Constant-volume heat capacity in a near-critical fluid from Monte Carlo simulations

Constant-volume heat capacity in a near-critical fluid from Monte Carlo simulations

Christopher D. Daub, Philip J. Camp, and G. N. Patey

Citation: J. Chem. Phys. **121**, 8956 (2004); doi: 10.1063/1.1795713
View online: http://dx.doi.org/10.1063/1.1795713
View Table of Contents: http://jcp.aip.org/resource/1/JCPSA6/v121/i18
Published by the AIP Publishing LLC.

Constant-volume heat capacity in a near-critical fluid from Monte Carlo simulations

Christopher D. Daub
Department of Chemistry, University of British Columbia, Vancouver, British Columbia, Canada V6T 1Z1

Philip J. Camp
School of Chemistry, University of Edinburgh, West Mains Road, Edinburgh EH9 3JJ, United Kingdom

G. N. Patey
Department of Chemistry, University of British Columbia, Vancouver, British Columbia, Canada V6T 1Z1

(Received 6 July 2004; accepted 28 July 2004)

We consider a near-critical fluid of hard spheres with short-range interactions ($\sim r^{-6}$) and obtain its constant-volume heat capacity C_V by means of Monte Carlo calculations in the canonical ensemble. The question addressed is whether or not the heat capacities of the finite-size systems studied in simulations can provide a reliable indication of nonclassical criticality. For the model fluid considered here this is found to be the case. The heat capacity along the critical isochore shows a peak near the critical temperature, with a system size dependence that is consistent with the known Ising universality class of the model. The relevance of our results to recent attempts to determine the universality class of ionic fluids through calculations of C_V is briefly discussed. © *2004 American Institute of Physics.* [DOI: 10.1063/1.1795713]

I. INTRODUCTION

Computer simulations yield valuable insights on the structure and dynamics of complex condensed-matter systems, yet some fundamental questions remain to be answered before such techniques become universally applicable. The question that concerns us here is, can simulation estimates of the constant-volume heat capacity provide reliable indications of the universality class to which a given system belongs?

The initial motivation for this work stems from Monte Carlo (MC) studies of liquid-vapor criticality in the restricted primitive model (RPM) of ionic fluids carried out by ourselves[1] and others.[2–8] Taken as a whole, this work has resulted in the critical point of the RPM being known with a high degree of accuracy. In addition, a large amount of evidence from finite-size scaling analyses suggests that the universality class of the RPM is that of the three-dimensional Ising model. However, simulation measurements of the constant volume heat capacity C_V have differed greatly, with some authors reporting a peak in the heat capacity consistent with Ising criticality,[6] while others found no sign of such behavior.[2,3]

In a recent paper dealing with the RPM and other model fluids,[1] we have demonstrated that the choice of statistical mechanical ensemble employed in the simulations can have large effects on the results obtained. Specifically, we found that estimates of C_V obtained in the grand-canonical (μVT) ensemble can give peaks near the critical point not only for the RPM, but also for systems known to exhibit classical criticality for which no ''divergent'' peaks are expected.[9–12] We therefore speculated that these peaks are artifacts arising from the influence of finite system size on the relevant grand-canonical fluctuations of the energy and the particle number. In contrast, estimates of C_V obtained in canonical (NVT) simulations gave no hint of a peak for the near-critical RPM, probably due to the suppression of density fluctuations and their coupling with energy fluctuations. These observations explained the qualitatively different results reported in the literature.[2,3,6]

In Ref. 1 we also considered a fluid of hard spheres interacting through a short-range attractive potential decaying as r^{-6}, where r is the interparticle separation. Renormalization group[11,12] and integral equation[13,14] studies provide strong evidence that such a system belongs to the 3D-Ising universality class,[15] and this is also supported by the mixed-field finite-size scaling (MFFSS) analysis of grand-canonical simulation data.[16] In our earlier NVT simulations employing relatively small systems, C_V for the short-ranged potential at the relevant critical density did show weak maxima in the vicinity of the critical temperature. However, due to the proximity of the freezing transition, these peaks could not be unambiguously identified with critical ''divergences.'' In the present paper we revisit this issue, and carry out a systematic investigation employing larger systems. This allows us to conclude that the peaks observed are clearly associated with the expected critical behavior. Hence, simulation measurements of C_V can be considered as a reliable indicator of the universality class of these systems. We note that a similar systematic study of C_V has been carried out for one- and two-dimensional continuous-spin Ising models.[17] In addition, Valleau and Torrie have reported C_V results consistent with Ising-like behavior for a Lennard-Jones fluid.[2]

TABLE I. Summary of the apparent finite-size critical parameters from the present work, and the bulk ($L=\infty$) critical temperature from Ref. 16.

