Liquid-vapour asymmetry in pure fluids: a Monte Carlo simulation study

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Abstract

Monte Carlo simulations within the grand canonical ensemble are used to obtain the joint distribution of density and energy fluctuations $p_L(\rho, u)$ for two model fluids: a decorated lattice gas and a polymer system. In the near critical region the form of $p_L(\rho, u)$ is analysed using a mixed field finite-size-scaling theory that takes account of liquid-vapour asymmetry. Field mixing transformations are performed that map $p_L(\rho, u)$ onto the joint distribution of critical scaling operators $\tilde{p}^\star(x, y)$ appropriate to the Ising fixed point. Carrying out this procedure permits a very accurate determination of the critical point parameters. By forming various projections of $\tilde{p}^\star(x, y)$, the full universal finite-size spectrum of the critical density and energy distributions of fluids is also obtained. In the sub-critical coexistence region, an examination is made of the influence of field mixing on the asymmetry of the density distribution.

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1 Introduction

Over the years, finite-size-scaling (FSS) techniques have proved themselves an indispensable tool for computer simulation investigations of critical phenomena in model systems, facilitating accurate estimates of infinite volume quantities from simulations of finite size. Of the many previous FSS simulation studies that have been performed [1], most have focussed on critical phenomena in lattice-based magnetic spin systems such as the Ising [2, 3], $\phi^4$ [4], XY [5] and Heisenberg models [3, 4]. Among the specific approaches employed to study such systems, use of the order parameter distribution function has proved itself one of the most powerful. The FSS properties of the order parameter distribution are now routin ely employed in studies of magnetic systems, facilitating both the accurate location of the critical point and the detailed elucidation of its character [8].

Only comparatively recently has attention turned to the task of applying FSS techniques to the simulation of critical fluids. Work to date has concentrated on attempting to carry over to fluids the order parameter block distribution techniques developed in the magnetic context [3, 10, 11]. In the process, however, it has been found necessary to generalise the FSS equations to take account of the absence in fluids of the energetic (‘particle-hole’ [12]) symmetry that prevails in magnetic systems such as the Ising model. Although this reduced symmetry is believed to have no bearing on the universal critical behaviour of fluids, (which for system with short-ranged interactions correspond to the Ising universality class), it has long been recognised that it leads to certain non-universal effects. The most celebrated of these is a weak energy-like singularity in the coexistence diameter on the approach to criticality, the existence of which constitutes a failure for the law of rectilinear diameter [13].

Within the renormalisation group framework, the critical behaviour of a given system is characterised by the values of its relevant scaling fields specifying the location of the effective hamiltonian with respect to the fixed point [14]. In models of the Ising symmetry, these scaling fields are simply identifiable with the thermodynamic fields, namely the (reduced) temperature and the applied field. By contrast for fluids, the absence of particle-hole symmetry implies that the scaling fields comprise mixtures (i.e. linear combinations) of the temperature and chemical potential. As a consequence of this ‘field mixing’, the fluid scaling operators (the quantities conjugate to the two relevant scaling fields) are also predicted to differ from those of the symmetric Ising systems. In the Ising model, the scaling operators are simply the order parameter (i.e. magnetisation) and the energy density. In fluids however, they are expected to be linear combinations of the order parameter (particle density) and the energy density.

The modified forms of the scaling variables have recently been incorporated within a FSS theory describing the interplay of energy and density fluctuations in near-critical fluids [10, 11]. This theory provides a potentially powerful framework for the detailed simulation study of critical phenomena in fluids. Hitherto, however, only a limited appraisal of the theory has been performed. Attention has focused on one predicted manifestation of field mixing, namely a finite size correction to the limiting form of the critical order parameter distribution. The existence of this correction has indeed been confirmed in detailed Monte-Carlo simulation studies of both the 2D Lennard-Jones fluid [11] and a 2D decorated lattice gas model [16]. To date, however, the full extent of the claims embodied in the mixed field FSS theory have not been closely scrutinised.

In the present paper we address this matter with simulation studies of two critical fluid systems: a decorated lattice gas model and a polymer model. The paper is broadly organised as follows. We begin by providing a short resumé of the mixed field FSS theory for the near-
critical density and energy fluctuations of fluids. We then present simulation measurements of the joint distribution of the density and energy fluctuations $p_L(\rho, u)$ at the liquid-vapour critical point of a 3D decorated lattice gas model. Field mixing transformations are performed that map $p_L(\rho, u)$ onto the fixed point distribution of scaling operators $\tilde{p}^*(x, y)$ appropriate to the Ising universality class. Effecting this data collapse yields estimates of the field mixing parameters that control the degree of field mixing, the values of which are found to be in excellent agreement with analytic calculations. Application of field mixing transformation to $\tilde{p}^*(x, y)$ are also used to generate the full universal finite-size spectrum of the density and energy density distributions of fluids. This analysis reveals, in particular, that (compared to models of the Ising symmetry) the presence of field mixing radically alters the limiting (large L) form of the critical energy distribution.

Consideration is then given to the role of field mixing in the sub-critical two phase regime of the decorated lattice gas model. An examination is made of the effect of applying field mixing transformations to the coexistence density and energy density distributions. For sub-critical temperatures down to approximately $0.9 T_c$, it is found that the observed asymmetries of the coexistence density distributions are well accounted for by the linear mixing of the energy density into the ordering operator.

Finally we apply the techniques developed in the context of the decorated lattice gas model, to a more realistic system, namely a 3D polymer model. Simulation studies of the bond fluctuation model within the grand canonical ensemble are used to obtain the joint distribution of density and energy on the liquid vapour coexistence curve. The critical temperature, chemical potential and field mixing parameters of the model are accurately determined by requiring the collapse of the measured scaling operator distributions onto their known universal fixed point forms. In the sub-critical region close to the critical point, the observed asymmetries of the density distribution are again found to be well described by field mixing transformations.

2 Background

In this section we provide a brief overview of the principal features of the mixed field FSS theory of reference [11], placing it within the context of the present work.

