Finite-size scaling for near-critical continuum fluids at constant pressure

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Abstract

We consider the application of finite-size scaling methods to isothermal-isobaric (constant-NpT) simulations of pure continuum fluids. A finite-size scaling ansatz is made for the dependence of the relevant scaling operators on the particle number. To test the proposed scaling form, constant pressure simulations of the Lennard-Jones fluid at its liquid-vapour critical point are performed. The critical scaling operator distributions are obtained and their scaling with particle number found to be consistent with the proposed behaviour. The forms of these scaling distributions are shown to be identical to their Ising model counterparts. The relative merits of employing the constant-NpT and grand canonical (constant-$\mu$VT) ensembles for simulations of fluid criticality are also discussed.
I. INTRODUCTION

The study of the phase behaviour of simple and complex fluids by computer simulation is a subject of much current research activity [1]. Of particular interest are the critical point properties of such systems [2]. In the vicinity of a critical point, the correlation length grows extremely large and may exceed the linear size of the simulated system. When this occurs, the singularities and discontinuities that characterise critical phenomena in the thermodynamic limit are shifted and smeared out [3]. Unless care is exercised, such finite-size effects can lead to serious errors in computer simulation estimates of critical point parameters.

To cope with these problems, finite-size scaling (FSS) techniques have been developed [4,3]. FSS methods enable one to extract accurate estimates of infinite-volume thermodynamic quantities from simulations of finite-sized systems. To date, their application to fluid criticality has been principally in conjunction with simulations in the constant-$\mu$VT or grand-canonical ensemble (GCE). The principal merit of this ensemble is that the particle density fluctuates on the scale of the system as a whole, thus enabling direct measurement of the large-scale density fluctuations that are the essential feature of fluid criticality. The GCE has proven its worth in FSS studies of criticality in a variety of fluid systems including the Lennard-Jones (LJ) fluid [5,6] and a 2D spin fluid model [7].

Notwithstanding its wide utility, however, there exist many complex fluids for which use of the GCE ensemble is by no means efficient. Systems such as semi-dilute polymer solutions are difficult to simulate in the GCE due to excluded volume effects which hinder chain insertions. While smart insertion techniques go some way to ameliorating this difficulty, the long chain lengths of greatest interest are currently inaccessible [8]. Similarly, electrolyte models such as the restricted primitive model show very poor acceptance rates for particle insertions due to the formation of bound ion clusters [9]. Thus it is interesting to ask whether one can deal with the near-critical density fluctuations in such systems without having to implement inefficient particle transfer operations.

The approach we consider here, is to employ an ensemble wherein the total particle number is fixed, but the density is allowed to fluctuate by virtue of volume transitions. Specifically, we consider how the FSS ideas, hitherto only applied to systems with constant volume, may be generalised to an isothermal-isobaric (NpT-ensemble) simulation. Since finite-size scaling usually rests on the idea of comparing the correlation length with the (fixed) linear dimensions of the system, the generalisation to systems whose linear dimensions are dynamically fluctuating is not completely obvious. We make a scaling ansatz for the near-critical scaling operator distributions and scaling fields, expressed in terms of powers of the particle number. This is then tested via a simulation study of the critical Lennard-Jones fluid, in which it found that the FSS predictions are indeed consistent with the simulation results. Finally we discuss the relative merits of the NpT- and $\mu$VT- (GCE) ensembles for simulation studies of fluid criticality.

II. FINITE-SIZE SCALING THEORY

We consider a classical single component fluid, whose configurational energy (which we write in units of $k_B T$) resides in a sum of pairwise interactions amongst the $N$ particles it
contains
\[ \Phi(\{\vec{r}\}) = \sum_{i<j=1}^{N} \phi(|\vec{r}_i - \vec{r}_j|) \] (1)

where \( \phi(|\vec{r}_i - \vec{r}_j|) \) is the interparticle potential which, for this work, we assign the Lennard-Jones form:
\[ \phi(r) = 4w[(\sigma/r)^{12} - (\sigma/r)^{6}] \] (2)

where \( w \) is the dimensionless well depth and \( \sigma \) serves to set the length scale.

