orkoulas and Panagiotopoulos²⁸ and Münger and Novotny²⁹ we expect this technique to be accurate if we are in the vicinity of the critical point. For each system size the necessary number of replicas has been established by analyzing the convergence of histograms and their moments; this number changed from 50 for the smallest system to 200 for the largest system. Thus, the number of replicas used in this study was considerably larger than that used in previous works.

Prior to data collection, equilibration periods of 10×10^6 Monte Carlo steps per site were utilized. To reduce correlations, sampling to evaluate histograms was then performed at intervals of 50 Monte Carlo steps. The final histograms of $P(\rho^*, u)$ comprised 3×10^7 entries for one matrix configuration. The aim of the simulations was to determine for various L the joint distribution $P_L(\rho^*, u)$. From the knowledge of this distribution, one can calculate all the moments, as required by the finite system scaling analysis.²²

In the order to initiate the investigations, we have performed a series of very short runs for smaller system sizes ($L=10$ and 12). In these runs, the temperature and chemical potential were tuned until the density distribution $P(\rho^*) = \sum_u P(\rho^*, u)$ exhibited a double-peaked structure with a shallow minimum. A longer run was then performed to accumulate better statistics. The coexistence curve was determined from a “two-state” approximation;³⁰ the precise location of coexistence was therefore achieved by tuning the chemical potential at any given temperature, until the areas under the two peaks of $P(\rho^*)$ became identical. It is important to emphasize that even the largest systems investigated in this work are not sufficiently large. Unfortunately, investigating larger systems is difficult because the number of

TABLE I. Liquid–vapor coexistence in the matrix of porosity 0.95 for the temperatures close to the critical point temperature in the case $L=14$. We show here the chemical potentials at the coexistence and gaseous and liquid densities.

T^*	μ^*	ρ_g^*	ρ_l^*
0.97	−2.962 45	0.1526	0.7617
0.98	−2.933 10	0.1666	0.7384
0.99	−2.904 39	0.1849	0.7090
0.995	−2.890 28	0.1964	0.6915
1.00	−2.876 33	0.2100	0.6722
1.001	−2.873 55	0.2129	0.6681
1.002	−2.870 78	0.2160	0.6639
1.003	−2.868 02	0.2191	0.6598
1.004	−2.865 27	0.2222	0.6555
1.005	−2.862 52	0.2255	0.6512
1.01	−2.848 87	0.2422	0.6293
1.015	−2.835 37	0.2594	0.6077

FIG. 4. Evaluation of the critical temperature (part a), of the fourth cumulant (part b), and of the critical exponents $1/\nu$ (part c) and $2\beta/\nu$ (part d).

replicas necessary to get convergent results increases rapidly with system size. Calculations have been carried out on a Compaq Alpha server with 21 624 processors, running at 500 MHz. The simulations for the system with $L=18$ required ca. 200 h of CPU time for one state point.

III. RESULTS AND DISCUSSION

We begin our discussion by presenting the histograms $P(\rho^*)$ and $P(u)$. In Fig. 1 we display the distributions $P(\rho^*)$ [parts (a) and (b)] and $P(u)$ [parts (c) and (d)], obtained for the smallest, $L=10$ [parts (a) and (c)], and for the largest, $L=18$ [parts (b) and (d)], system. Different symbols correspond to different temperatures.

By comparing the relevant density or energy distributions for two system sizes we realize that the functions evaluated for the smaller systems are more symmetric. Increasing the system size causes an increase of the height of the distribution maxima and, as expected, leads to a narrowing of the entire distributions. The gaseous-state peaks of the distributions for $L=18$ are narrow and high, whereas the liquid-state peaks for the same system size are much lower and diffuse. The difference in the shape of the gaseous- and liquid-state maxima for the system with $L=10$ are less pronounced. The curves shown here have been obtained by averaging over 50 (for $L=10$) and over 200 (for $L=18$) matrices.

We estimated the value of the critical temperature for an

TABLE II. Critical temperatures, chemical potentials, values of U^* , and critical exponents for the quenched-annealed system of porosity 0.95 (QA) and for three-dimensional (Ref. 32) (3D) and for two-dimensional (Ref. 33) (2-D) Ising models.

	QA	3-D	2-D
T_c^*	1.004	1.127 80	0.567 296 3
μ_c^*	-2.8645	-2.6600	-3.5255
ρ_c^*	0.435	0.5	0.5
U^*	0.591	0.44	0.61
$1/\nu^a$	1.38 ± 0.01	1.5944	1.00
β/ν^a	0.35 ± 0.02	0.518	0.125

^aThe errors in the values of the critical exponents have been estimated from Figs. 4(c) and 4(d).

infinite system to be equal to $T_c^* = 1.004 \pm 0.001$. Note, however, that for $L=10$ there are still well-defined liquid and gaseous peaks on the distributions evaluated at $T^* = 1.01$. At the same temperature, but for a larger system, $L=18$, the peaks associated with the gas and liquid phases practically vanish, and the relevant distributions $P(\rho^*)$ and $P(u)$ exhibit a broad plateau. This illustrates the dependence of the phase transition on the system size. The dependence of the coexistence curve on the system size is also illustrated in Fig. 2, where we have displayed the phase diagrams in the $1/T^* - \mu^*$ plane for different sizes of the system. The difference between the values of the chemical potential at coexistence evaluated for the system size $L=18$ (open circles) and for the system with $L=12$ (white triangles) is rather small. As expected, the plot of μ^* vs $1/T^*$ is linear in the vicinity of the critical temperature.³¹

To determine the “final” phase diagram, the values of the chemical potential were refined, using histogram reweighting, to achieve equal weights of the two peaks in $P(\rho^*)$. The final data for the coexistence in the vicinity of the critical point are collected in Table I.