L/σ	Range of T^* for Padé fits	$T_c^*(L)$	C_V/Nk_B
6	0.30–0.60	0.384 ± 0.020	9.90 ± 0.23
10	0.36–0.60	0.475 ± 0.010	11.66 ± 0.45
12	0.42–0.60	0.501 ± 0.010	12.47 ± 0.64
17	0.45–0.60	0.534 ± 0.010	13.5 ± 1.3
22	0.45–0.60	0.545 ± 0.010	14.2 ± 1.0
∞		0.5972 ± 0.0001	

II. MONTE CARLO COMPUTER SIMULATIONS

The pair potential $u(r)$ is given by

$$u(r)=\begin{cases}\infty & r<\sigma \\ -\epsilon(\sigma/r)^6 & r\geqslant\sigma,\end{cases} \tag{1}$$

where r is the pair separation, σ is the hard sphere diameter, and ϵ is the well depth. We define a reduced temperature $T^*=k_BT/\epsilon$ and a reduced density $\rho^*=N\sigma^3/V$, where N is the number of particles and V is the total volume.

MC simulations in cubic cells of side L were carried out in the NVT ensemble at densities as close as possible to the critical density [$\rho_c^*=0.3757$ (Ref. 16)] and over a temperature range that encompassed the critical temperature [$T_c^*=0.5972$ (Ref. 16)]. Periodic boundary conditions were imposed, and the spherical potential was truncated at $L/2$. The system sizes considered were $L/\sigma=6$, 10, 12, 17, and 22; the largest system contained $N=4000$ particles in the simulation cell. The systems were well equilibrated at each temperature before statistics were gathered.

For each system size the average configurational energy per particle $U^{\mathrm{ex}}/N\epsilon$ was obtained as a function of temperature and the results were fitted using a [4,4] Padé approximant,

$$\frac{U_{\mathrm{ex}}}{N\epsilon}=\frac{f_0+f_1x+f_2x^2+f_3x^3+f_4x^4}{1+g_1x+g_2x^2+g_3x^3+g_4x^4}, \tag{2}$$

where $x=\sqrt{T^*}$. At low temperatures ($T^*=0.3$–0.4, depending on L) there is a ''freezing'' transition to a solidlike structure which causes a sharp change in the energy; the Padé function cannot accommodate this feature and so we carried out the fitting over restricted temperature ranges as indicated in Table I. The results of the calculations and the fits are shown in Fig. 1. Clearly, the Padé fits provide accurate descriptions of the simulation results.

The canonical heat capacity was calculated in two ways; directly from the fluctuations in energy [$C_V=(\langle U^2\rangle-\langle U\rangle^2)/k_BT^2$], and through temperature differentiation of the Padé approximant fit to the energy. The results obtained are shown in Fig. 2; the kinetic contribution, $(3/2)Nk_B$, has been included. It is apparent that the two methods arrive at similar results, though the fluctuation calculations are subject to larger statistical errors. Also included in Fig. 2 are indications of the apparent finite-size critical temperatures $T_c^*(L)$ being defined by the positions of the maxima in C_V; these values are also given in Table I.

In the thermodynamic limit the heat capacity of an Ising-like system in three dimensions should diverge near T_c^* with

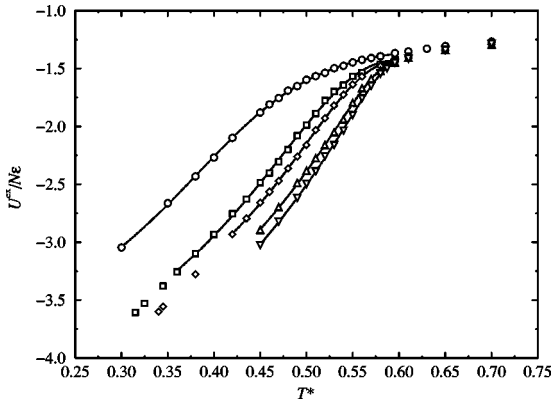

FIG. 1. The average configurational energy per particle, $U^{\mathrm{ex}}/N\epsilon$, as a function of T^* for all system sizes (points), and the respective [4,4] Padé fits (lines): $L/\sigma=6$ (circles); $L/\sigma=10$ (squares); $L/\sigma=12$ (diamonds); $L/\sigma=17$ (up triangles); $L/\sigma=22$ (down triangles).

