

# **Molecular Simulation of Phase Coexistence: Finite-Size Effects and Determination of Critical Parameters for Two- and Three-Dimensional Lennard-Jones Fluids<sup>1</sup>**

**A. Z. Panagiotopoulos<sup>2, 3</sup>**

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The subject of this paper is the investigation of finite-size effects and the determination of critical parameters for a class of truncated Lennard-Jones potentials. Despite significant recent progress in our ability to model phase equilibria in multicomponent mixtures from direct molecular simulations, the accurate determination of critical parameters remains a difficult problem. Gibbs ensemble Monte Carlo simulations with systems of controlled linear system size are used to obtain the phase behavior in the near-critical region for two- and three-dimensional Lennard-Jones fluids with reduced cutoff radii of 2, 2.5, and 5. For the two-dimensional systems, crossover of the effective exponent for the width of the coexistence curve from mean field ( $\beta = 1/2$ ) in the immediate vicinity of the critical point to Ising-like ( $\beta = 1/8$ ) farther away is observed. Critical parameters determined by fitting the data that follow Ising-like behavior are in good agreement with literature values obtained with finite-size scaling methods. For the three-dimensional systems, no crossover to mean field-type behavior was apparent. Extrapolated results for the critical parameters are consistent with literature estimates for similar fluids. For both two- and three-dimensional fluids, system size effects on the coexistence curves away from the critical point are small, normally within simulation statistical uncertainties.

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**KEY WORDS:** critical exponents; critical point; critical temperature; finite-size effects; Gibbs ensemble; Lennard-Jones; Monte Carlo simulation.

## **I. INTRODUCTION**

The determination of phase coexistence properties of systems by means of molecular simulations is an area that has experienced significant growth in

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<sup>2</sup> School of Chemical Engineering, Cornell University, Ithaca, New York 14853, U.S.A.

<sup>3</sup> Work performed while the author was a visiting scientist at the Demokritos National Research Center, 15310 Athens, Greece.

recent years. The availability of new algorithms for this purpose, such as the Gibbs ensemble methodology for determination of phase equilibria of pure fluids and mixtures [1, 2] or free-energy calculation methods for solids [3], has contributed to this growth. The interest in these calculations stems from the importance of the phase behavior for industrial and technological applications and the appeal of establishing a direct connection between phase behavior and intermolecular forces acting in a system.

Some years ago, the author presented a paper entitled "Exact Calculations of Fluid-Phase Equilibria by Monte Carlo Simulations in a New Statistical Ensemble" to a previous Symposium on Thermophysical Properties [4]. By the word "exact," I tried to emphasize the distinction between computer simulation methods and approximate theoretical techniques. In retrospect, this was an unfortunate choice of words. Simulations can, in principle, provide accurate numerical results for a system but are *never* exact. Among the many possible pitfalls for simulators, especially those interested in phase transitions, are the effects of the finite extent of simulated systems on the observed results.

Finite-size effects are clearly present in the vicinity of critical points, where correlation lengths for the macroscopic systems diverge and such divergences cannot be captured in a simulation of a finite system. Finite-size scaling theory [5] has allowed the accurate estimation by simulation of the location and universality class of critical points for many physically interesting models. Unfortunately, the techniques of finite-size scaling as developed to date are much easier to apply to lattice models than to continuous-space models of the type often of interest to engineers. A subsystem-block-density distribution analysis [6] based on finite-size scaling theory has been used to determine the critical point of a two-dimensional Lennard-Jones system. The block-density distribution technique is based on observing a large system under conditions of constant volume, and focusing on smaller subsystems of progressively larger size. For systems just below a vapor-liquid critical point, large density fluctuations are observed inside the subsystems, corresponding to the transient formation of "droplets" and "bubbles" of liquid and gas, respectively. A different and potentially very powerful approach based on grand-canonical Monte Carlo simulations at a range of temperatures [7] has been recently formulated and applied to a two-dimensional Lennard-Jones system. It must be emphasized that although finite-size scaling theory can provide quite accurate estimates for the critical points of model fluids, the computational requirements for continuous potentials are heavy. The study of Rovere *et al.* [6] took "several hundred CPU hours on CRAY-XMP supercomputers" and Wilding and Bruce [7] used long Monte Carlo runs on a massively parallel machine.

