Critical point field mixing in an asymmetric lattice gas model

N. B. Wilding
Institut für Theoretische Physik, Philosophenweg 19,
Universität Heidelberg, D-6900 Heidelberg, Germany

Abstract

The field mixing that manifests broken particle-hole symmetry, is studied for a 2-D asymmetric lattice gas model having tunable field mixing properties. Monte Carlo simulations within the grand canonical ensemble are used to obtain the critical density distribution for different degrees of particle-hole asymmetry. Except in the special case when this asymmetry vanishes, the density distributions exhibit an antisymmetric correction to the limiting scale-invariant form. The presence of this correction reflects the mixing of the critical energy density into the ordering operator. Its functional form is found to be in excellent agreement with that predicted by the mixed-field finite-size-scaling theory of Bruce and Wilding. A computational procedure for measuring the significant field mixing parameter is also described, and its accuracy gauged by comparing the results with exact values obtained analytically.

PACS numbers 64.70, 64.70F
1 Introduction

It has long been appreciated [1] that the lack of symmetry between the liquid and vapour phases of a fluid leads to a mixing of the temperature and chemical potential in the two relevant scaling fields close to the critical point. This is in marked contrast to the situation for models of the Ising symmetry such as the ordinary lattice gas [2], which as a consequence of their so-called ‘particle-hole’ symmetry\(^1\) exhibit no field mixing. Although the reduced symmetry of fluids has no consequences for their universal properties (which for systems with short-ranged interactions correspond to the Ising universality class), it is predicted that certain non-universal effects are engendered by field mixing. Principal among these, is the existence of a weak energy-like singularity of the coexistence diameter on the approach to criticality. The presence of this singularity, now firmly established experimentally [3, 4], constitutes a failure for the century-old empirical ‘law of rectilinear diameter’. Indeed, some theoretical progress has been made towards an understanding of the microscopic factors governing the amplitude of the diameter singularity [5, 6].

Recently however, a new finite-size-scaling theory has been developed that relates the mixed character of the fluid scaling fields to the interplay of the near-critical energy and density fluctuations [7, 8]. The theory predicts that as a result of field mixing, the energy operator features in the critical density distribution, giving rise (as outlined below) to a correction to the limiting (large \(L\)) universal form of the density distribution. This correction is subdominant to the limiting form and dies away with increasing \(L\). To leading order in the theory, its functional form is prescribed by independently known functions characteristic of the Ising universality class. Moreover the symmetry of the correction (an antisymmetric function) differs from that of the limiting form (a symmetric function). Its presence in the density distribution is therefore a potentially distinctive signature of the field mixing phenomenon, one that can in principle be isolated and analysed by means of computer simulation measurements of the density fluctuations. Indeed, the potential utility of the theory in facilitating simulation studies of field mixing was clearly demonstrated in an extensive Monte Carlo investigation of the 2-D Lennard-Jones fluid near the liquid-vapour critical point [8]. Measurements of the near-critical density distribution yielded an antisymmetric field mixing component that mapped quite well onto the predicted universal form. In addition, a computational prescription was set out for estimating the more significant of the two field mixing parameters (that which controls the extent to which the chemical potential features in the thermal scaling field).

Notwithstanding the successes of the study reported in [7, 8], one is still confronted with a number of difficulties if one wishes to assess the quantitative validity of the new theory. The most severe problem is the computational burden imposed by simulations of realistic fluid models (such as the Lennard-Jones system), which owing to their continuous, long-ranged interaction potential, require intensive floating-point calculations. The computational demands of such simulations far exceed those of lattice-based particle or spin systems. Moreover, since exact values of the critical couplings are not generally available for realistic fluid models, it is difficult to probe the asymptotic critical region. This can complicate the isolation of the field mixing correction to the density distribution, which must be identified amidst other corrections associated with small departures from criticality. The analytical intractability of realistic fluid models also precludes an assessment of the accuracy of any computational

---

\(^1\)A lattice gas possesses particle-hole symmetry if the Hamiltonian, a function of the site occupation numbers \(\sigma_i = 0, 1\) satisfies the relation \(\mathcal{H} \rightarrow \mathcal{H} + A \sum_i \sigma_i + B\) (with \(A, B\) constants) under the transformation \(\sigma_i \rightarrow 1 - \sigma_i\). Real (continuous) fluids lack particle-hole symmetry ipso-facto since a hole is not defined.
procedure for measuring the significant mixing parameter.