The systems we consider are assumed to be contained in a volume $L^d$ (with $d = 3$ in the simulations described below) and thermodynamically open so that the particle number can fluctuate. The observables on which we shall focus are the particle number density:

$$\rho = L^{-d} N$$

and the dimensionless energy density:

$$u = L^{-d} w^{-1} \Phi(\{r\})$$

(2.2)

where $\Phi(\{r\})$ is the configurational energy of the system which we assume takes the general two-body form:

$$\Phi(\{r\}) = \sum_{i,j} \phi(|r_i - r_j|),$$

(2.3)

with $\phi(r)$ the two-body interaction potential (e.g. square-well or Lennard-Jones) whose associated coupling strength (well-depth) we denote $w$. 

Within the formalism of the grand canonical ensemble (GCE), the joint distribution of density and energy fluctuations, \( p_L(\rho, u) \), is controlled by the reduced chemical potential \( \mu \) and the coupling strength \( w \) (both in units of \( k_B T \)). The critical point of the system is located by critical values of the chemical potential \( \mu_c \) and coupling \( w_c \). Deviations of \( w \) and \( \mu \) from their critical values control the sizes of the two relevant scaling field that characterise the critical behaviour \[14\]. In the absence of the special symmetry prevailing in the Ising model, the relevant scaling fields comprise (asymptotically) linear combinations of the coupling and chemical potential difference \[15\]:

\[
\tau = w_c - w + s(\mu - \mu_c) \quad h = \mu - \mu_c + r(w_c - w) \quad (2.4)
\]

where \( \tau \) is the thermal scaling field and \( h \) is the ordering scaling field. The parameters \( s \) and \( r \) are system-specific quantities controlling the degree of field mixing. In particular \( r \) is identifiable as the limiting critical gradient of the coexistence curve in the space of \( \mu \) and \( w \).

The role of \( s \) is somewhat less tangible; it controls the degree to which the chemical potential features in the thermal scaling field, manifest in the widely observed critical singularity of the coexistence curve diameter of fluids \[13\].

Conjugate to the two relevant scaling fields are scaling operators \( \mathcal{M} \) and \( \mathcal{E} \), which comprise linear combinations of the particle density and energy density \[10, 11\] :

\[
\mathcal{M} = \frac{1}{1-sr}[\rho - su] \quad \mathcal{E} = \frac{1}{1-sr}[u - r\rho] \quad (2.5)
\]

The operator \( \mathcal{M} \) (which is conjugate to the ordering field \( h \)) is termed the ordering operator, while \( \mathcal{E} \) (conjugate to the thermal field) is termed the energy-like operator. In the special case of models of the Ising symmetry, (for which \( s = r = 0 \)), \( \mathcal{M} \) is simply the magnetisation while \( \mathcal{E} \) is the energy density.

The joint distribution of density and energy is simply related to the joint distribution of mixed operators:

\[
p_L(\rho, u) = \frac{1}{1-sr} p_L(\mathcal{M}, \mathcal{E}) \quad (2.6)
\]

Near criticality, and in the limit of large system size, \( p_L(\mathcal{M}, \mathcal{E}) \) is expected to be describable by a finite-size-scaling relation of the form \[11\] :

\[
p_L(\mathcal{M}, \mathcal{E}) \simeq \Lambda^+_\mathcal{M} \Lambda^+_\mathcal{E} \tilde{p}(\Lambda^-\mathcal{M} \delta\mathcal{M}, \Lambda^-\mathcal{E} \delta\mathcal{E}, \Lambda\mathcal{M} h, \Lambda\mathcal{E} \tau) \quad (2.7a)
\]

where

\[
\Lambda_{\mathcal{E}} = a_{\mathcal{E}} L^{1/\nu} \quad \Lambda_{\mathcal{M}} = a_{\mathcal{M}} L^{d-\beta/\nu} \quad \Lambda_{\mathcal{M}} \Lambda^+_\mathcal{M} = \Lambda_{\mathcal{E}} \Lambda^+_\mathcal{E} = L^d \quad (2.7b)
\]

and

\[
\delta\mathcal{M} \equiv \mathcal{M} - <\mathcal{M}>_c \quad \delta\mathcal{E} \equiv \mathcal{E} - <\mathcal{E}>_c \quad (2.7c)
\]

The subscripts \( c \) in equations \[2.7c\] signify that the averages are to be taken at criticality. Given appropriate choices for the non-universal scale factors \( a_{\mathcal{M}} \) and \( a_{\mathcal{E}} \) (equation \[2.7b\]), the function \( \tilde{p}^* \) is expected to be universal.

Precisely at criticality, equation \[2.7a\] implies simply

\[
p_L(\mathcal{M}, \mathcal{E}) \simeq \Lambda^+_\mathcal{M} \Lambda^+_\mathcal{E} \tilde{p}^*(\Lambda^-\mathcal{M} \delta\mathcal{M}, \Lambda^-\mathcal{E} \delta\mathcal{E}) \quad (2.8)
\]

where \( \tilde{p}^*(x, y) = \tilde{p}(x, y, 0, 0) \) is a function describing the universal and statistically scale invariant operator fluctuations characteristic of the critical point.
In what follows, we shall employ Monte Carlo simulations to explicitly test the prediction of equation 2.8 for a decorated lattice gas model and a polymer system, both members of the Ising universality class. To do so, however, we first require an independent estimate of the fixed point function $\tilde{p}^*(x,y)$ appropriate to the 3D Ising universality class. In practice, this is most readily obtained by considering the prototype member of the Ising class, namely the 3D Ising model itself. Owing to its lack of field mixing, the scaling operators of the Ising model are simply $M \to m$ (the magnetisation) and $E \to u$ (the energy density). Moreover, the availability of highly accurate estimates for the Ising model critical temperature, circumvents the need to perform a time consuming search for the critical point.