To locate the critical temperature in simulations, it turns out to be most convenient to use the normalized fourth-order cumulant of the distribution. This cumulant is given by²²

$$U_L = 1 - \langle m^4 \rangle_L / (3 \langle m^2 \rangle_L^2) \quad (2)$$

where $m = \rho^* - \langle \rho^* \rangle$ and $\langle \dots \rangle_L$ denotes an average evaluated from a distribution for the system with size L . Far above T_c^* the distribution is a single Gaussian $U_L = 0$, and we have $U_L = \frac{2}{3}$ for T^* far below T_c^* . However, at T_c^* , U_L tends to a nontrivial “fixed point value,” U^* . If we thus plot U_L vs. T^* for different choices of L , these curves should have a unique intersection point U^* ; the temperature where this occurs is T_c^* . In this way, an estimate of T_c^* can be obtained which is not biased by any assumptions about critical exponents. Originally, this method was successfully demonstrated for Ising models.^{14–16} The plots of the cumulants U_L versus temperature are shown in Fig. 3. Curves for consecutive system sizes intersect almost at the same point. As we have already mentioned, the critical temperature evaluated from the analysis of the curves shown in Fig. 3 is 1.004 ± 0.001 . The fixed point value of U^* is equal to 0.591 for the system

FIG. 5. Examples of the functions $P(\rho^*)$ (without reweighting) for a small system. Solid line denotes the function averaged over 50 replicas. Different symbols denote functions $P(\rho^*)$ for some selected replicas. Temperature is $T^* = 1$ and the chemical potential is $\mu^* = -2.874$.

under study. Note that, for the three-dimensional Ising universality class, $U^* = 0.44$, whereas the exact value of U^* for the two-dimensional Ising model is 0.61.²²

There exists²² an alternative route to the value of U^* , namely we may plot $U_{L'} = U_L(U_L)$ for various choices of U_L , where the curve $U_{L'}(U_L)$ is constructed treating temperature, T^* , as a parameter of the curve. The fixed point estimate, U^* , is found when $U_{L'} = U_L \equiv U^*$. If the values of L are big enough, corrections to scaling are negligible²² and the estimate for U^* should be independent of $b = L'/L$. The functions $U_{L'} = U_L(U_L) \equiv U_{bL}(U_L)$ could be approximated well by straight lines, thereby allowing reasonably accurate estimates of U^* . The critical temperature can then be evaluated from the condition $(U_{bL}/U_L)_{T_c=T^*} = 1$. Also, from the slope of $U_{bL} = U_{bL}(U_L)$ at the intersection point one can obtain an estimate for the critical exponent ν

$$\nu^{-1} = [\ln[\delta U_{bL} / \delta U_L] / \ln(b)]_{U^*}. \quad (3)$$

The value of the exponent β/ν can be then obtained from

$$2\beta/\nu = -\ln[\langle m^2 \rangle_{bL, T_c} / \langle m^2 \rangle_{L, T_c}] / \ln(b). \quad (4)$$

Figure 4 shows results corresponding to the analysis of the evaluation of critical temperature, the fixed point value of the fourth cumulant, and the critical exponents. The curves shown in Fig. 4 also serve to illustrate the precision with which these quantities can be evaluated. The values that characterize the critical behavior of the Ising fluid in a microporous matrix are collected in Table II, together with data for a conventional three-dimensional Ising reported by Ferrenberg and Landau,³² and with exact results for the two-dimensional Ising model.³³

The critical temperature of the model studied here is only slightly lower than that of the two-dimensional Ising system. However, the estimated critical exponent $1/\nu$ is drastically different from that for the three-dimensional Ising universality class. Similarly, the estimated value of the exponent β/ν is intermediate between the two- and three-

dimensional cases. For the zero matrix concentration, the system belongs to the three-dimensional Ising universality class; our findings indicate that the presence of even a small number of frozen obstacles gives rise to changes of the critical properties. Note that qualitatively similar effects were also observed in the case of Ising random field models.³⁴

We stress that our studies have been carried out using a much larger number of system replicas than previous simulations, and that we have evaluated the necessary number of replicas from the convergence of the histograms and their moments. Our results show that it is essential to work with a large enough number of replicas if meaningful and reasonably accurate estimates of the critical properties are to be obtained. This point is further illustrated by Fig. 5, which shows examples of the five functions $P(\rho^*)$ (without reweighting, evaluated for small system). The final average, displayed as solid line, has been obtained by averaging over 50 replicas. Different symbols show the results computed for five *ad hoc* selected system replicas. The calculations have been done at $T^*=1$ and at the chemical potential $\mu^* = -2.874$. We realize huge differences between results for consecutive replicas: the maximum of the gaseous peak changes by a factor of approximately 8; that of the liquid peak by a factor of 4. Moreover, not only does the height change, but also the position of the liquid state peak changes.

Let us summarize the obtained results. In this article we have carried out extensive Monte Carlo simulations of three-dimensional fluid on a cubic lattice with nearest-neighbor interactions. Some lattice sites were occupied by obstacles. The concentration of the obstacles was 5%. The number of system replicas used in our simulations was controlled by checking the convergence of the histograms and the convergence of the histograms' moments. Consequently, the calculations have been carried out by an enormously large (when compared with previous studies) number of replicas. This number ranged from 50 for the smallest system size to 200 for the largest system size. We have found that the presence of such a small number of obstacles reduces the three-dimensional Ising critical temperature by approximately 11%. Instantaneously, the critical exponents $1/\nu$ and β/ν are reduced by 13% and 31%, respectively. However, we expect the critical behavior of the system to be strongly dependent on the matrix concentration. This problem is currently under study.

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