Clearly, in order to facilitate a more detailed assessment of the mixed-field finite-size-scaling theory, it would be beneficial to work with a model system having fewer of the drawbacks listed above. One such system is the 2-D asymmetric lattice gas model, originally proposed by Mermin, which whilst being comparatively much easier to tackle computationally than e.g the Lennard-Jones fluid, is also analytically solvable for the critical point couplings and field mixing parameters. It therefore provides an ideal test-bed for the theory, permitting an accurate determination of the field mixing correction, and providing a benchmark against which, the accuracy of any computational method for determining the field mixing parameters can be gauged.

Below we describe the results of field mixing studies of Mermin’s asymmetric lattice gas model. The layout of the paper is as follows: the model is described in section 2 and set within the framework of the mixed-field finite-size-scaling theory. Exact values for the significant mixing parameter of the model are also calculated. In section 3, Monte Carlo measurements of the critical density distribution are presented. The antisymmetric component of these distributions is isolated and compared with the predicted form of the field mixing correction. Estimates of the significant mixing parameter are also deduced from the simulation data and compared with the exact results. Section 4 details our conclusions.

2 Background

The asymmetric lattice gas model forming the focus of the present work, was first proposed by Mermin [9] as an example of a system exhibiting a singular coexistence diameter. The model consists of an ordinary 2-D square lattice gas (whose nearest neighbour coupling we denote \( J \)) in which particle-hole symmetry is manually destroyed by forbidding occupation of sites whose row and column numbers are both even. By this action one creates two types of sites: odd-odd sites having coordination number 4, and odd-even (or even-odd) sites having coordination number 2. 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 sets of inequivalent sublattices in the asymmetric lattice gas, clearly violates this condition and leads to field mixing. It transpires, however, that if one introduces an additional coupling \( K \), between atoms on the sublattice of odd-odd sites, then the degree of particle-hole asymmetry can be tuned. Indeed for the special choice \( K = -J/2 \), the average energy per site becomes equal for both sublattices and consequently particle-hole symmetry is once more restored.

Aside from its field mixing properties, the chief asset of Mermin’s asymmetric lattice gas, 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, for which in turn a wealth of exact results are known in two dimensions [2]. Specifically, one finds [9]:

\[
\Omega(\mu, T) = (1 + e^{\mu/kT})^{2N} \Omega(\mu, T)
\]

where \( \Omega \) is the partition function of the asymmetric model and \( \mu \) and \( T \) are the chemical potential and temperature respectively. Bars denotes quantities in the ordinary lattice gas and

\[\text{We note in passing, that the model also possesses a rich phase structure that has been investigated in detail by other workers [10, 11, 12, 13].}\]
\( \overline{N} = N/3 \) where \( N \) is the number of allowed sites in the asymmetric model.

Introducing the dimensionless chemical potential \( \xi = \mu/k_bT \) and dimensionless coupling parameters \( \eta = J/k_bT, \lambda = K/k_bT \), equation [9] leads to the following relationships [3]:

\[
\xi = \xi + 4 \ln \left[ \frac{1 + e^{\xi + \eta}}{1 + e^\xi} \right] \quad (2a)
\]

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

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

Now, it transpires [2] that in the ordinary lattice gas the liquid-vapour coexistence line is specified by \( \overline{\xi} = -2\overline{\eta} \), while the critical point that terminates this line is given by the solutions to the relations:

\[
\sinh(\eta_c/2) = 1, \quad \overline{\xi}_c = -2\overline{\eta}_c \quad (3)
\]

Setting \( \overline{\xi} = -2\overline{\eta} \) in equations [2a] and [2b] then yields the coexistence condition for the asymmetric model:

\[
\xi + 2\lambda + 2 \ln \left[ \frac{1 + e^{\xi + 2\eta}}{1 + e^\xi} \right] = 0 \quad (4)
\]

which represents a surface in the space of \( \xi, \eta \) and \( \lambda \). Note however, that since \( \lambda \) and \( \eta \) both enter only as multiplicative factors in the configurational energy (see equation [8] below), this coexistence surface can be represented in terms of a family of coexistence curves in the space of \( \xi \) and \( \eta \), each curve being parameterised by a different value of the coupling ratio \( \lambda/\eta \). This ratio is consequently the crucial parameter controlling the coexistence and field mixing properties.