3 Monte Carlo simulations

3.1 The 3D Ising model and the form of $\tilde{p}^*(x,y)$

Using a vectorised algorithm on a Cray YMP supercomputer, we have performed high precision Monte Carlo simulation measurements of the joint magnetisation and energy density distribution for the 3D Ising model on a periodic lattice of side $L = 20$. The measurements were performed at the estimated (reduced) critical coupling $K^c_I = 0.2216595(26)$, as obtained in a previous high precision Monte Carlo study [3]. Following an initial equilibration period of $2 \times 10^6$ Monte Carlo steps per spin (MCS), the magnetisation and energy density were sampled at intervals of 50 MCS (in order to reduce correlations), and the results accumulated in a histogram. The final histogram (comprising $2 \times 10^7$ entries) was formed from 12 independent runs, thereby allowing the statistical independence of the data to be assessed and statistical errors to be assigned to the results. The resulting form of $\tilde{p}^*(x,y)$, normalised to unit integrated weight and scaled to unit variance along both axes, is shown in figure 1. The associated ordering operator distribution $\tilde{p}^*(x) = \int \tilde{p}^*(x,y)dy$, and energy operator distribution $\tilde{p}^*(y) = \int \tilde{p}^*(x,y)dx$ are shown in figure 2. One observes that while the form of $\tilde{p}^*(x)$ is doubly peaked and symmetric, that of $\tilde{p}^*(y)$ is singly peaked and asymmetric.

3.2 The 3D decorated lattice gas model

The decorated lattice gas model was first proposed in its two dimensional form by Mermin as an example of a system exhibiting a singular coexistence diameter [17]. The model was subsequently generalised to simple, body, and face centred cubic lattices by other workers [18, 19, 20] and studied for its interesting coexistence properties. The simple cubic form of the model, on which we shall focus in the present work, consists of an ordinary simple cubic lattice gas (whose sites we term the primary sites), augmented (decorated) by additional secondary sites on the interstitial bonds. Particles on primary sites are assumed to interact with one another via a dimensionless coupling of strength $\lambda$, while particles on the secondary sites interact with those on primary sites via a dimensionless coupling $\eta$, but do not interact with each other. A schematic representation of a unit cell of the model is shown in figure 3.

The configurational energy $\Phi(\{\sigma\})$ of the decorated lattice gas model is given by

$$\Phi(\{\sigma\}) = \sum_{<i,j>} \eta \sigma_i \sigma_j + \sum_{[m,n]} \lambda \sigma_m \sigma_n \quad (3.1)$$

with $\sigma_i = 0, 1$. The site indices $i$ and $j$ are taken to run over nearest neighbour primary and
secondary sites of the model, while \( m \) and \( n \) run only over nearest neighbour primary sites. It is straightforward to show that the particle-hole symmetry that obtains in the ordinary lattice gas is equivalent to the requirement that all sites have the same average energy environment. The presence of two inequivalent sublattices in the decorated model clearly violates this condition and leads to field mixing.

Aside from its field mixing properties, the chief asset of the decorated lattice gas model, is its analytic tractability. The grand partition function of the asymmetric model can be related by means of analytic transforms to that of the ordinary lattice gas model which is itself isomorphic to the Ising model. Specifically, one finds:

\[
\Omega(\mu, T) = (1 + e^{\mu/kT})^{3N} \overline{\Omega}(\overline{\mu}, \overline{T})
\]  

where \( \Omega \) is the partition function of the decorated model and \( \mu \) and \( T \) are the chemical potential and temperature respectively. Bars denote quantities in the ordinary lattice gas and \( N \) is the number of primary sites in the model.

Introducing the dimensionless chemical potential \( \xi = \mu/k_bT \) equation 3.2 leads to the following relationships [19]:

\[
\overline{\xi} = \xi + 6 \ln \left[ \frac{1 + e^{\xi+\eta}}{1 + e^{\xi}} \right]  
\]

\[
\overline{\lambda} = \lambda + \ln \left[ \frac{(1 + e^{\xi})(1 + e^{\xi+2\eta})}{(1 + e^{\xi+\eta})^2} \right]
\]

where \( \overline{\xi} = \overline{\mu}/k_b\overline{T} \) and \( \overline{\lambda} = \overline{\lambda}/k_b\overline{T} \) are respectively the dimensionless chemical potential and dimensionless nearest neighbour coupling constant of the ordinary lattice gas.

In the 3D ordinary lattice gas the liquid-vapour coexistence line is specified by the condition \( \overline{\xi} = -3\overline{\lambda} \) [21]. The location of critical point that terminates this line is not known exactly, but is trivially related to that of the Ising model:

\[
\overline{\lambda}_c = 4K_{\text{Ising}}^c, \quad \overline{\xi}_c = -3\overline{\lambda}_c
\]

where

\[
K_{\text{Ising}}^c = 0.2216595(26) \quad (3.5)
\]

is the estimated dimensionless critical coupling of the simple cubic Ising model [3]. Estimates for the critical point parameters are thus obtainable by feeding this value of \( K_{\text{Ising}}^c \) into equations 3.3a and 3.3b. Similarly, the coexistence curve of the decorated model is obtainable by setting \( \xi = -3\lambda \) in equations 3.3a and 3.3b to find:

\[
\xi + 3\lambda + 3 \ln \left[ \frac{1 + e^{\xi+2\eta}}{1 + e^{\xi}} \right] = 0
\]

Note however, that since \( \lambda \) and \( \eta \) both enter only as multiplicative factors in the configurational energy (equation 3.1), the coexistence curve is uniquely parameterised by the value of the coupling ratio \( \lambda/\eta \). Varying this ratio allows one to tune the degree of field mixing [14]. Indeed for the special choice \( \lambda/\eta = -1/3 \), the average energy environment is identical for atoms on both sublattices of the model and particle-hole symmetry is restored.

Knowledge of the mapping between the decorated lattice gas and the ordinary lattice gas also permits an analytic calculation of the field mixing parameters \( r \) and \( s \) for the model. The
value of $r$ is obtainable from equation (3.6) simply by calculating the limiting critical gradient of the coexistence curve. A calculation of $s$ proceeds from the observation that in the ordinary lattice gas, the field-like scaling field $h$ coincides with the line $\overline{\lambda} = \overline{\lambda}_c$ in the space of $\xi$ and $\overline{\lambda}$. It follows that in the decorated lattice gas model, the direction of $h$ can be obtained from equation (3.3b) by setting $\overline{\lambda} = \overline{\lambda}_c$, $\eta = \eta(\lambda)$ and solving for $\lambda$. The value of $s$ is then given by

$$s = \left( \frac{\partial \lambda}{\partial \xi} \right)_c$$

(3.7)

where the derivative is to be evaluated at criticality.