Despite the existence of numerous observations and a firmly grounded theory of finite-size effects at both second- and first-order phase transitions, one often finds in simulation studies of detailed atomistic models statements that “system size effects were negligible.” The confusing situation with respect to finite-size effects for simulations in the Gibbs ensemble is a case in point. Studies of lattice models [8] and a symmetric square-well mixture at constant density [9] have found significant shifts of the apparent coexistence curves with system size, especially for two-dimensional systems, while many Gibbs-ensemble simulations of continuous-space models have not detected effects of system size on the observed phase coexistence behavior [1, 9]. The results for a symmetric square-well mixture [9] were obtained without using the volume fluctuation step normally required for pressure equilibration in the Gibbs ensemble, because of the special symmetry. A subsequent study for a similar system performed at constant pressure [10] did not find finite-size effects. There are no accepted general guidelines regarding the likely importance of finite-size effects in Gibbs ensemble simulations.

A related important question is the determination of critical parameters for a model fluid from simulations. The results of Mon and Binder [8] and of Recht and Panagiotopoulos [9] throw some doubt on the validity of commonly used extrapolations of coexistence curves obtained from Gibbs-ensemble simulations to the critical point using scaling relationships [2, 10–12]. The “order parameter” for the vapor–liquid phase coexistence is the difference in density of the liquid and gas phases. On approach to the critical point, the width is described by a characteristic exponent,  $\beta$ ,

$$(\rho_L - \rho_G) \propto (T_C - T)^\beta \quad (1)$$

where  $\rho_L$  and  $\rho_G$  are the liquid and gas densities,  $T$  is the temperature, and  $T_C$  is the critical temperature. The exponent  $\beta$  depends on the universality class of the transition. For macroscopic systems  $\beta = 1/8$  in two dimensions and  $\beta \approx 1/3$  in three [13]. However, as Mon and Binder [8] point out, the “effective” exponents observed in simulations conform to these expectations only when the correlation length is much less than the simulation box size. On approach to the critical point, the correlation length diverges. Therefore, sufficiently close to the (macroscopic) critical point, we expect to see a crossover of the effective exponents to their mean-field value, namely,  $1/2$ . For continuous potentials, typical statistical uncertainties for Gibbs-ensemble simulations close to critical points are large and the observation of the crossover of the exponents quite difficult.

The main goal of this paper is to present a systematic study of finite-size effects and the approach to the critical point for a class of Lennard–Jones

potentials in two and three dimensions. We attempt to answer the two questions implicitly posed in the previous paragraphs, namely, (a) Which potentials are likely to show significant finite-size effects in Gibbs-ensemble simulations? and (b) What are valid ways to estimate critical parameters for a given model potential, and how uncertain are these parameters? The method we use is to obtain numerical estimates for the phase coexistence envelopes and critical parameters of Lennard–Jones fluids with various cutoffs, ranging from two to five molecular diameters. We use a range of linear system sizes and pay particular attention to maintaining the linear dimensions of both regions in the simulations constant, something that has not been the usual practice in previous Gibbs-ensemble simulations.

## 2. MODEL SYSTEMS AND SIMULATION METHOD

The much studied Lennard–Jones intermolecular potential model is the natural choice for the present study. The potential,  $\mathcal{U}_{LJ}$ , is of the form

$$\mathcal{U}_{LJ}(r) = 4\epsilon \left[ \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^6 \right] \quad (2)$$

where  $\epsilon$  is the potential well depth parameter,  $\sigma$  is the size parameter, and  $r$  the distance between particles. Reduced (dimensionless) quantities that are indicated by a superscript asterisk are defined so that distances are scaled by  $\sigma$  and temperatures by  $\epsilon/k_B$ , where  $k_B$  is Boltzmann's constant. Since we are interested in studying systems of varying size, we would like to avoid using long-range corrections for the part of the intermolecular potential that extends beyond the simulation box edge. The potential is thus truncated at a cutoff distance,  $r_c$ ,

$$\mathcal{U}'_{LJ}(r) = \begin{cases} \mathcal{U}_{LJ}(r), & r \leq r_c \\ 0, & r > r_c \end{cases} \quad (3)$$

The additional benefit of using a cutoff potential is that detailed comparisons can be made with previous finite-size scaling studies of the critical properties of Lennard–Jones systems which were performed with the two-dimensional version of the model and  $r_c^* = 2.5$  [6] and  $r_c^* = 2$  [7]. In addition to these two cutoffs,  $r_c^* = 5$  was selected for this study in an attempt to come as close as possible to the behavior of the “full” (untruncated) potential without having to use excessively large simulation boxes.