Within the isothermal-isobaric ensemble, the partition function is given by
\[ Z_N = \prod_{i=1}^{N} \left\{ \int d\vec{r}_i \right\} \int dV e^{[-\Phi(\{\vec{r}\}) - pV]} \] (3)

where \( p = P/k_B T \) is the pressure, and \( V = L^d \) is the homogeneously fluctuating system volume. The associated (Helmholtz) free energy is
\[ G = -k_B T \ln Z_N = k_B T(\Phi(\{\vec{r}\}) + pV) \] (4)

In the vicinity of the liquid-vapour critical point, the coarse-grained properties of the system are expected to exhibit scaling behaviour. For simple fluids with short-ranged interactions, this behaviour is Ising-like \[3\] and is controlled by two relevant scaling fields \( \tau \) and \( h \) that measure deviations from criticality. In general (in the absence of the special Ising ‘particle-hole’ symmetry), these scaling fields comprise linear combinations \[10\] of the reduced chemical potential \( \mu \) and well depth \( w \):
\[ \tau = w_c - w + s(\mu - \mu_c), \quad h = \mu - \mu_c + r(w_c - w) \] (5)

where subscripts denote critical values, and \( s \) and \( r \) are non-universal field mixing parameters, the values of which depend on the specific system under consideration.

The respective conjugate operators are defined by
\[ \langle \mathcal{E} \rangle = \frac{1}{\langle V \rangle} \frac{\partial \ln Z_N}{\partial \tau}, \quad \langle \mathcal{M} \rangle = \frac{1}{\langle V \rangle} \frac{\partial \ln Z_N}{\partial h} \] (6)

whereupon, utilizing equation \[3\], and noting that \( dP = gdT + \rho d\mu \) (with \( g \equiv S/V \), the entropy density), one finds
\[ \mathcal{E} = \frac{1}{1 - sr}[u - r\rho], \quad \mathcal{M} = \frac{1}{1 - sr}[ho - su] \] (7)

where \( \rho \equiv N/V \) is the particle density and \( u \equiv \Phi(\{\vec{r}\})/V \) is the energy density. We term \( \mathcal{M} \) the ordering operator, while \( \mathcal{E} \) is termed the energy-like operator.

For the finite-size scaling behaviour of the joint distribution \( P_N(\mathcal{M}, \mathcal{E}) \) we make the following ansatz:
\[ P_N(\mathcal{M}, \mathcal{E}) \simeq a^{-1}_M a^{-1}_e N^x N^y \tilde{p}(a^{-1}_M N^x(\mathcal{M} - \mathcal{M}_c), a^{-1}_e N^y(\mathcal{E} - \mathcal{E}_c), a_{\mathcal{M}} N^{1-x}\tau, a_{\mathcal{E}} N^{1-y}\tau) \] (8)
where $a_M$ and $a_E$ are non-universal metric factors and $\tilde{P}$ is a universal function in the sense that it is identical for all members of a given universality class and a given choice of boundary conditions. Here we have chosen simply the particle number $N$ rather than the volume $V$ as a measure of the ‘finite-size’ of the systems, using now suitable powers of $N$ in the scaling assumption.

The unspecified exponents $x$ and $y$ in equation \[8\] can be related to the standard critical indices $\beta$ and $\nu$ by an argument analogous to that invoked by Binder \[11\] for the Ising model in the canonical ensemble. Consider the generalised isothermal compressibility, $\kappa_\tau$, defined by

$$\kappa_\tau \equiv -\frac{1}{V} \left( \frac{\partial^2 G}{\partial h^2} \right)_\tau$$

This may be reexpressed as a fluctuation relation by appeal to equations \[3\] and \[4\], whence one finds

$$\kappa_\tau = \beta \langle \rho \rangle^{-1} N \langle (\mathcal{M} - \mathcal{M}_c)^2 \rangle$$

From equation \[8\], the scaling of the fluctuation in the ordering operator $\mathcal{M}$ at finite $\tau$ is given by

$$\langle (\mathcal{M} - \mathcal{M}_c)^2 \rangle = a^{-1}_M N^x \int d\mathcal{M} (\mathcal{M} - \mathcal{M}_c)^2 \tilde{p}_N(a^{-1}_M N^x(\mathcal{M} - \mathcal{M}_c), N^{1-y} \tau)$$

$$= N^{-2x} a^2_M \int dz z^2 \tilde{p}_N(z, N^{1-y} \tau)$$

$$\equiv N^{-2x} a^2_M f(N^{1-y} \tau)$$

where $f(N^{y} \tau)$ is an unspecified scaling function.

Now in the critical ($\tau \to 0$) and thermodynamic limits ($N \to \infty$), one requires for consistency that $\kappa_\tau \sim \tau^{-\gamma}$. Accordingly $f(N^{y} \tau) \sim (N^{1-y} \tau)^{-\gamma}$, and matching powers of $N$ in equation \[10\] and \[13\] then yields

$$-2x - \gamma(1 - y) = 1,$$

a relation that is satisfied by the assignments

$$x = \frac{\beta}{d\nu},$$

$$y = 1 - \frac{1}{d\nu},$$

where we have employed the hyperscaling relation $d\nu = \gamma + 2\beta$ to eliminate $\gamma$ from equation \[14\].