Compared to more realistic fluid models such as the Lennard-Jones fluid, the great simplicity of the decorated lattice gas model renders it highly computationally tractable. Moreover the prior availability of accurate values for the critical parameters obviates the need for a time consuming search of parameter space for the critical point, and simplifies the task of data analysis. The model therefore provides an ideal test-bed for simulation studies of critical point field mixing.

3.2.1 The critical limit

Using a Metropolis algorithm within the grand canonical ensemble (GCE) [22], we have performed detailed simulation measurements of the joint density and energy distribution $p_L(\rho, u)$ of the decorated lattice gas model, at the estimated critical parameters obtained as described above. All simulations were performed for a choice of the coupling ratio $\lambda/\eta = 0.1$, for which it is known that the coexistence curve of the model closely resembles those of many real fluids [19]. In the course of the simulations, three system sizes were studied having linear extent $L = 12$, $L = 20$ and $L = 32$. Periodic boundary conditions were employed throughout. Prior to data collection, equilibration periods of $5 \times 10^6$ MCS were utilised. Samples of the density and energy density were then performed at intervals of 50 MCS (to reduce correlations) and the data stored in histograms. For each system size, 12 independent runs were performed in order to test the statistical independence of the data and to assign statistical errors to the results. The final histograms of $p_L(\rho, u)$ comprised $2 \times 10^7$ entries for the $L = 12$ and $L = 20$ system sizes, and $1 \times 10^7$ entries for the $L = 32$ system size.

The measured form of $p_L(\rho, u)$ for the decorated lattice gas model is presented in figure 4 for the $L = 20$ system size. Clearly apart from a general overall double peaked structure, the form of this distribution bears little resemblance to that of $\tilde{p}^*(x, y)$ (c.f. figure 1) which represents the joint critical order parameter and energy density distribution in the absence of field mixing. To illustrate the differences it is instructive to compare the fluid density distributions $p_L(\rho) = \int p_L(\rho, u) du$ with $\tilde{p}^*(x)$, and the fluid energy density distribution $p_L(u) = \int p_L(\rho, u) d\rho$ with $\tilde{p}^*(y)$.

The forms of $p_L(\rho)$ for all three system sizes are shown in figure 4a. In contrast to $\tilde{p}^*(x)$ (figure 2a), all the density distributions exhibit a pronounced asymmetry, qualitatively similar in form to that observed in the 2D version of the same model [18]. Even more conspicuous, however, are the differences between the finite-size forms of $p_L(u)$ (figure 4b), and that of $\tilde{p}^*(y)$ (figure 2b). Clearly while the latter is singly peaked, the former are doubly peaked, with a form (were one to plot $p_L(-u)$), reminiscent of the density distribution. As we shall show, the explanation of these differences is to be found in the field mixing that manifests the lack of particle-hole symmetry in fluids.
In order to expose the universality linking the critical point of the decorated lattice gas model to that of the Ising model, it is necessary to recast \( p_L(\rho, u) \) in terms of the joint distribution of scaling operators \( p_L(\mathcal{M}, \mathcal{E}) \), cf. equation 2.8. To do so however, requires specification of the field mixing parameters \( s \) and \( r \) featuring in the definitions of \( \mathcal{M} \) and \( \mathcal{E} \) (equation 2.5). In practice, these values may be readily found by requiring that the single scaling operators distributions \( p_L(\mathcal{M}) \) and \( p_L(\mathcal{E}) \) match their respective fixed point forms \( \tilde{\rho}^*(x) \) and \( \tilde{\rho}^*(y) \). Carrying out this procedure yields the matchings shown in figure 6a and 6b. The associated estimates for the field mixing parameters are \( s = -0.143(8) \) and \( r = -3.11(1) \). These values compare very favourably with those calculable analytically, for which one finds \( s = -0.1428 \cdots \), \( r = -3.1163 \cdots \) Such a high level of accord indicates that the matching of the operator distributions to the universal Ising forms is a potentially very accurate method for determining the field mixing parameters.

Having obtained estimates for \( s \) and \( r \), one may then construct the joint distribution of scaling operators \( p_L(\mathcal{M}, \mathcal{E}) \). The resulting form is shown in figure 7, and should be compared with that of \( \tilde{\rho}^*(x, y) \) shown in figure 1. Clearly the agreement between the operator distributions and the universal fixed point form is gratifying, providing substantial corroboration of the mixed field FSS theory.

3.2.2 The subcritical region

As the critical point is approached along the line of phase coexistence, the known symmetries of the Ising problem imply that

\[
\langle \mathcal{M} \rangle^\pm - \langle \mathcal{M} \rangle_c = \pm a |\tau|^\beta, \quad (3.8a)
\]

\[
\langle \mathcal{E} \rangle^\pm - \langle \mathcal{E} \rangle_c = b |\tau|^{1-\alpha} + \text{terms analytic at criticality} \quad (3.8b)
\]

where \( a \) and \( b \) are critical amplitudes and \( \pm \) denote limits as the coexistence curve is approached from above (\( h \to 0^+ \)) or below (\( h \to 0^- \)). Recalling that \( \mathcal{M} = \rho + s\mathcal{E} \) then yields the two branches of the coexistence curve densities near criticality:

\[
\rho_\pm - \rho_c = \pm a |\tau|^\beta + sb |\tau|^{1-\alpha} + \text{terms analytic at criticality}, \quad (3.9)
\]

which displays a singular diameter:

\[
\rho_d - \rho_c = \frac{1}{2}(\rho_+ + \rho_-) - \rho_c \sim sb |\tau|^{1-\alpha} \quad (3.10)
\]

as is indeed observed experimentally [13].

At temperatures outside the critical region, the relations 3.8a and 3.8b are not generally expected to hold and a crossover description to regular classical behaviour is more appropriate [23, 24, 25, 26, 27, 28]. Nevertheless as observed in many computer simulations of various simple fluids, the temperature dependence of the order parameter is quite accurately described by Ising critical exponents over a remarkably wide range of subcritical temperatures [29], without the need to introduce higher order (non-linear) terms in the Wegner expansion of the scaling fields [14]. In view of this it seems of interest to examine the range of applicability of the scaling form 2.7a in the subcritical two-phase region.