In order to investigate finite-size effects, control of the linear dimensions of the simulations cells is necessary. The size of each of the two boxes

fluctuates in Gibbs-ensemble simulations, and system size can only be approximately controlled. Approximate control of system size was achieved by varying the number of particles and initial densities of the two regions. This required preliminary estimates of the equilibrium densities for each system and temperature studied. The preliminary estimates were obtained from shorter exploratory runs. The target linear system sizes studied were  $L^* = 16, 24,$  and  $32$  in two dimensions and  $L^* = 6, 9,$  and  $12$  in three. For performing finite-size scaling analysis, a wide range of linear system sizes is desirable. However, much larger systems could not be studied because of the large number of particles required and, perhaps more seriously, because of the extremely long simulation runs required. Much smaller systems also are not feasible, because the system size cannot be smaller than twice the cutoff distance. The system with the larger cutoff ( $r_c^* = 5$ ) could not be studied in any but the larger linear system size—no finite-size scaling analysis is possible in this case.

The simulation method used in this work is the Gibbs-ensemble Monte Carlo method [1]. For the one-component systems of interest to the present study, the method is based on performing a simulation in two regions at a constant temperature, total volume, and number of particles. Particle displacements within each region, volume changes, and particle transfers from one region to the other are performed in a way that establishes internal equilibrium, equality of pressures, and equality of the chemical potentials of the two regions. The acceptance criteria for the Monte Carlo steps and further details of program organization are given in the original papers [1, 2] and a recent review paper [14] that also lists applications of the method until 1992. The simulations were performed so that the type of step to be taken every time is decided at random with fixed probabilities, so that microscopic reversibility is strictly satisfied. Typical ratios of displacements:volume change:particle transfer steps were 100:1:100. Because the potential is truncated, volume change steps are computationally quite expensive, as the potential does not scale simply with box size. Typical lengths of the runs were  $10^7$  Monte Carlo steps. Typical computing time requirements for the larger systems, which contained up to 1200 particles, were 10 h on a Convex 3800 system.

For simulations significantly below the critical point, the identities of the coexisting phases do not change in the course of the simulations and a region that started as a liquid phase retains its identity despite the statistical fluctuations in density. For such cases, the statistical uncertainties of the results are obtained by dividing the configurations obtained after initial equilibration into five blocks of equal length and calculating the uncertainties of the block averages. For simulations closer to the critical point, the identities of the coexisting regions change, sometimes frequently,

and the coexisting densities are obtained by constructing histograms of the frequency of observing a certain density. The statistical uncertainties in this case were obtained by dividing the configurations after equilibration into two blocks and constructing the corresponding histograms.

### 3. RESULTS AND DISCUSSION

#### 3.1. Two-Dimensional Systems

Results for the phase coexistence densities of the two-dimensional systems are given in Table I. Statistical uncertainties of the liquid- and

**Table I.** Simulation Results for the Phase Coexistence Properties for Two-Dimensional Lennard-Jones Systems<sup>a</sup>

$T^*$	$L^* \approx 16$		$L^* \approx 24$		$L^* \approx 32$	
	$\rho_G^*$	$\rho_L^*$	$\rho_G^*$	$\rho_L^*$	$\rho_G^*$	$\rho_L^*$
$r_c^* = 5$						
0.42	0.018(4)	0.753(8)	0.023(4)	0.760(4)	0.020(6)	0.756(2)
0.44	0.032(6)	0.738(6)	0.034(5)	0.737(6)	0.040(9)	0.741(3)
0.46	0.046(11)	0.715(7)	0.042(8)	0.708(11)	0.044(4)	0.711(5)
0.48	0.063(10)	0.675(20)	0.065(8)	0.673(20)	0.078(10)	0.685(6)
0.49	0.067(7)	0.656(7)	0.080(16)	0.652(13)	0.110(22)	0.658(9)
0.50	0.120(30)	0.650(10)	0.130(3)	0.640(20)	0.179(15)	0.621(24)
0.51	0.140(70)	0.575(75)	0.160(22)	0.600(33)	0.143(22)	0.553(10)
0.52			0.190(40)	0.500(20)	0.220(30)	0.470(30)
$r_c^* = 2.5$						
0.42	0.022(4)	0.755(17)	0.023(4)	0.755(5)	0.032(6)	0.755(3)
0.44	0.034(4)	0.722(12)	0.037(7)	0.727(9)	0.039(10)	0.730(7)
0.46	0.065(11)	0.708(10)	0.072(18)	0.700(8)	0.091(14)	0.710(3)
0.48	0.128(42)	0.662(13)	0.180(10)	0.690(10)	0.210(10)	0.670(10)
0.50	0.190(30)	0.610(20)	0.230(40)	0.600(30)	0.350(50)	0.530(50)
$r_c^* = 2$						
0.41	0.035(2)	0.731(5)	0.042(10)	0.728(8)	0.037(7)	0.716(8)
0.42	0.041(4)	0.708(7)	0.041(7)	0.692(11)	0.049(8)	0.704(9)
0.43	0.054(8)	0.691(10)	0.065(18)	0.679(8)	0.087(20)	0.697(8)
0.44	0.065(6)	0.669(4)	0.096(25)	0.642(37)	0.078(8)	0.618(40)
0.45	0.080(10)	0.650(10)	0.206(25)	0.611(32)	0.148(21)	0.604(30)
0.46	0.110(20)	0.530(30)	0.288(28)	0.605(38)	0.260(30)	0.530(30)
0.47	0.150(20)	0.380(40)				