Thus precisely at criticality, where $\tau = h = 0$, equation \[11\] can be written:

$$P_N(\mathcal{M}, \mathcal{E}) \simeq a^{-1}_M a^{-1}_E N^{\beta/d\nu} N^{(dv-1)/d\nu} \tilde{P}^\star(a^{-1}_M N^{\beta/d\nu}(\mathcal{M} - \mathcal{M}_c), a^{-1}_E N^{(dv-1)/d\nu}(\mathcal{E} - \mathcal{E}_c)),$$

where $\tilde{P}^\star$ is a universal function characterising the Ising fixed point. We note that this scaling behaviour is simply related to that for the $\mu VT$-ensemble \[3\] by the substitution $L^d \to N$. In what follows we will test the validity of equation \[17\] via simulations of the 3D Lennard-Jones fluid at its liquid-vapour critical point.
III. MONTE-CARLO STUDIES

Monte-Carlo simulations of the Lennard-Jones fluid were carried out within the NpT-ensemble using a Metropolis algorithm [12]. In common with many other simulation studies of the model, the potential was cutoff at a distance $r_c = 2.5 \sigma$, and was not shifted. In the course of the simulations, three separate periodic systems comprising $N = 216, 363$ and $512$ particles were studied. In order to minimise fluctuations in the acceptance rate for volume moves, the method of Eppenga and Frenkel [14] was employed. Within this scheme the system performs a random walk in $\ln V$ rather than in $V$ itself, thereby automatically adjusting the step size in the volume to be larger at lower densities than higher densities. This technique is particularly useful in the coexistence region, due to the large volume fluctuations.

From a previous detailed simulation study of the LJ fluid in the grand-canonical ensemble [6], the critical temperature is known to lie at $T_c \equiv 4/w_c = 1.1876(3)$. Using this value of $w$, a number of short runs were performed in which the pressure $p$ was tuned in order to locate approximately the coexistence curve. Once a near-critical value of $p$ had been obtained, a long run comprising $6 \times 10^6$ volume change attempts and an equal number of displacements attempts per particle were performed. During this run, the histogram of the joint distribution $P_N(\rho, u)$ was accumulated.

In order to locate more precisely the critical pressure, the ordering operator distribution $P_N(M)$ was studied for each value of $N$. Precisely at criticality, and for the correct choice of the field mixing parameter $s$, $P_N(M)$ is expected to be a symmetric function by virtue of the fact that the field mixing transformation restores the Ising symmetry of the critical fluid [6]. The value of the field mixing parameter $s$ and the pressure $p$ were therefore tuned simultaneously using the histogram reweighting scheme [15], until a symmetric function was obtained. This occurred for values $s = -0.10(1)$ and $p = 0.1093(6)$. This value of $s$ is in accord with that obtained previously in the GCE study of the same model [6]. The resulting form of $P_N(M)$ for each system size, expressed in terms of the scaling variable $x = a_M^{-1}N^{\beta/\nu}(M - M_c)$, is plotted in figure 1. The non-universal scale factor $a_M$ was chosen so that the data for the $N = 512$ system has unit variance, while the exponent ratio $\beta/\nu$ was assigned the Ising estimate $\beta/\nu = 0.518$ of reference [17]. Also shown for comparison (solid line) is the scaled critical magnetisation distribution of the 3D Ising model obtained in a separate study [16]. Clearly the data for each system size collapse well on to one another and are thus consistent with the proposed scaling form. They also agree well with the universal form of the Ising magnetisation distribution. We attribute the small deviations to corrections-to-scaling associated with the rather small numbers of particles. These discrepancies are comparable in size and form with those observed in reference [6]. Unfortunately, owing to these corrections-to-scaling, as well as to the somewhat poor statistical quality (a point to which we return in section IV), it was not possible to obtain a reliable independent estimate of the exponent ratio $\beta/\nu$.

A procedure similar to that outlined above was also carried out for the energy-like operator $P_N(E)$. In this case, however, there is no symmetry requirement for the critical form of the function $P_N(E)$. However, we found that by assigning the field mixing parameter $r$, the value $r = -1.02$ found in the previous GCE study of the LJ fluid [6], the function matched closely the form of the critical Ising model energy distribution. Again the scaling of the
$P_N(\mathcal{E})$ with $N$ was found to be consistent with the scaling form eq. [17].