We shall also find it useful to obtain the critical density of the asymmetric lattice gas, which can be calculated by appeal to the relation:

\[
\rho_c = \left. \frac{1}{N} \frac{\partial \ln \Omega(\mu, T)}{\partial \mu} \right|_c \quad (5)
\]

from whence, one obtains [3]:

\[
\rho_c = \frac{2}{3} \left[ 1 + e^{-\xi} \right]^{-1} + \frac{1}{3} \overline{\rho}_c \left( \frac{\partial \overline{\xi}}{\partial \overline{\xi}} \right)_c + \frac{1}{3} \overline{\rho}_c \left( \frac{\partial \overline{\eta}}{\partial \overline{\xi}} \right)_c \quad (6)
\]

where the subscript \( c \) on the derivatives signifies that they are to be evaluated at criticality. The quantities \( \overline{\rho}_c \) and \( \overline{\rho}_c \) are respectively the critical energy density and number density of the ordinary lattice gas model, the particle-hole symmetry of which implies \( \overline{\rho}_c = 0.5 \). The value of \( \overline{\rho}_c \) is also known exactly; it is related to the critical energy density \( u_I^c \) of the 2-D Ising model by the relation \( \overline{\rho}_c = \frac{1}{4}[2 + u_I^c] \), where from Onsager’s solution, \( u_I^c = \sqrt{2}/2 \). The derivatives in equation [8] can be calculated straightforwardly to yield

\[\text{Note that we might equally well have chosen } \lambda \text{ instead of } \eta \text{ as the independent coupling variable.} \]
\[
\frac{\partial \xi}{\partial \xi} = \frac{1 + 5e^{\xi + \eta} - 3e^{\xi} + e^{2\xi + \eta}}{(1 + e^\xi)(1 + e^{\xi + \eta})} \quad (7a)
\]

\[
\frac{\partial \eta}{\partial \xi} = \frac{e^\xi - e^{2\xi + \eta} + 2e^{2\xi + 2\eta} + e^{\xi + 2\eta} - e^{2\xi + 3\eta} - 2e^{\xi + \eta}}{(1 + e^\xi)(1 + e^{\xi + 2\eta})(1 + e^{\xi + \eta})} \quad (7b)
\]

Substituting for \( \eta_c \) and \( \xi_c \) in equations 2a and 2b, and feeding the results for \( \eta_c \) and \( \xi_c \) into equation 6, one readily obtains the critical density \( \rho_c \) as a function of \( \lambda/\eta \). This relationship is shown in figure 1 for values of \( \lambda/\eta \) in the range \((-1/2, 1/2)\), which, as will be seen, encompasses a wide range of field mixing behaviour. The figure clearly demonstrates that when \( \lambda/\eta = -1/2 \) the critical density is that of the ordinary lattice gas (\( \rho_c = 0.5 \)), thus confirming that particle hole symmetry is restored for this value of the coupling ratio. It is also evident that increasing \( \lambda/\eta \) causes the critical density to decrease monotonically. The nature of this density shift finds illustration in the simulation results to be described later.