<sup>a</sup> Numbers in parentheses indicate statistical uncertainties in units of the last decimal point shown: 0.018(4) means  $0.018 \pm 0.004$ .

gas-phase densities are indicated in parentheses in units of the last decimal point for the corresponding quantity. In some cases, at the highest temperatures studied for each cutoff, results are missing because no stable runs could be obtained.

An interesting observation was made in the course of performing simulations for systems with  $r_c^* = 2$ . For the larger system size studied ( $L^* \approx 32$ ), for simulations with initial density of the low-density region inside the coexistence region, the system equilibrated extremely slowly. Even after a  $10^7$  Monte Carlo steps for a temperature some distance from the critical point ( $T^* = 0.43$ ), the region was found to contain a mixture of liquid and gas, as shown in Fig. 1. This is likely due to the low interfacial tension in the two-dimensional systems, which makes the free-energy penalty for formation of an interface small. This event is particularly likely to occur for the larger systems because then sizable, stable regions of the "wrong" phase can form. This particular run was discarded, and a new simulation was initiated at a lower initial density, resulting in stable coexistence densities shown in Table I.

To determine the effective exponents appropriate for the description of the width of the coexistence curves, we plot the results as  $(\rho_L^* - \rho_G^*)^x$  and  $(\rho_L^* - \rho_G^*)^2$  versus  $T^*$  [8, 9]. In order to bring the values in approximately the same numerical range, the  $(\rho_L^* - \rho_G^*)^x$  curves were shifted up by multiplying by 5. Typical results are presented in Figs. 2 and 3, corresponding,

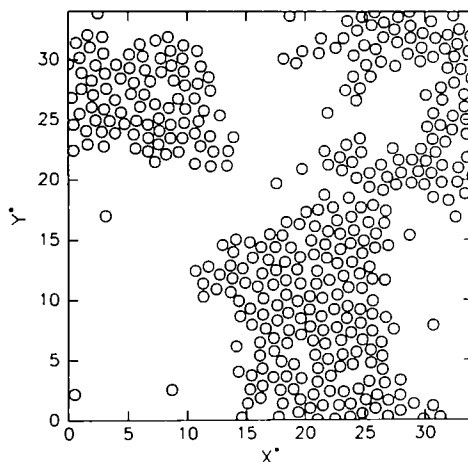
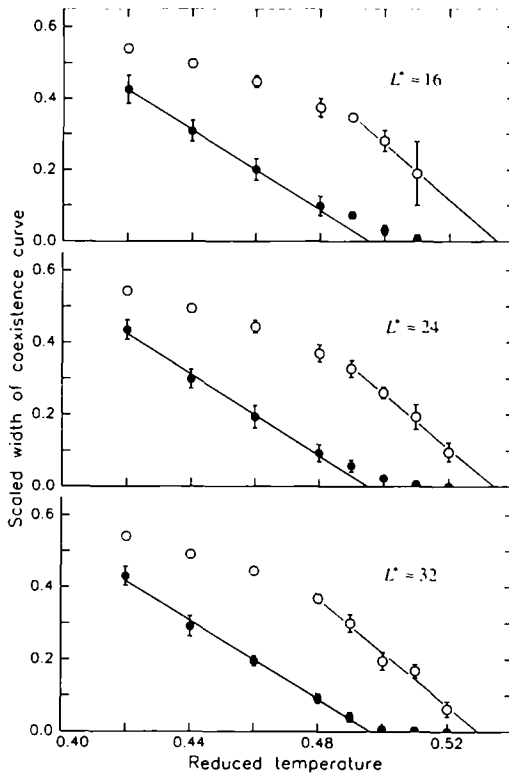


Fig. 1. A configuration of one region in a Gibbs-ensemble simulation of a two-dimensional system with  $r_c^* = 2$  at  $T^* = 0.43$ .  $X^*$  and  $Y^*$  are the reduced coordinates of the particles, shown as circles.