To this end we have obtained the joint density and energy density distribution of the decorated lattice gas model at temperatures \( T = 0.9T_c \) and \( T = 0.8T_c \), for a system of side \( L = 20 \). In order to circumvent the prohibitively large ‘tunneling’ times between the coexisting phases...
that normally plague GCE simulations in the two-phase region, we have employed the multicanonical preweighting scheme \[30\]. This scheme uses weighted transitions to encourage the system to sample those interfacial configurations that would otherwise occur only very rarely. The weight factors are chosen such that the sampled density distribution is approximately flat in the density region between the peaks of the two coexisting phases. After the simulation, the correct (‘unweighted’) coexistence distribution is regained by dividing out the weight factors from the sampled distribution. In this manner the effective tunneling frequency between the coexisting phases may be increased by many orders of magnitude, thereby facilitating very accurate estimates of the coexistence form of \(p_L(\rho, u)\).

Using the multicanonical preweighting scheme, samples of the density and energy were accumulated every 20 MCS and stored in histograms. The final histograms for \(p_L(\rho, u)\) comprised approximately \(5 \times 10^7\) entries. In figure 8a we present the measured coexistence forms of \(p_L(\rho)\) for \(T = 0.9T_c\) and \(T = 0.8T_c\). Also included in the figure is the critical point form of \(p_L(\rho)\) for the \(L = 20\) system size, as obtained previously (c.f. subsection 3.2.1). Clearly the distributions are all asymmetric, those for the two subcritical temperatures having a form similar to those observed in an asymmetric version of the 2D Blume-Emery-Griffiths spin model \[31\]. Although the two peaks of the sub-critical distributions have equal weight, (reflecting the thermodynamic condition for coexistence \[32\]), one observes that the high density peak is much broader and shorter than the low density peak. Moreover the magnitude of the change in position of the high density peak on lowering the temperature is much greater than that in the low density peak. It is this effect that gives rise to the asymmetric form of the temperature-density phase diagram of fluids.

In figure 8b we present the corresponding forms of the ordering operator distribution \(p_L(M)\). For each temperature the value of the field mixing parameter \(r\) was obtained as the gradient of the coexistence curve, while the value of \(s\) was obtained by applying the prescription of equation 3.7. One sees that in this choice of variables, the distributions at \(T = T_c\) and \(T = 0.9T_c\) are largely symmetric i.e. both peaks have the same height and width. Only the distribution for \(T = 0.8T_c\) exhibits small deviations from symmetry, these being attributable to the non-singular (and non-Ising) part of the partition function (equation 3.2). Thus it would appear that in the present case at least, the validity of the scaling form 2.7a extends some 10% or more below the critical temperature. In this temperature range, the asymmetry of the density distribution can therefore be accurately ascribed to the linear mixing of the energy density into the ordering operator. It remains to be seen however, to what extent this finding holds true in more realistic fluid models as well as those possessing very large coexistence curve asymmetries, such as polar \[34\], ionic \[35\] or metallic fluids \[36, 37, 38\].

It is also instructive to compare the simulation results with analytic calculations of the coexistence density diameter \(\rho_d\) and the ordering operator diameter \(M_d\). The latter can be calculated exactly, while the former may be obtained approximately by employing the tabulated values of the Padé Approximants for the temperature dependence of the Ising model energy density \[33\]. Performing these calculations for fractional temperatures \(t = T/T_c\) in the range \(0.7 \leq t \leq 1.0\) yields the results shown in figure 4. The weak critical singularity in the coexistence diameter is readily discernible from the figure although, as expected, no such singularity obtains for \(M_d(t)\), which is analytic at the critical point. Some variation in \(M_d\) is seen as a function of temperature, however, but this again arises from the non-singular, non-Ising part of the partition function \[3.2\]. Also included in the figure are the simulation estimates of \(\langle M \rangle(t)\) and \(\langle \rho \rangle(t)\) obtained from the multicanonical simulations at \(T = 0.9T_c\) and

\[8\]
\( T = 0.8T_c \), as well as the conventional simulations at the critical point. Clearly a very good overall agreement between the simulations and the analytical predictions is apparent.

### 3.3 The universal critical finite-size spectrum of \( p_L(\rho) \) and \( p_L(u) \)

In this subsection we return to a consideration of the critical point forms of \( p_L(\rho) \) and \( p_L(u) \) in fluids, with the aim of gaining an understanding of their shapes and finite-size-scaling behaviour. To this end it is expedient to reexpress \( \rho \) and \( u \) in terms of the scaling operators. Appealing to equation 2.5, one finds

\[
    u = \mathcal{E} - r \mathcal{M} \quad \rho = \mathcal{M} - s \mathcal{E},
\]

so that the critical density and energy density distributions are

\[
    p_L(u) = p_L(\mathcal{E} - r \mathcal{M}) \quad p_L(\rho) = p_L(\mathcal{M} - s \mathcal{E})
\]

Now the structure of the scaling form 2.7 shows that the typical size of the fluctuations in the energy-like operator will vary with system size like \( \delta \mathcal{E} \sim L^{-(1-\alpha)/\nu} \), while the typical size of the fluctuations in the ordering operator vary like \( \delta \mathcal{M} \sim L^{-\beta/\nu} \). It follows that for a given \( L \), the shape of the energy and density distributions can be identified with the distribution of the variable

\[
    X_\Theta = a_{\mathcal{M}}^{-1} \delta \mathcal{M} \cos \Theta + a_{\mathcal{E}}^{-1} \delta \mathcal{E} \sin \Theta,
\]

with

\[
    \tan \Theta_u = \frac{a_{\mathcal{E}}}{ra_{\mathcal{M}}} L^{-(1-\alpha-\beta)/\nu} \quad \text{and} \quad \tan \Theta_\rho = \frac{sa_{\mathcal{E}}}{a_{\mathcal{M}}} L^{-(1-\alpha-\beta)/\nu}
\]

where the subscripts \( u \) and \( \rho \) signify that the value of \( \Theta \) corresponds to the energy density and density distributions respectively.