We turn now to the field mixing properties of the asymmetric lattice gas model, which we analyse within the framework of the mixed-field finite-size-scaling theory of references [7, 8]. To this end, we consider a 2-D system of side \( L \), having a maximum available volume \( V = 3L^2/4 \). The configurational energy \( \Phi(\{\sigma\}) \) is given by

\[
\Phi(\{\sigma\}) = \sum_{i,j} \eta \sigma_i \sigma_j + \sum_{[m,n]} \lambda \sigma_m \sigma_n \quad (8)
\]

with \( \sigma_i = 0, 1 \). The site indices \( i \) and \( j \) are taken to run over all allowed nearest neighbour sites, while \( m \) and \( n \) run only over nearest neighbours on the sublattice of odd-odd sites. We assume also that the system is thermodynamically open so that the particle number density \( \rho = \sum_i \sigma_i / V \) can fluctuate. In this paper, we shall be concerned with the statistical behaviour of both the number density \( \rho \), and the configurational energy density \( u = V^{-1} \eta^{-1} \Phi(\{\sigma\}) \), the latter of which we write in units of the coupling parameter \( \eta \).

For a given choice of the coupling ratio \( \lambda/\eta \), the critical point is located by critical values of the reduced chemical potential \( \xi_c \) and reduced coupling \( \eta_c \). Deviations of \( \xi \) and \( \eta \) from their critical values determine the size of the two relevant scaling fields [14]. In the absence of particle-hole symmetry, it is expected [1] that the relevant scaling fields comprise (asymptotically) linear combinations of these deviations:

\[
\tau = \eta_c - \eta + s(\xi - \xi_c) \quad h = \xi - \xi_c + r(\eta_c - \eta) \quad (9)
\]

where \( \tau \) is the temperature-like scaling field and \( h \) is the field-like 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 slope of the coexistence curve in the space of \( \xi \) and \( \eta \) [14]. The role of the parameter \( s \) (which controls the degree to which the chemical potential features in the thermal scaling field) is, however, more significant: it determines the size of the diameter singularity. We term \( s \) the significant mixing parameter.

Conjugate to the two relevant scaling fields are scaling operators \( \mathcal{E} \) and \( \mathcal{M} \), which are found to comprise linear combinations of the energy and number densities [8]:

\[
\mathcal{E} = \frac{1}{1-sr} [u - r\rho] \quad \mathcal{M} = \frac{1}{1-sr} [\rho - su] \quad (10)
\]
where $E$ is the energy-like operator and $M$ the ordering operator. In the Ising context (for which $s = r = 0$), $M$ is simply the magnetisation while $E$ is the energy density.

Near criticality, the joint probability distribution $p_{M,E}(M,E)$ of the operators $E$ and $M$ is expected to exhibit scaling behaviour. In particular, in the limit of large system size $L$, the distribution of the ordering operator $p_{M}(M) = \int p_{M,E}(M,E)dE$ is expected to be describable by a finite-size-scaling relation having the form [13]:

$$p_{M}(M) \approx a_{M}^{-1}L^{d-\lambda_{M}}\tilde{p}_{M}(a_{M}^{-1}L^{d-\lambda_{M}}\delta M, a_{M}L^{\lambda_{M}}h, a_{E}L^{\lambda_{E}}\tau)$$

where $\delta M \equiv M - M_{c}$ and the function $\tilde{p}_{M}$ is predicted to be universal, modulo the choice for the scale-factors $a_{M}$ and $a_{E}$ of the two relevant fields, whose scaling indices are $\lambda_{M} = d - \beta/\nu$ and $\lambda_{E} = 1/\nu$ respectively. This scaling form (which has its basis in the renormalisation group scaling properties of the multi-point correlation functions [10]) is well-supported by Monte Carlo studies of 2-D Ising and $\phi^{4}$ models, where the ordering operator $M$ is simply the magnetisation [17].

In asymmetric systems, the mixing of the energy density into $M$ precludes direct simulation measurements of $p_{M}(M)$, since in general the value of $s$ will not be known a-priori. Instead, it is expedient to focus on the distribution of the density, which is obtained from the joint distribution of the mixed operators by integrating over the energy spectrum and expanding in the mixing parameter $s$:

$$p_{L}(\rho) = \int p_{M,E}(\rho - sE,E)dE$$

from which one finds [8]

$$p_{L}(\rho) \approx a_{M}^{-1}L^{d-\lambda_{M}}\tilde{p}_{M}(a_{M}^{-1}L^{d-\lambda_{M}}[\rho - \rho_{c}], a_{M}L^{\lambda_{M}}h, a_{E}L^{\lambda_{E}}\tau) + \Delta p_{L}(\rho)$$

with

$$\Delta p_{L}(\rho) = -s\frac{\partial}{\partial \rho} \{p_{L}(\rho) [< u(\rho) > - u_{c} - r(\rho - \rho_{c})] \} + O(s^{2})$$

where $< u(\rho) >$ (hereafter referred to as the energy function) is the mean energy density for a given $\rho$.