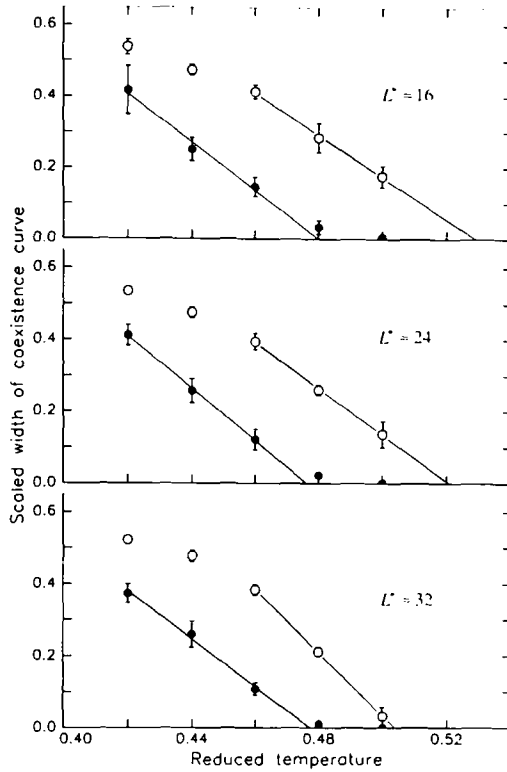
respectively, to  $r_c^* = 5$  and 2.5. A clear crossover from an effective value of the exponent of  $1/8$  away from the critical point to  $1/2$  closer to it is seen in all cases. This crossover was also observed for the two-dimensional Ising [8] and the symmetric square-well mixture in two dimensions [9].

Away from the critical point the effect of system size on the coexistence densities is relatively small, often within the statistical uncertainties of the simulations. A possible reason for the relative small magnitude of size effects away from the critical point in both two-dimensional and three-dimensional Lennard-Jones systems discussed later can be found in the analysis of Smit and Frenkel [15] on finite-size corrections to the chemical potential obtained from Widom test particle insertions. These finite-size corrections scale simply as  $1/N$ , but their absolute magnitude for the three-dimensional Lennard-Jones system is the suggestion of Green *et al.* [10]



**Fig. 2.** Scaled width of the coexistence curves versus reduced temperature for two-dimensional systems with  $r_c^* = 5$  and  $L^* \approx 16, 24,$  and  $32$ . (●)  $(\rho_L^* - \rho_G^*)^2$ ; (○)  $5 \times (\rho_L^* - \rho_G^*)^8$ .





**Fig. 3.** Scaled width of the coexistence curves versus reduced temperature for two-dimensional systems with  $r_c^* = 2.5$  and  $L^* \approx 16, 24,$  and  $32$ . (●)  $(\rho_L^* - \rho_G^*)^2$ ;  $(\circ) 5 \times (\rho_L^* - \rho_G^*)^8$ .

on the importance of “density fluctuations” on the relative strength of finite-size effects. In contrast to the two-dimensional continuous systems studied by Recht and Panagiotopoulos [9], the Lennard–Jones systems studied here require density fluctuations for equilibration and do not show strong finite-size effects.

Estimates for the critical point can, in principle, be obtained based on finite-size scaling analysis [8]. This involves using the data close to the critical point that show “mean field-like” behavior ( $\beta = 1/2$ ) to obtain an estimate for the apparent critical temperature as a function of the linear system size. This extrapolation is shown by the straight least-squares lines through the open circles in Figs. 2 and 3. An estimate for the infinite-system size critical temperature can then be obtained by extrapolating the results at finite system lengths using the appropriate correlation-length

exponents [8, 9]. Unfortunately, this method is not easily applicable to the data for the systems of interest to the present study, because of the inherent instabilities of linear system size close to the critical point and the resulting large statistical uncertainties.