The distributions \( p(X_\Theta) \) constitute a one-parameter class of universal functions describing the density and energy distributions of fluids at finite \( L \). Geometrically, \( \Theta \) can be interpreted as defining a direction \( OX_\Theta \) in the basal plane formed by the \( Ox \) and \( Oy \) axes of figure 1, making an angle \( \Theta \) with the \( Ox \) axis. The form of \( p(X_\Theta) \) is then obtainable by projecting \( \tilde{p}^*(x, y) \), onto the vertical plane which includes the line \( OX_\Theta \). A representative selection of such projections is shown in figure 10. For \( \Theta = 0^\circ \) one obtains simply the ordering operator distribution \( \tilde{p}^*(x) \), while for \( \Theta = 90^\circ \) the form is that of the energy-like operator \( \tilde{p}^*(y) \) distribution. Intermediate between these values a range of behaviour is obtained, representing the finite \( L \) forms of \( p_L(\rho) \) and \( p_L(u) \).

Asymptotically (i.e. as \( L \to \infty \)), equation 3.14 implies that both \( \Theta_u \) and \( \Theta_\rho \) approach zero so that in this limit

\[
    p_L(u) = p_L(-r \mathcal{M}) \simeq a_{\mathcal{M}}^{-1} r L^{\beta/\nu} \tilde{p}_\mathcal{M}^*(-a_{\mathcal{M}}^{-1} r L^{\beta/\nu} \delta \mathcal{M})
\]

\[
    p_L(\rho) = p_L(\mathcal{M}) \simeq a_{\mathcal{M}}^{-1} L^{\beta/\nu} \tilde{p}_\mathcal{M}^*(a_{\mathcal{M}}^{-1} L^{\beta/\nu} \delta \mathcal{M})
\]

It follows that for any finite \( s \) and \( r \), the limiting critical point forms of \( p_L(\rho) \) and \( p_L(u) \) both match the critical ordering operator distribution \( \tilde{p}^*(x) \). The approach to this limiting
behaviour is indeed clearly evident in the distributions of figure 5. We note however that the limiting form of \( p_L(u) \) differs drastically from that of the Ising model where, owing to the absence of field mixing, \( \lim_{L \to \infty} p_L(u) = \tilde{p}^{*}(y) \). The profound influence of field mixing on the critical behaviour of fluids should therefore be apparent [11].

Finally in this subsection, we point out that precise knowledge of the location of the critical point (obtained e.g. from the data collapse of the scaling operators onto their fixed point forms), does not imply the possibility of directly measuring the infinite-volume density and energy density. To appreciate this, recall that

\[
\langle u \rangle_c = \langle \mathcal{E} \rangle_c - r \langle \mathcal{M} \rangle_c \\
\langle \rho \rangle_c = \langle \mathcal{M} \rangle_c - s \langle \mathcal{E} \rangle_c
\]

(3.17)

Now, while symmetry considerations dictate that the value of \( \langle \mathcal{M} \rangle_c = \int p_L(\mathcal{M})d\mathcal{M} \) is independent of system size, no such symmetry condition pertains to \( p_L(\mathcal{E}) \), whose average value \( \langle \mathcal{E} \rangle_c = \int d\mathcal{E} p_L(\mathcal{E}) \) at criticality is expected to vary with system size like

\[
\langle \mathcal{E} \rangle_c(L) - \langle \mathcal{E} \rangle_c(\infty) \sim L^{-(1-\alpha)/\nu}
\]

(3.18)

It follows that in order to extract infinite volume estimates of \( \rho_c \) and \( u_c \) from simulations at the critical point, it is necessary to extrapolate data from a number of different system sizes to the thermodynamic limit. This procedure is illustrated in figure [11] for the decorated lattice gas model, using critical point data from the three system sizes \( L = 12, 20, 32 \). The measured values of \( \langle \rho \rangle_c(L) \) and \( \langle u \rangle_c(L) \) are plotted against \( L^{-(1-\alpha)/\nu} \). A least squares fit to the data yields the infinite volume estimates \( \rho_c = 0.3371(1) \) and \( u_c = -0.8385(6) \). We remark that the existence of these finite-size shifts imply that the equal weight criterion [32, 31] for the order parameter distribution, while correctly identifying the coexistence curve in the subcritical regime, must fail close to the critical point [32].

3.4 Liquid-vapour equilibria of a polymer model

We now apply the techniques developed in the foregoing sections to the study of critical phenomena and phase coexistence in a more realistic model fluid, namely a polymer system. The model we consider is the bond fluctuation model, a coarse grained lattice-based polymer model which combines the essential qualitative features of real polymer systems — monomer excluded volume and connectivity — with computational tractability. Within the framework of the model, each monomer occupies a whole unit cell of a periodic simple cubic lattice. Excluded volume interactions are catered for by requiring that no lattice site can simultaneously be occupied by two monomer corners. Monomers along the polymer chains are connected by bond vectors which can assume one of 108 possible values, providing for 87 distinct bond angles and 5 distinct bond lengths. For a more detailed description of the model, the reader is referred to the literature [12].

Using a grand canonical simulation algorithm, we have simulated chains of length \( N = 20 \) monomers, interacting via a short range square well potential, the range of which was set at \( \sqrt{6} \) (in units of the lattice spacing). Chain insertions and deletions were facilitated by use of the configurational bias Monte Carlo (CBMC) method of Siepmann [43]. The essential idea behind the CBMC method is to improve the low acceptance rate associated with random trial chain insertion, by ‘growing’ chains of favourable energy into the system. A bookkeeping scheme maintains a record of the statistical bias associated with choosing favourable chain conformations, and this bias is subsequently removed when the acceptance probability is calculated.
The CBMC technique has also recently been used in conjunction with Gibbs ensemble Monte Carlo simulations of liquid-vapour phase coexistence of off-lattice alkanes models [44].

The quantities measured in the simulations were the monomer density:

$$\rho = 8nN/V$$  \hspace{1cm} (3.19)

and the dimensionless energy density:

$$u = 8w^{-1}\Phi(\{r\})/V$$  \hspace{1cm} (3.20)

where \(n\) is the number of chains, \(\Phi(\{r\})\) is the configurational energy, \(w\) is the well depth and \(V\) is the system volume which was set at \(V = 40^3\). Here the factor of 8 derives from the number of lattice sites occupied by one monomer. In the course of the simulations, measurements of \(\rho\) and \(u\) were performed at intervals of 5000 chain insertion attempts and accumulated in the joint histogram \(p_L(\rho, u)\). The final histogram comprised some \(3 \times 10^5\) entries.