The function $\Delta p_{L}(\rho)$ describes (to linear order in $s$) the component of the critical density distribution associated with field mixing. Precisely at criticality, equation [13] may be written in the form:

$$p_{L}(\rho) \approx a_{M}^{-1}L^{\beta/\nu} \left[ \tilde{p}_{M}^{*}(x) - sa_{E}a_{M}^{-1}L^{-(1-\alpha-\beta)/\nu} \frac{\partial}{\partial E} (\tilde{p}_{M}^{*}(x)\tilde{e}^{*}(x)) \right]_{x=a_{M}^{-1}L^{\beta/\nu}[\rho - \rho_{c}]} + O(s^{2})$$

where $\tilde{p}_{M}^{*}(x) \equiv \tilde{p}_{M}(x,0,0)$ and

$$\tilde{e}^{*}(x) \equiv \left. \frac{\partial \ln \tilde{p}_{M}(x,0,z)}{\partial z} \right|_{z=0} = a_{E}^{-1}L^{d-1/\nu} [< u(\rho) > - u_{c} - r(\rho - \rho_{c})] + O(s)$$

is a universal function whose form has (like that of $\tilde{p}_{M}^{*}$) been previously established in Monte Carlo studies of the critical 2-D Ising model [17], where it is simply the energy function for the magnetisation.
To leading order in $s$, the critical density distribution can thus be expressed as a sum of two independently-known universal components. The first of these, $\tilde{p}_M^*(x)$, is a function having the same form as the critical magnetisation distribution of the Ising model. The second, $\frac{\partial}{\partial x} (\tilde{p}_M^*(x)\tilde{e}^*(x))$, is a function characterising the critical energy operator and represents (to linear order in $s$) the field mixing contribution to the density distribution. This field mixing term is down on the first term by a factor $L^{-1-(\alpha-\beta)/\nu}$ and therefore represents a correction to the large $L$ limiting behaviour. Given further the symmetries of $\tilde{e}(x)$ and $\tilde{p}_M^*(x)$, both of which are even (symmetric) in the scaling variable $x$, the field mixing correction is the leading antisymmetric contribution to the density distribution. Accordingly, it can be isolated from measurements of the critical density distribution, simply by antisymmetrising around $\rho_c$.

In addition to furnishing the functional form of the field mixing correction, equation 14 also constitutes a computational prescription for estimating the significant mixing parameter $s$. The value of $s$ is simply the single scale factor required to match the critical point form of the measured function $\Delta p_L(\rho) = -s \frac{\partial}{\partial \rho} \{ p_L(\rho) \{ u(\rho) - u_c - r(\rho - \rho_c) \} \}$ to the measured antisymmetric component of the critical density distribution. In the present case, the accuracy of this procedure can be gauged, since the exact value of $s$ is obtainable analytically.

An exact calculation of $s$ follows from the observation that in the ordinary lattice gas, the field-like scaling field $h$ coincides with the line $\eta = \eta_c$ in the space of $\xi$ and $\eta$. It follows that in the asymmetric model, the direction of $h$ in the space of $\xi$ and $\eta$ can be obtained from equation 2b by setting $\eta = \eta_c$, $\lambda = \lambda(\eta)$ and solving for $\eta$. The value of $s$ is then given by

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

(17)

where the derivative is to be evaluated at criticality. The results of this calculation are displayed in figure 2 as a function of $\lambda/\eta$ in the range $(-1/2, 1/2)$. As anticipated, $s$ vanishes for $\lambda/\eta = -1/2$. We note also the presence of a broad minimum in the value of $s$ at $\lambda/\eta \simeq -0.08$.