an exponent $\alpha\simeq0.11$ (Ref. 18). According to the finite-size scaling analysis,[19] in a finite system this divergence is replaced with a rounded peak with a maximum at a temperature $T_c^*(L)$ somewhat removed from the bulk-system critical temperature $T_c^*(\infty)$ with the peak getting sharper as the system size increases. In the canonical ensemble the position of this peak should scale with system size like,[20]

$$T_c^*(L)=T_c^*(\infty)+a_1L^{-1/\nu}(1+a_2L^{-\theta/\nu}+a_3L^{-2\beta/\nu}), \tag{3}$$

where a_n are nonuniversal constants. For an Ising-like critical point, $\nu\simeq0.630$,[18] $\theta\simeq0.54$,[21] and $\beta\simeq0.326$ (Ref. 18) are the correlation length, Wegner correction-to-scaling,[22] and order-parameter critical exponents, respectively. The last two terms in brackets in Eq. (3) have exponents of similar magnitudes, being $\theta/\nu\simeq0.86$ and $2\beta/\nu\simeq1.03$. The number and range of system sizes considered in this work are not sufficient to fit both of the coefficients a_2 and a_3 reliably, and so we have used an approximate expression for $T_c^*(L)$ with a single correction-to-scaling term, i.e.,

$$T_c^*(L)=T_c^*(\infty)+a_1L^{-1/\nu}(1+a_2L^{-1}). \tag{4}$$

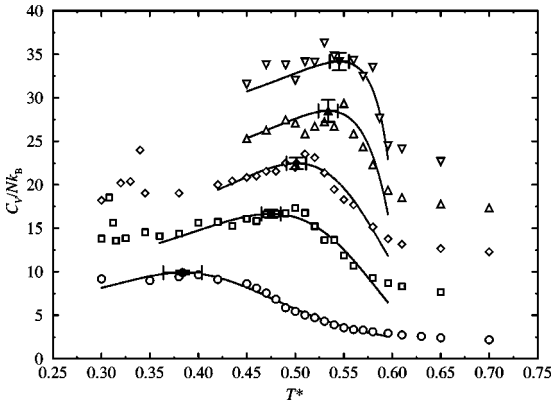

FIG. 2. C_V/Nk_B as a function of T^* for all system sizes, calculated directly from the fluctuations in energy (open symbols) and from the derivative of the Padé fits to the average energies (lines): $L/\sigma=6$ (circles); $L/\sigma=10$ (squares); $L/\sigma=12$ (diamonds); $L/\sigma=17$ (up triangles); $L/\sigma=22$ (down triangles). The solid symbols indicate $T_c^*(L)$. The results for each system size are displaced by five units along the ordinate for clarity.

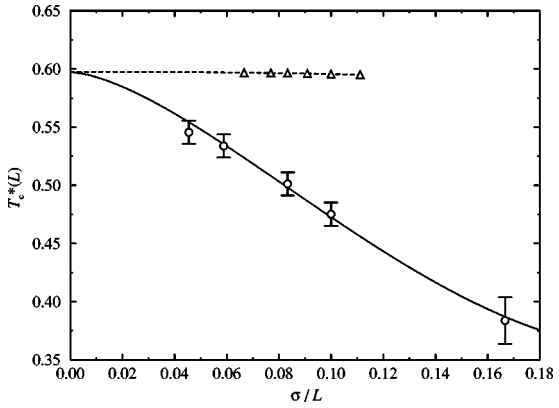

FIG. 3. Apparent finite-size critical temperature, $T_c^*(L)$, as a function of σ/L: present simulation results (circles) and fit [Eq. (4)] with $T_c^*=0.5972$ (Ref. 16); MFFSS results (triangles) and fit [Eq. (5) of Ref. 16] (dashed line).