In contrast to the decorated lattice gas model considered in previous sections, the line of liquid-vapour phase coexistence is not known \textit{a-priori} for the polymer system and must therefore be identified empirically. The precise location of the coexistence curve is prescribed by the equal weight criterion for the two peaks of the density distribution [32]. Unfortunately, the task of identifying the coexistence curve using this criterion is an extremely time consuming and computationally demanding one, since the density distribution is generally very sensitive to small deviations from coexistence. In practice, however, it suffices to obtain data for only a few points close to the coexistence curve. The full coexistence curve between these points can subsequently be constructed using histogram reweighting techniques [45, 46]. Provided that the measured density distributions are doubly peaked and the temperatures studied are not too widely separated, this technique permits a very accurate determination of the coexistence curve locus.

Starting with an initial well-depth \(w = 0.569\), the approximate value of the coexistence chemical potential was determined by tuning \(\mu\) until the density distribution exhibited two peaks. Again the multicanonical preweighting scheme [30] was employed in order to overcome the otherwise very large tunnelling times between the coexisting phases. A histogram extrapolation based on this data was then used to estimate the value of the coexistence chemical potential for a well-depth \(w = 0.56\), which lies close to the critical well-depth. A further long runs was carried out at this near-coexistence point. By extrapolating the measured near-coexistence histograms of \(p_L(\rho, u)\) in conjunction with the equal weight criterion, we were then able to construct a sizeable portion of the coexistence curve (and its analytic extension). Representative forms of the density distributions along the line of coexistence and its analytic continuation are shown in figure 12a. The coexistence curve, expressed as a function of the well-depth \(w\) and chemical potential \(\mu\) is shown in figure 13.

To locate the critical point along the line of phase coexistence, we utilised the universal matching condition for the operator distributions \(p_L(\mathcal{M})\) and \(p_L(\mathcal{E})\). Again applying the histogram reweighting technique, the well-depth, chemical potential and field mixing parameters were tuned until the forms of \(p_L(\mathcal{M})\) and \(p_L(\mathcal{E})\) most accurately matched the universal critical Ising forms of figure 2. The results of performing this procedure are shown in figure 14. Given that the system contains an average of only about 100 polymer chains, the quality of the data collapse is remarkable. The mappings shown were effected for a choice of the parameters

$$w_c = 0.5584(1), \quad \mu_c = -5.16425(2), \quad s = -0.135(4), \quad r = -2.55(2)$$  \hspace{1cm} (3.21)
where we have defined $\mu$ to be the chemical potential per monomer. The corresponding critical density and energy density distributions are shown in figure 15. They yield the (finite-size) estimates $\rho_c = 0.199(3)$ and $u_c = -0.304(4)$.

Turning lastly to the subcritical two-phase regime, we have again considered the effect of forming linear combinations of the density and energy density. Figure 14b shows the form of the ordering operator distribution $p_L(M)$ obtained at coexistence using the histogram reweighting technique for the same values of $w$ shown in figure 14a. In each instance the values of $s$ was chosen so that the two peaks of $p_L(M)$ had both equal heights and equal weights, while the value of $r$ was chosen so that $p_L(E)$ was singly peaked. As was the case for the decorated lattice gas model, simple field mixing transformations also appear to account for the subcritical coexistence curve asymmetries of the polymer density distribution, at least over the limited range of $w$ studied here.

4 Conclusions

In summary we have provided explicit demonstration of the field mixing transformations that link the fluctuation spectra of the order parameter and energy in the critical fluid to those of the critical Ising magnet. The results serve to underline the profound influence of field mixing on the non universal critical behaviour of fluids. This influence is manifest most notably as a finite-size shift to the measured critical density, and as an alteration to the limiting (large L) form of the critical energy distribution. Field mixing is also found to account for the observed asymmetries of the coexistence density distribution over a sizeable portion of the sub-critical region.

With regard to the general computational issues raised in this study, it has been seen that effecting the data collapse of the fluid scaling operator distributions onto their (independently known) universal fixed point forms, provides a very powerful method for accurately locating the critical point and determining the field mixing parameters of model fluids. This use of the scaling operator distributions represents the natural extension to fluids of the order parameter distribution method deployed so successfully in the study of symmetric spin models. Thus, in principle at least, there would appear to be no barriers to attaining similar degrees of accuracy in the study of critical fluids as has previously been achieved for lattice spin systems.

The successes of the present work (and of an earlier FSS study of the 2D Lennard-Jones fluid [1]) also attest to the utility of the grand canonical ensemble for simulation studies of near-critical fluids. The benefits of this ensemble stem principally from the fact that density fluctuations are observable on the scale of the system size itself, thus freeing the method of the interfacial effects and additional length scales that complicate use of the ‘sub-block’ finite-size scaling technique within the canonical (NVT) ensemble [3, 17]. High quality results can therefore be obtained using comparatively much smaller system sizes, with concomitant savings in computational effort.

The ability to perform a full finite size scaling analyses in the near-critical region also represents an important advantage of the GCE approach over the Gibbs ensemble Monte Carlo (GEMC) simulation technique [29]. In the GEMC method, the fluctuating box size seems to preclude a rigorous FSS analysis [18, 19], thus seriously hindering the accurate location of the critical point. The GEMC is, nevertheless, very efficient for locating the temperature-density phase diagram in the sub-critical regime. For this task, use of the bare GCE method is only feasible for temperatures within a few percent of the critical temperature because the other-
wise high interfacial free energy results in prohibitively large ‘tunneling’ times between the coexisting phases. Nonetheless, as we have shown, this problem is surmountable by combining the GCE with recently developed multicanonical preweighting and histogram reweighting techniques, thereby enabling accurate studies of the coexistence density and energy fluctuations even well below the critical temperature.