## 3 Monte Carlo studies

### 3.1 Computational details

The Monte Carlo simulations reported here, were all performed using a Metropolis algorithm within the grand canonical ensemble. Two system sizes were studied, having linear dimension $L = 20$ and $L = 30$. Periodic boundary conditions were employed throughout. The basic observables recorded were the probability distribution of the number density $P_L(\rho)$ and the energy function $< u(\rho) >$. The distribution of the density was obtained initially as a histogram. The energy function was accumulated as an average of the energy for each value of $\rho$ explored in the course of the simulation. All simulations were performed at the exact critical point of the model, obtained (for a given choice of $\lambda/\eta$) from equations 2a, 2b and 3. The $L = 20$ systems consisted of $1 \times 10^6$ lattice sweeps for equilibrium, followed by a sequence of $2 \times 10^5$ observations with 100 sweeps between each observation. For the $L = 30$ system, equilibration times of $4 \times 10^6$ sweeps were used with $2 \times 10^5$ observations separated by 200 lattice sweeps. In each instance the whole procedure was repeated 12 times to test the statistical independence of the data and to assign statistical errors to the results.
3.2 Results

Measurements of the critical density distribution were collected for the $L = 20$ system at five distinct values of $\lambda/\eta$, namely $-1/2, -1/4, 0, 1/4, 1/2$. For the $L = 30$ system, measurements were made with $\lambda/\eta = -5/12$ and $\lambda/\eta = 0$. The $L = 20$ distributions are shown in figure 3, where each has been normalised to unit integrated weight. With the exception of the case $\lambda/\eta = -1/2$, the distributions display a marked asymmetry. Also apparent, is a pronounced shifting of the high density peak to successively lower densities as $\lambda/\eta$ is increased. By contrast, however, the position of the low density peak is relatively unaffected by changes in $\lambda/\eta$. Measurements of the critical density (calculable simply as the first moment of these distributions), agree well with the exact values obtained from equation 6.

That the asymmetry of the distributions vanishes for $\lambda/\eta = -1/2$, is demonstrated in figure 4 where a comparison is shown between the critical density distribution and the magnetisation distribution of the 2-D spin-$1/2$ Ising model at its exact critical point, as previously obtained by Nicolaides and Bruce [17]. The density data has been expressed in terms of the scaling variable $x = a_M^{-1}L^{\beta/\nu}r(\rho - \rho_c)$, and the data collapse has been effected by a single scaling (choice of the non-universal scale factor $a_M$) such that both distributions have unit variance. Clearly, the overall quality of the data collapse is impressive, except for small departures near the vestiges of the density distribution. These however, can be traced to the fact that the $L = 20$ system is not quite sufficiently large to allow proper sampling of the high and low density tails of the density distribution. For this reason, detailed analysis of the corrections to the density distributions was carried out for the $L = 30$ system where this problem is much less evident.

As previously noted, the antisymmetric component of the density distributions may be isolated simply by antisymmetrising the density distribution about $\rho_c$, whose value is obtainable from equation 3. The results of applying this procedure are depicted in figure 5 for the $L = 30$ system at $\lambda/\eta = -5/12$ and $\lambda/\eta = 0$. In the former case, the size of the antisymmetric component is quite small, while in the latter it is considerably larger. These antisymmetric components are replotted as functions of the scaling variable $x$ in figure 6, together with the predicted universal form of the field mixing correction, prescribed in equation 15 and obtained from Ising model studies [17, 8]. The data have all been brought into coincidence by single scalings of the non-universal scale factor $a_M$ and the ordinate. In both instances the antisymmetric component of the density distribution maps extremely well onto the predicted universal form.

Turning now to measurements of the significant mixing parameter, the value of $s$ can be estimated according to the procedure outlined in the previous section. We shall describe this procedure for the case $\lambda/\eta = -5/12$, for which the antisymmetric component of the density distribution is rather small. Some additional complications arise when the antisymmetric component is larger, and these are discussed separately in the context of the $\lambda/\eta = 0$ data.