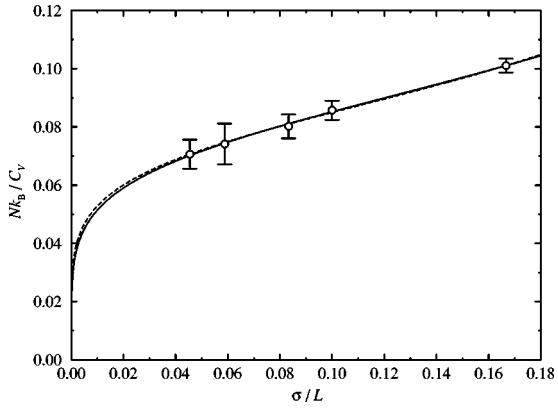

FIG. 4. Reciprocal of the peak height of C_V/Nk_B at $T^*=T_c^*(L)$ as a function of σ/L: present simulation results (circles); from Eq. (5) with $\nu=0.189(28)$ (solid line); from Eq. (5) with $\nu=0.175$ (dashed line).

In Fig. 3 we plot $T_c^*(L)$—obtained from the peaks in C_V—as a function of σ/L. Simulation results obtained from a MFFSS analysis,[16] and the appropriate fit [Eq. (5) in Ref. 16] are included for comparison. The finite-size corrections in the current analysis are clearly much greater than in the MFFSS case. In order to show consistency between our finite-size simulation results and the Ising-like finite-size corrections in Eq. (4), we have performed a fit with the bulk critical temperature being fixed at the value obtained from a MFFSS study,[16] $T_c^*(\infty)=0.5972$. The fit parameters are $a_1=-6.63(39)$ and $a_2=-2.73(32)$; the resulting curve is included in Fig. 3. We have also carried out a fit with $T_c^*(\infty)$ being an additional adjustable parameter, which gives $T_c^*(\infty)=0.5808(43)$, $a_1=-4.96(47)$, and $a_2=-1.89(36)$. This estimate of $T_c^*(\infty)$ is about 3% lower than that obtained from the MFFSS analysis. Clearly, in the present situation, the C_V route to the finite-size critical parameters is not reliable for estimating $T_c^*(\infty)$, largely because of the pronounced finite-size corrections and the large statistical uncertainties associated with calculating C_V (either by differentiating U, or by using the fluctuation formula). Nonetheless, the results show that the finite-size scaling of $T_c^*(L)$ is at least consistent with Ising-like criticality.

We now turn to a finite-size scaling analysis of the peak height of C_V. The values of C_V at $T=T_c^*(L)$ are reported in Table I, and the reciprocals are plotted in Fig. 4 as a function σ/L. We have fitted curves of the form,

$$\frac{C_V}{Nk_B}=b(L+\delta L)^{\alpha/\nu}, \tag{5}$$

where b is a nonuniversal constant, and δL is an aid to extrapolation[23] which accounts for corrections to scaling, albeit in an approximate manner. When the exponent ratio α/ν is fixed at its Ising value ($\alpha/\nu\simeq 0.175$) the fit parameters obtained are $b=8.506(60)$ and $\delta L=-3.63(12)$; the resulting curve is shown in Fig. 4 and provides a good description of the simulation results. When α/ν is treated as an adjustable parameter the results are $\alpha/\nu=0.189(28)$, $b=8.17(65)$, and $\delta L=-3.26(75)$; the value of α/ν is very close to the Ising value, but this agreement is likely to be fortuitous. Nonetheless, Fig. 4 shows that the corresponding curve is of comparable quality to that obtained with the Ising value of α/ν. These results serve to demonstrate that measurements of thermodynamic properties near the critical point in canonical ensemble simulations can be used to discriminate between classical and nonclassical criticality. Recall that for a classical critical point $\alpha=0$ and hence the peak-height of C_V is not expected to increase with increasing system size. Despite the sizable statistical errors in C_V, Fig. 4 shows that the observed finite-size scaling is at least consistent with Ising-like criticality.

III. SUMMARY AND CONCLUSIONS

We have investigated the behavior of C_V in a near-critical fluid of hard spheres with an attractive interaction proportional to r^{-6}. Our simulations, carried out in the canonical ensemble, show the expected finite-size scaling behavior for a system belonging to the Ising universality class; C_V clearly has a peak near $T_c^*(\infty)$ which increases in height and moves closer to $T_c^*(\infty)$ with increasing system size. The finite-size dependence of the apparent critical temperature is much stronger than that observed in a MFFSS analysis.[16] This is most likely due to the strong suppression of density fluctuations that is inherent to the canonical ensemble. For this reason, the estimate of $T_c^*(\infty)$ obtained using grand-canonical ensemble simulations and the MFFSS method[16] would appear to be more trustworthy (subject to the effects of pressure mixing being small[24,25]).