An alternative is provided by the following observations. In all cases studied, there is an extensive range away from the critical point over which the data show "Ising-like" ( $\beta = 1/8$ ) behavior. On strict theoretical grounds Eq. (1) is valid only in the immediate neighborhood of the critical point. However, it has been confirmed empirically for many simulated [e.g., Refs. 9 and 18] and real fluids that, over a surprisingly wide range of temperatures, the coexistence curves can be described by effective exponents close to the appropriate universal exponents. The fitted curves to the data away from the critical point do not show much dependence on system size, as illustrated in Figs. 2 and 3. We can thus obtain useful critical temperature estimates by *ignoring* the data close to the critical point and extrapolating using the Ising exponents. The resulting critical temperatures are shown in Table II, together with data for the critical temperatures of comparable systems from previous investigations. Given the critical temperatures, approximate estimates for the critical densities can be obtained from the "rectilinear diameter" rule, which states that the average of the liquid and gas coexisting densities fall on a straight line in a temperature-density diagram [16]. The weak divergence of the quantity  $(\rho_L + \rho_G - 2\rho_C)$  very close to the critical point is difficult to observe even with high-precision experimental measurements and the limited accuracy of the simulation data does not justify taking it into account. There is no clear trend in the calculated critical densities for the different cutoffs.

It is of interest to compare our estimated critical temperatures with available literature data. Wilding and Bruce [7] have obtained accurate estimates of the critical parameters of the fluid with  $r_c^* = 2$  using finite-size scaling techniques and extremely long grand canonical Monte Carlo simulations. The results are in good agreement with our estimates. Also in

Table II. Critical Properties of Two-Dimensional Lennard-Jones Fluids

$r_c^*$	$T_c^*$	$\rho_c^*$	Source
None	$0.515 \pm 0.002$	$0.355 \pm 0.003$	Smit and Frenkel [11]
None	0.472	$0.33 \pm 0.02$	Singh <i>et al.</i> [17]
5	$0.497 \pm 0.003$	$0.38 \pm 0.01$	This work
2.5	$0.472 \pm 0.010$	$0.35 \pm 0.01$	Rovere <i>et al.</i> [6]
2.5	$0.477 \pm 0.003$	$0.38 \pm 0.02$	This work
2	$0.44 \pm 0.005$	$0.368 \pm 0.003$	Wilding and Bruce [7]
2	$0.446 \pm 0.003$	$0.37 \pm 0.01$	This work

good agreement are our results and those of Rovere *et al.* for  $r_c^* = 2.5$ , who used a finite-size scaling analysis of subsystem-block-density distributions. There are no directly comparable data for  $r_c^* = 5$ , but there are two sets of literature results for the "full" potential. The estimate of Singh *et al.* [17] is clearly too low. Following a suggestion of Wilding and Bruce [7], we have calculated the Boyle temperatures at which the second virial coefficient for the corresponding fluids vanishes, and we have found that the *ratio* of the critical temperatures calculated from our work to the Boyle temperature of the corresponding fluid is approximately constant. The Boyle temperature of the "full" potential is only 0.3% higher than the one with  $r_c^* = 5$ , which suggests that the difference between the estimate of Smit and Frenkel [1] and our own is too high by an order of magnitude to be explained by the different cutoff. Since we observe here that for finite-size systems phase coexistence can be observed at temperatures higher than the infinite-system critical point, this may explain why the result of Smit and Frenkel is higher than our estimates.

**Table III.** Simulation Results for the Phase Coexistence Properties for Three-Dimensional Lennard-Jones Systems<sup>a</sup>

$T^*$	$L^* \approx 6$		$L^* \approx 9$		$L^* \approx 12$	
	$\rho_G^*$	$\rho_L^*$	$\rho_G^*$	$\rho_L^*$	$\rho_G^*$	$\rho_L^*$
$r_c^* = 5$						
1.10					0.636(4)	0.062(4)
1.15					0.594(6)	0.080(9)
1.20					0.558(7)	0.112(8)
1.25					0.477(34)	0.165(15)
$r_c^* = 2.5$						
0.95	0.037(3)	0.689(2)	0.035(1)	0.687(2)	0.035(2)	0.688(4)
1.00	0.051(3)	0.652(9)	0.049(2)	0.650(3)	0.053(6)	0.645(4)
1.05	0.072(6)	0.610(6)	0.069(7)	0.610(6)	0.074(8)	0.613(5)
1.10	0.090(10)	0.590(10)	0.104(11)	0.567(7)	0.111(4)	0.574(9)
1.15	0.120(20)	0.520(20)	0.140(20)	0.490(20)	0.156(8)	0.521(3)
1.17			0.160(30)	0.430(30)	Homogeneous	
$r_c^* = 2$						
0.85	0.030(1)	0.691(3)	0.033(3)	0.694(4)	0.032(3)	0.690(4)
0.90	0.048(6)	0.652(8)	0.048(3)	0.656(3)	0.050(3)	0.657(5)
0.95	0.067(2)	0.600(13)	0.070(8)	0.611(4)	0.073(3)	0.615(8)
1.00	0.119(17)	0.559(6)	0.111(14)	0.557(10)	0.103(10)	0.548(10)
1.05	0.170(30)	0.510(30)	0.215(35)	0.495(21)	0.252(22)	0.468(23)

<sup>a</sup> Numbers in parentheses indicate statistical uncertainties in units of the last decimal point shown: 0.636(4) means  $0.636 \pm 0.004$ .