In order to measure $s$, both the energy function $u(\rho) > -u_c$ and the density distribution $p_L(\rho)$ are required. The energy function is displayed in figures 7 for the case $\lambda/\eta = -5/12$. Also included in figure 7 is the function $r(\rho - \rho_c)$, where $r$ (cf equation 3) is the limiting critical slope of the coexistence curve in the plane of $\eta$ and $\xi$, whose value (for a particular choice of $\lambda/\eta$) is calculable from equation 4. For the present case, $\lambda/\eta = -5/12$, one finds $r = -1.054092$. Now, according to equation 15, $s$ is simply the single scale factor required to match the function $\Delta p_L(\rho) = -s\frac{\partial}{\partial \rho} \{p_L(\rho)[u(\rho) > -u_c - r(\rho - \rho_c)]\}$ to the antisymmetric component of the density distribution. To the extent that $O(s)$ correction to the energy function and the
density distribution can be neglected, the function $\Delta p_L(\rho)$ will itself be antisymmetric and thus comparison of the scales of the two functions can be effected directly, notwithstanding the relative enhancement of statistical uncertainties in $\Delta p_L(\rho)$ that results from taking the numerical derivative. Figure 8 shows both $\Delta p_L(\rho)$ and the measured antisymmetric component of the density distribution. The two data sets have been brought into correspondence by a single scaling (choice of the ordinate) implying a value $s = -0.23(2)$. This estimate is in quite good agreement with the exact value of $-0.204$.

Finally, we address briefly the situation where the antisymmetric component of the density distribution is not small. Under these circumstances, $O(s)$ terms make a significant contribution to both $p_L(\rho)$ and $u(\rho)$. These terms (manifesting themselves as $O(s^2)$ corrections to $\Delta p_L(\rho)$) prevent a direct comparison of $\Delta p_L(\rho)$ with the measured antisymmetric component since $\Delta p_L(\rho)$ will no longer itself be antisymmetric in $\rho - \rho_c$. Notwithstanding this, an estimate of $s$ can be obtained by the simple expedient of antisymmetrising $\Delta p_L(\rho)$ about $\rho_c$, and comparing the scales of the two functions. Carrying out this procedure for the $\lambda/\eta = 0$ data yields an estimate $s = -0.38(1)$ to be compared with the exact value $s = -0.331$. The bulk of this discrepancy, some 15%, is presumably attributable to the neglect of field mixing terms of order $s^2$ and higher, which are not included in equation 4.

4 Conclusions

The simulation results presented in this paper confirm that in systems with broken particle-hole symmetry, the field mixing phenomenon gives rise to an antisymmetric correction to the limiting form of the critical density distribution. An accurate determination of the functional form of this correction has demonstrated it to be in excellent quantitative agreement with the prediction of the mixed-field finite-size-scaling theory of references [7, 8]. As such the results constitute substantial corroboration of that theory.

A method for estimating the significant mixing parameter $s$ was also assessed, and found to yield accurate results, provided the overall magnitude of the field mixing correction is not too large. In view of the finding [8] that the size of the field mixing correction in the Lennard-Jones fluid is indeed rather small (constituting only approximately 5% by weight of the density distribution for a system of 400 particles), the method described should in principle permit quite accurate evaluation of $s$ in realistic (off-lattice) fluid models. Of course (and as noted in the introduction), the feasibility of such studies is contingent upon an ability to first locate accurately the critical point for the model of interest. However, as was demonstrated in reference [8], this can also be achieved via a finite-size-scaling analysis of the density distribution, provided one works within an ensemble (such as the grand canonical ensemble) that affords adequate sampling of density fluctuations.

With these points in mind, it would be of considerable interest to extend the present programme of simulation studies to an investigation of the microscopic factors influencing the degree of field mixing in realistic fluid models. Recent theories have predicted that the size of the significant mixing parameter is strongly influenced by three-body forces [4, 6]. Such interactions could certainly (albeit at greater computational expense) be incorporated into off-lattice fluid simulations, allowing their role in the field mixing process to be assessed.
Acknowledgement

The author is grateful to A D Bruce for helpful communications and for making available the results of Ising model studies.