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Figure 1: Estimates of the fixed point form of the joint scaling operator distribution $\tilde{p}^\star(x, y)$ appropriate to the 3D Ising universality class, obtained as the joint magnetisation and energy density distribution of the $L = 20$ periodic 3D Ising model at the estimated critical coupling $K = 0.2216595$. The data is expressed in terms of the scaling variables $x = a_M^{-1}L^{3/\nu}(M - M_c)$ and $y = a_E^{-1}L^{(1-\alpha)/\nu}(E - E_c)$, with the scale factors $a_M^{-1}$ and $a_E^{-1}$ chosen so that the distribution has unit variance along both axes.

Figure 2: (a) The ordering operator distribution $\tilde{p}^\star(x)$ appropriate to the 3D Ising universality class, obtained as the magnetisation distribution of the $L = 20$ 3D periodic Ising model at the assigned value of the critical coupling $K^I_c = 0.2216595$, and expressed in terms of the scaling variable $x = a_M^{-1}L^{3/\nu}(M - M_c)$. (b) The corresponding energy operator distribution $\tilde{p}^\star(y)$, expressed in terms of the scaling variable $y = a_E^{-1}L^{(1-\alpha)/\nu}(E - E_c)$. In both cases, the value of the non-universal scale factors $a_E^{-1}$ and $a_M^{-1}$ were chosen so that the distributions have unit variance. Statistical errors do not exceed the symbol sizes.

Figure 3: Schematic representation of a unit cell of the decorated lattice gas model. The primary sites have been shaded, while the secondary (decoration) site have not. Primary sites interact with other nearest neighbour primary sites with a coupling $\lambda$, and with nearest neighbour secondary sites with a coupling $\eta$. 

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Figure 4: Estimates of the normalised joint distribution of density and energy density $p_L(\rho, u)$ of the 3D decorated lattice gas model for $L = 20$, at the assigned value of the critical parameters.

Figure 5: (a) The density distributions of the 3D decorated lattice gas model at the assigned values of the critical parameters, for system sizes $L = 12, L = 20$ and $L = 32$. (b) The corresponding energy density distributions. Statistical errors do not exceed the symbol sizes.

Figure 6: (a) The critical ordering operator distribution $p_L(M)$ of the decorated lattice gas model for the system sizes $L = 20$ and $L = 32$. The $L = 12$ data has been omitted for clarity. Also shown for comparison is the universal ordering operator distribution $\tilde{p}^*(x)$ (c.f. figure 2a). (b) The critical energy operator distribution $p_L(E)$ compared with the universal fixed point form $\tilde{p}^*(y)$ (figure 2b). In both cases, the non-universal scale factors $a^{-1}_E$ and $a^{-1}_M$ have been chosen to give unit variance for the $L = 32$ data set. The exponent ratios were taken to be $\beta/\nu = 0.5176$ and $\alpha/\nu = 0.177$. Statistical errors do not exceed the system sizes.

Figure 7: The joint critical distribution of scaling operators $p_L(M, E)$ for the 3D decorated lattice gas model, obtained by applying appropriate field mixing transformation to the distribution of figure 4. The data is expressed in terms of the scaling variables $x = a^{-1}_M L^{\beta/\nu}(M - M_c)$ and $y = a^{-1}_E L^{(1-\alpha)/\nu}(E - E_c)$. The values of the non-universal scale factors $a^{-1}_E$ and $a^{-1}_M$ have been chosen to give unit variance along both axes.

Figure 8: (a) Estimates of the coexistence density distributions of the $L = 20$ decorated lattice gas model at $T = T_c$, $T = 0.9T_c$ and $T = 0.8T_c$. (b) The corresponding forms of the ordering operator distribution $p_L(M)$. Statistical errors do not exceed the symbol sizes.

Figure 9: Comparison of the calculated (lines) and measured (points) temperature dependence of the coexistence density and ordering operator diameters. The calculated temperature dependence was obtained from exact and series expansion methods, as described in the text. The data points were obtained from the simulations, except the estimate for $\rho_c$, which derives from the finite-size extrapolation of figure 11. Statistical errors do not exceed the symbol sizes.

Figure 10: Selections from the universal finite-size spectrum of critical density and energy density distributions of fluids. The distributions were obtained according to the procedure described in the text. The values of the non-universal scale factors $a^{-1}_E$ and $a^{-1}_M$ have been chosen to ensure that the distributions have unit variance.
Figure 11: (a) The measured average density $\langle \rho \rangle_c(L)$ of the decorated lattice gas model at the critical point, expressed as a function of $L^{-(1-\alpha)/\nu}$. The least-squares fit yields an infinite volume estimate $\rho_c = 0.3371(1)$. (b) The measured average energy density $\langle u \rangle_c(L)$ of the decorated lattice gas model at the critical point, expressed as a function of $L^{-(1-\alpha)/\nu}$. The least-squares fit yields an infinite volume estimate $u_c = -0.8385(6)$.

Figure 12: (a) The monomer density distribution for a selection of well-depths $w$ along the line of liquid-vapour coexistence. The distributions were obtained by applying the histogram reweighting technique to measured near-coexistence data for $w = 0.56$ and $w = 0.569$. (b) The corresponding distributions of the ordering operator $p_L(M)$.

Figure 13: The line of liquid-vapour phase coexistence and its analytic extension in the space of $\mu$ and $w$, for values of $w$ in the range $0.555 - 0.575$. The results were obtained by implementing the equal weight criterion for the density distribution. Also shown are the measured directions of the relevant scaling fields.

Figure 14: (a) The ordering operator distribution $p_L(M)$ of the polymer model at the assigned critical parameters. Also shown for comparison is the universal fixed point form $\tilde{p}^*(x)$ (cf. figure 2a). (b) The energy-like operator distribution $p_L(E)$ compared with the universal fixed point form $\tilde{p}^*(y)$ (cf. figure 2b). In both cases the non-universal scale factors $a^{-1}_E$ and $a^{-1}_M$ have been chosen to give unit variance. Statistical errors are indicated by representative error bars.

Figure 15: (a) Estimates for the polymer monomer density distribution $p_L(\rho)$ at the assigned values of the critical well-depth and chemical potential. (b) Corresponding estimates for the polymer energy density distribution $p_L(u)$. Representative error bars are shown.