### 3.2. Three-Dimensional Systems

Our results for the three-dimensional systems are presented in Table III. A sample plot of the scaled coexistence curves versus temperature is shown in Figs. 4 and 5, which correspond to  $r_c^* = 2.5$  and 2. As observed previously [9], there does not seem to be a crossover between “mean-field” and “Ising-like” values of the effective exponents for the three-dimensional systems. Away from the critical point we could obtain almost as good a least-squares fit of the data with either exponent. However, if points close to the critical point are included, especially for the larger systems, curvature for the points corresponding to  $\beta = 1/2$  appears, indicating that the data are better described with  $\beta = 1/3$ . The curvature is most apparent for the data for  $L^* \approx 9$  in Fig. 4 and for all lengths in Fig. 5.

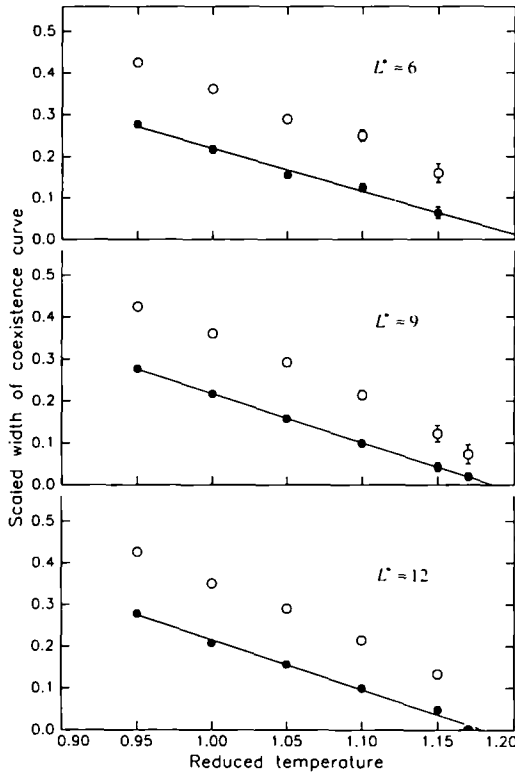


Fig. 4. Scaled width of the coexistence curves versus reduced temperature for three-dimensional systems with  $r_c^* = 2.5$  and  $L^* \approx 6, 9,$  and  $12$ . (●)  $(\rho_L^* - \rho_G^*)^2$ ; (□)  $(\rho_L^* - \rho_G^*)^3$ .

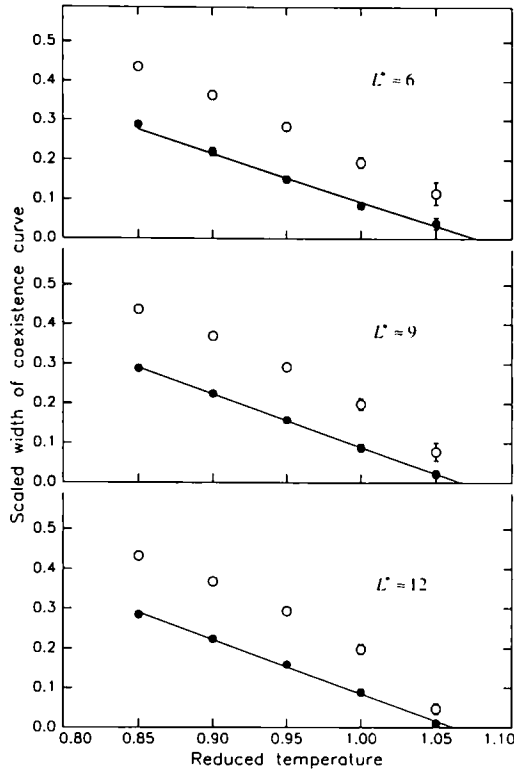


Fig. 5. Scaled width of the coexistence curves versus reduced temperature for three-dimensional systems with  $r_c^* = 2$  and  $L^* \approx 6, 9,$  and  $12$ . (●)  $(\rho_L^* - \rho_G^*)^2$ ; (○)  $(\rho_L^* - \rho_G^*)^3$ .