References

[1] Rehr, J.J. and Mermin, N.D.: Phys. Rev. A 8, 472 (1973)
[2] Lee, T.D. and Yang, C.N.: Phys. Rev. 87, 410 (1952)
[3] Sengers, J.V. and Levelt-Sengers, J.M.H.: Ann. Rev. Phys. Chem. 37, 189 (1986)
[4] Jungst, S., Knuth, B. and Hensel, F.: Phys. Rev. Lett. 55, 2167 (1985)
[5] Goldstein, R.E., Parola, A., Ashcroft, N.W., Pestak, M.W., Chan, M.W.H., de Bruyn, J.R. and Balzarini, D.A.: Phys. Rev. Lett. 58, 41 (1987)
[6] Goldstein, R.E. and Parola, A.: J. Chem. Phys. 88, 7059 (1988)
[7] Bruce, A.D. and Wilding, N.B.: Phys. Rev. Lett. 68, 193 (1992)
[8] Wilding, N.B. and Bruce, A.D.: J. Phys. Condens. Matter 4, 3087 (1992)
[9] Mermin, N.D.: Phys. Rev. Lett. 26, 957 (1971)
[10] Rehr, J.J. and Mermin, N.D.: Phys. Rev. A 7, 379 (1973)
[11] Zollweg, J.A. and Mulholland, G.W.: J. Chem. Phys. 57, 1021 (1972)
[12] Mulholland, G.W. and Rehr, J.J.: J. Chem. Phys. 60, 1297 (1974)
[13] Mulholland, G.W., Zollweg, J.A. and Levelt-Sengers, J.M.H.: J. Chem. Phys. 62, 2535 (1975)
[14] Wegner, F.J.: Phys. Rev. B. 5, 4529 (1972)
[15] Binder, K.: Z. Phys. B 43, 119 (1981)
[16] Bruce, A.D.: J. Phys. C 14, 3667 (1981)
[17] Nicolaides, D. and Bruce, A.D.: J. Phys. A. 21, 233 (1988)
Figure 1: The critical density $\rho_c$ of the asymmetric lattice gas model expressed as a function of the coupling ratio $\lambda/\eta$.

Figure 2: The significant field mixing parameter ‘s’ expressed as a function of the coupling ratio $\lambda/\eta$.

Figure 3: The $L = 20$ critical density distribution for various values of the coupling ratio $\lambda/\eta$. Statistical uncertainties are smaller than symbol sizes; the curves are simply guides to the eye. All distributions are normalised to unit integrated weight.
Figure 4: The critical density distribution for the $L = 20$ system at $\lambda/\eta = -1/2$, expressed as a function of the scaling variable $x = L^{\beta/\nu} a_M^{-1} (\rho - \rho_c)$. Also shown (full curve) is the critical magnetisation distribution of the 2-D Ising model obtained in [17]. The non-universal scale factor implicit in the definition of the scaling variable, has been chosen so that both distributions have unit variance.

Figure 5: The measured antisymmetric component of the $L = 30$ critical density distributions at $\lambda/\eta = -5/12$ and $\lambda/\eta = 0$. The lines are guides to the eye.

Figure 6: The data of figure 5 re-expressed in terms of the scaling variable $x = L^{\beta/\nu} a_M^{-1} (\rho - \rho_c)$ and shown as the data points. The solid curve represents the prediction following from equation 15, utilising predetermined Ising forms [17]. The measured correction data have been brought into coincidence with the predicted form via appropriate choices of the non-universal scale factor $a_M$ and the ordinate.

Figure 7: The measured form of the critical energy function $\langle u(\rho) \rangle - u_c$ for the $L = 30$ system at $\lambda/\eta = -5/12$. Statistical uncertainties do not exceed the symbol sizes. Also shown (solid line) is the function $r(\rho - \rho_c)$, with $r = -1.054092$.

Figure 8: The measured function $\Delta p_L(\rho) = -s \frac{\partial}{\partial \rho} \{ p_L(\rho) [\langle u(\rho) \rangle - u_c - r(\rho - \rho_c)] \}$ for the $L = 30$ system at $\lambda/\eta = -5/12$ and shown as crosses ($\times$). Also shown as circles ($\circ$) is the measured antisymmetric component of the critical density distribution, cf. figure 5. The matching shown was effected by a choice of the ordinate implying $s = -0.23(2)$. 

11