IV. DISCUSSIONS AND CONCLUSIONS

The aim of this work was to develop a FSS formalism for simulations of near-critical fluids at constant pressure. A scaling form was proposed and tested for the Lennard-Jones fluid, whose critical point parameters are known to high precision. Good consistency with the scaling prediction was found. Additionally, it was shown that the forms of the critical scaling operator distributions are the same as those for the $\mu VT$-ensemble (and hence the canonical ensemble of the critical Ising model), despite the very different nature of the simulation ensembles. As is well known, finite-size effects may differ in various ensembles of statistical mechanics: the microcanonical ensemble, canonical and grand canonical ensembles of fluids are known to have distinct finite-size properties, and are characterized by different scaling functions. Our interpretation of the equivalence of the constant-$NpT$ and constant-$\mu VT$ ensemble scaling functions, is that in the thermodynamic limit, $p = p(T, \mu)$, and therefore it is immaterial whether one uses $\mu T$ or $pT$ as the pair of given intrinsic thermodynamic variables. All that matters is that both ensembles have a single extensive variable ($N$ or $V$). Different scaling properties are obtained when two extensive variables are used, such as in the constant-NVT (canonical) ensemble of fluids. It follows that the GCE-based FSS techniques developed in reference [6] for accurately locating fluid critical point parameters, carry over directly to the NpT-ensemble. It is hoped that use of this latter ensemble will prove beneficial in situations where the GCE is highly inefficient, such as for long-chain polymer or electrolyte models. We add the further comment that finite-size scaling with $N$ rather than $V$ is well known in mean-field spin systems, when every spin interacts with every other spin, and geometry and space have no meaning [18].

While use of the NpT-ensemble is likely to be much more efficient than the GCE in cases where particle insertions have a low acceptance probability, we believe that for simple fluids, use of the grand canonical ensemble is much to be preferred. The present study of the LJ fluid consumed circa 300 hours CPU time on a Cray-YMP, using a vectorized program. By contrast, the previous GCE study of the same model was performed with considerably less computational effort using workstations. Moreover, it was possible to study much larger systems (comprising up to $\sim 1800$ particles), with considerably greater statistical accuracy than attainable here. The reasons for this difference in efficiency seem to be manifold. Owing to the fluctuating volume, it is not possible to easily implement a cell structure for efficiently locating neighbouring particles within the cutoff range. A calculation of all particle separations prior to a trial volume transition involves an $O(N^2)$ operation, which can only be avoided if no potential cutoff is employed [13]. By contrast, use of a cell structure in the GCE leads to a $O(N)$ growth in computational complexity. A second disadvantage of the NpT-ensemble, is that both volume changes and particle moves must be performed. For each particle move, two partial energy calculations are required, while for a volume change (with finite interaction cutoff), a total energy calculation is required. By contrast, only particle insertions need be implemented in a GCE scheme [6], each of which requires only a single partial energy calculation. Additionally it seems likely that for a given $\langle \rho \rangle$ the random walk in $V$ required to pass from one phase to the other at coexistence is longer than that in $N$ for the GCE, even if one employs a dynamically adjusting volume step size.
such as that of reference [14]. Consequently the correlation time in the NpT-ensemble is considerably greater than that of the GCE.

Finally we note that another recent study has also attempted to apply finite-size scaling methods to the LJ fluid in the NpT-ensemble [19]. In this study the authors focused on the distribution of the specific volume \( v = \frac{V}{N} \) and attempted to locate the critical point by requiring scale invariance in \( P_N(v) \), subject to the requirement that \( P_N(v) \) has two peaks of equal height at coexistence. However, as we have shown in this work, the volume distribution is not the scaling counterpart for fluids of the Ising magnetisation, rather it is the operator \( M \). Moreover, the limiting (large \( N \)) critical point form of \( P_N(v) \) does not have two peaks of equal heights, and is in fact highly asymmetric in form, as figure 2 shows. We therefore ascribe the rather low accuracy in the estimates for \( T_c \) and the difficulties in obtaining the surface tension exponent in reference [19] to this incorrect choice of the scaling operator.

Acknowledgements

Helpful correspondence with A.D. Bruce and G. Orkoulas is acknowledged. NBW is supported by the Max-Planck Institute für Polymerforschung, Mainz.
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FIG. 1. The critical scaling operator distributions $P_N(M)$ for the three system sizes $N = 216, 363$ and $N = 512$, expressed in terms of the scaling variable $x = a_M^{-1}N^{\beta/d\nu}(M - M_c)$. The solid line is the critical magnetisation distribution of the 3D Ising model [16].
FIG. 2. The specific volume distribution $P_N(v)$ for the $N = 512$ system, measured at the assigned values of the critical parameters.