We have demonstrated that with sufficient care, direct measurements of C_V by simulation can indeed be used to rule out classical criticality for a continuous, three dimensional fluid interacting with a short-range potential. The important question remains, however, why similar investigations of model ionic systems show no such peak. The most prosaic explanation is simply that, despite ionic screening, the long-range Coulombic interactions suppress critical energy fluctuations in the ''small'' systems simulated to date. This explanation is supported by the fact that the MFFSS analyses of the ionic systems show very small finite-size effects and no deviations from Ising-type criticality, just as the MFFSS analysis of the present system shows far smaller

finite-size effects than the analysis of C_V. The recent study of the RPM by Caillol *et al.*[7] extending up to $L/\sigma=34$ suggests that the question of the lack of a "diverging" C_V peak may not be resolved by simulations, at least not without an order of magnitude increase in system size.

ACKNOWLEDGMENTS

P.J.C. would like to thank Professor M. E. Fisher for a valuable discussion. This research was enabled by the use of WestGrid computing resources, which were funded in part by the Canada Foundation for Innovation, Alberta Innovation and Science, BC Advanced Education, and the participating research institutions. WestGrid equipment was provided by IBM, Hewlett Packard, and SGI. The financial support of the National Science and Engineering Research Council of Canada is gratefully acknowledged.

[1] C. D. Daub, P. J. Camp, and G. N. Patey, J. Chem. Phys. **118**, 4164 (2003).
[2] J. Valleau and G. Torrie, J. Chem. Phys. **108**, 5169 (1998).
[3] J. Valleau and G. Torrie, J. Chem. Phys. **117**, 3305 (2002).
[4] Q. Yan and J. J. de Pablo, J. Chem. Phys. **111**, 9509 (1999).
[5] G. Orkoulas and A. Z. Panagiotopoulos, J. Chem. Phys. **110**, 1581 (1999).
[6] E. Luijten, M. E. Fisher, and A. Z. Panagiotopoulos, J. Chem. Phys. **114**, 5468 (2001).
[7] J.-M. Caillol, D. Levesque, and J.-J. Weis, J. Chem. Phys. **116**, 10794 (2002).
[8] E. Luijten, M. E. Fisher, and A. Z. Panagiotopoulos, Phys. Rev. Lett. **88**, 185701 (2002).
[9] G. Stell, Phys. Rev. B **5**, 981 (1972).
[10] G. Stell, Phys. Rev. B **8**, 1271 (1973).
[11] M. E. Fisher, S.-K. Ma, and B. G. Nickel, Phys. Rev. Lett. **29**, 917 (1972).
[12] J. Sak, Phys. Rev. B **8**, 281 (1973).
[13] G. Stell, Phys. Rev. Lett. **20**, 533 (1968).
[14] G. Stell, Phys. Rev. B **1**, 2265 (1970).
[15] J. Hubbard and P. Schofield, Phys. Lett. **40A**, 245 (1972).
[16] P. J. Camp and G. N. Patey, J. Chem. Phys. **114**, 399 (2001).
[17] E. Bayong and H. T. Diep, Phys. Rev. B **59**, 11919 (1999).
[18] R. Guida and J. Zinn-Justin, J. Phys. A **31**, 8103 (1998).
[19] M. N. Barber, in *Phase Transitions and Critical Phenomena*, edited by C. Domb and J. L. Lebowitz (Academic, London, 1983), Vol. 8, Chap. 2.
[20] Y. C. Kim and M. E. Fisher, Phys. Rev. E **68**, 041506 (2003).
[21] J. H. Chen, M. E. Fisher, and B. G. Nickel, Phys. Rev. Lett. **48**, 630 (1982).
[22] F. J. Wegner, Phys. Rev. B **5**, 4529 (1972).
[23] G. Orkoulas, A. Z. Panagiotopoulos, and M. E. Fisher, Phys. Rev. E **61**, 5930 (2000).
[24] Y. C. Kim, M. E. Fisher, and G. Orkoulas, Phys. Rev. E **67**, 061506 (2003).
[25] Y. C. Kim and M. E. Fisher, J. Phys. Chem. B **108**, 6750 (2004).