The determination of the critical parameters for the three-dimensional fluids can proceed in the same way as previously, by extrapolating the data corresponding to  $\beta = 1/3$ . In contrast to the situation for the two-dimensional systems, some size dependence remains for the critical point parameters, with the smaller systems having slightly higher apparent critical points. This is clear in Figs. 4 and 5 by the shift of the intercepts of the straight lines going through the data points and the axis lines corresponding to zero width of the coexistence curve. The accuracy of the data does not justify sophisticated extrapolations, so a simple  $1/N$  dependence was assumed to obtain the critical parameters listed in Table IV. For the  $r_c^* = 5$  system, only a single system size could be meaningfully studied, so we report the critical temperature for that system size in Table IV.

**Table IV.** Critical Properties of Three-Dimensional Lennard-Jones Fluids

$r_c^*$	$T_c^*$	$\rho_c^*$	Source
None	$1.316 \pm 0.003$	$0.304 \pm 0.006$	Smit [18]
None	1.310	0.314	Lotfi <i>et al.</i> [19]
5	$1.281 \pm 0.005$	$0.32 \pm 0.01$	This work
2.5	$1.176 \pm 0.008$	$0.33 \pm 0.01$	This work
2	$1.061 \pm 0.005$	$0.32 \pm 0.01$	This work

Comparisons of the results with literature data is complicated by the fact that most previous literature studies were for the full [1, 2] or the cut-and-shifted potentials [18], not for the truncated potential. If we assume that the ratio of the critical to the Boyle temperatures of each fluid is the same for all fluids (a reasonable assumption based on our calculated critical temperatures), then we can perform the following approximate comparisons. From Smit's estimate [2] of  $T_c^* = 1.316$  for the full potential, we obtain an extrapolated value  $T_c^* = 1.300$  for the potential cut at  $r_c^* = 5$ . This estimate is somewhat higher than our own, but the difference is just outside the combined simulation uncertainties. In even better agreement with our estimate would be an extrapolation of the data of Lotfi *et al.* [19]. From Smit's estimate [18] of  $T_c^* = 1.085$  for the cut-and-shifted potential at  $r_c^* = 2.5$ , we obtain  $T_c^* = 1.201$  for potential cut at  $r_c^* = 2.5$ , which is also close to but higher than our own estimate. The extrapolation procedure itself may be partly to blame for the differences and it seems justified to clarify whether this small discrepancy can be resolved by detailed calculations with controlled linear system sizes.

#### 4. CONCLUSIONS

One of the main conclusions of this work is that finite-size effects in phase equilibrium calculations of continuous-space models are important for systems of low dimensionality. For such systems, calculation of the phase behavior, especially close to critical points, should be done with extreme care and preferably by means of simulation techniques for which precise control of system linear dimensions is possible. Simulations in the Gibbs ensemble cannot achieve the high precision required for detailed finite-size scaling analysis because of the variability in number of particles and density of each of the two regions. In three dimensions finite-size effects are present, but not very pronounced for potentials of the Lennard-Jones type, even for relatively short cutoffs.

Away from the critical point, there are no significant effects of system size on the location of the coexistence curves for potentials of the

Lennard–Jones type. This is in contrast to the large effects of system size on the coexistence curves observed for two- and three-dimensional symmetric square-well mixtures simulated under constant-volume conditions [9], for which no density fluctuations are necessary for reaching equilibrium in Gibbs-ensemble simulations.

This procedure for the determination of critical constants, namely, the use of Eq. (1) with the appropriate Ising exponents together with the rectilinear diameter rule, has been used in most previous Gibbs-ensemble studies to determine critical temperatures. The analysis shown here suggests that this is a valid procedure only if data in the immediate vicinity of the critical point that follow mean-field-like behavior are discarded. Critical temperatures can be determined within an accuracy of  $\pm 1\%$  or better using this procedure. Critical densities obtained from the rectilinear diameter rule are subject to significantly larger uncertainties than the critical temperatures.

Finally, it seems that the apparent critical exponents obtained in Gibbs-ensemble simulations depend on the linear system size and the distance from the critical point. In the light of this finding, it is hard to justify using Gibbs-ensemble simulations to determine apparent critical exponents for different potential models without precise control of system size and explicit consideration of possible crossover behavior in the immediate vicinity of the critical point.

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