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1996 J. Phys.: Condens. Matter 8 9637

(http://iopscience.iop.org/0953-8984/8/47/076)

J. Phys.: Condens. Matter **8** (1996) 9637–9641. Printed in the UK

Tricritical phenomena in a two-dimensional fluid

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Received 15 July 1996

Abstract. We consider the application of finite-size scaling methods to simulations of tricritical phenomena in a two-dimensional symmetrical binary fluid. A simulation strategy is described which together with the scaling framework enables the accurate determination of both the universal and non-universal tricritical point properties of the model. The results also provide insight into the character of the tricritical fluctuations.

The present understanding of fluid phase equilibria owes much to computer simulation studies. Simulations are valuable because they can provide new insights into the relevant physical phenomena, and may even lead to new discoveries. They also provide a useful benchmark for testing analytical theories.

Currently, there is considerable interest in using simulation to study the critical point regime of fluid systems. The theoretical problems posed by the critical region fall naturally into two categories. First, one may wish to establish the universality class to which the phase transition belongs, thereby identifying the values of the universal quantites characterizing the critical behaviour. Second, one may wish to determine the non-universal critical parameters of the system, and try to relate them to the interatomic forces.

Before undertaking a serious simulation study of critical phenomena, it is necessary to have in place a reliable framework for accurately locating the critical point. This necessitates taking account of finite-size effects, which are particularly pronounced in the critical region due to the divergent correlation length. Failure to do so can lead to serious errors in estimates of critical point parameters. For lattice-based spin models, the standard technique for achieving this is to employ finite-size scaling (FSS) methods [1], which permit estimates of bulk critical properties from simulations of finite-sized systems. Recently much attention has also been given to extending FSS techniques to off-lattice fluid models [2–6].

In this paper we describe the application of FSS methods to a simulation study of tricriticality [7] in a two-dimensional (2D) symmetrical binary fluid model [8]. Experimentally, the phase diagrams of binary fluids exhibit a rich topology, dependent on the specific forms of the microscopic interactions [9]. For the symmetrical system considered in this work, however, the two component species posess a special Ising model type symmetry and it is possible to arrange for the topology shown schematically in figure 1. At high temperatures there is a line of second-order demixing transitions, while at low temperature there is a (triple) line of first-order liquid–vapour transitions. The two lines of transitions meet one another at the liquid–vapour critical point, which is thus a tricritical point.

The particular model we consider is a 2D symmetrical square-well fluid in which the two particle species A and B interact with one another via the potential:

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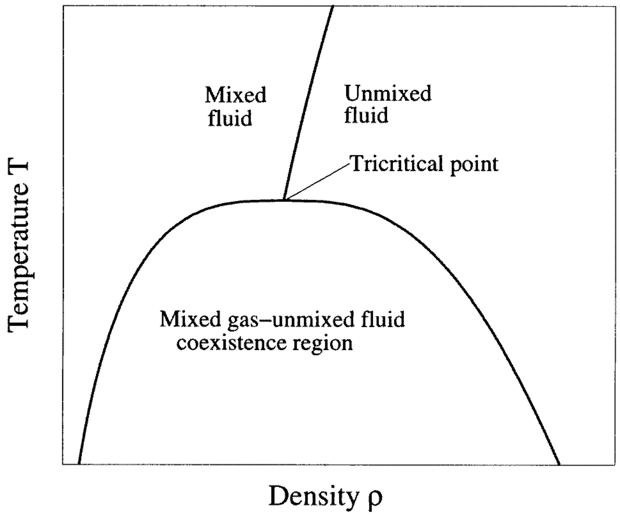

Figure 1. A schematic phase diagram of a symmetrical binary fluid in the T–ρ plane.

$$\begin{aligned} U(r) &= \infty \qquad && r < \sigma \\ U(r) &= -J && \sigma \leqslant r \leqslant 1.5\sigma \\ U(r) &= 0 && r > 1.5\sigma \end{aligned} \tag{1}$$

with $J_{AA} = J_{BB} = -J_{AB} = J > 0$. Owing to the symmetry of this potential with respect to A–A and B–B interactions, the phase diagram is symmetric with respect to positive and negative values of the chemical potential difference $\mu_A - \mu_B$. Also by virtue of this symmetry, there is a tricritical point which lies in the symmetry plane $\mu_A = \mu_B$ of the phase diagram.

Monte Carlo simulations of this model were performed in the grand canonical (constant-μVT) ensemble, and both particle transfers (insertions and deletions) and identity changes (A $\rightarrow$ B, B $\rightarrow$ A) were implemented. To locate the tricritical point, the approach adopted was to study the FSS properties of the scaling operator distributions along the first-order line of liquid–vapour coexistence. In general, owing to the lack of symmetry between the coexisting phases, these operators will comprise linear combinations of the bare physical observables [5], namely the particle density ρ, the energy density u and the excess concentration $\psi = (N_A - N_B)/V$. For the symmetric binary fluid, the scaling operators on which we shall focus are

$$\begin{aligned} \mathcal{M} &\sim \psi \\ \mathcal{D} &\sim \rho - su \end{aligned} \tag{2}$$

where s is a non-universal 'field mixing' parameter, which controls the degree to which the energy and density fluctuation couple to one another [5].

Precisely at tricriticality, the probability distribution functions of the scaling operators are expected to be both universal and scale invariant. This scale invariance can be exploited to locate the tricritical point using the cumulant intersection method [11]. The fourth-order cumulant ratio, U_L, is a quantity that characterizes the form of a distribution, and is defined in terms of the fourth and second moments of a given distribution:

$$U_L = 1 - \frac{\langle m^4 \rangle}{3\langle m^2 \rangle^2}. \tag{3}$$

At criticality, the value of U_L should become independent of the system size.

We have studied the behaviour of U_L for the operator distribution $p_L(\mathcal{D})$, along the liquid–vapour coexistence curve and its analytical extension. Simulations were carried out at a reduced temperature of $k_BT/J = 0.58$, and the histogram reweighting technique [10] was used to estimate $U_L(T)$ for other temperatures along the coexistence curve. The results are shown in figure 2 for three system sizes. The data exhibit a clear crossing at $k_BT/J = 0.581(1)$, which we therefore adopt as our estimate of the tricritical temperature. The associated estimate for the tricritical chemical potential is $\mu/k_BT = -1.916(2)$.

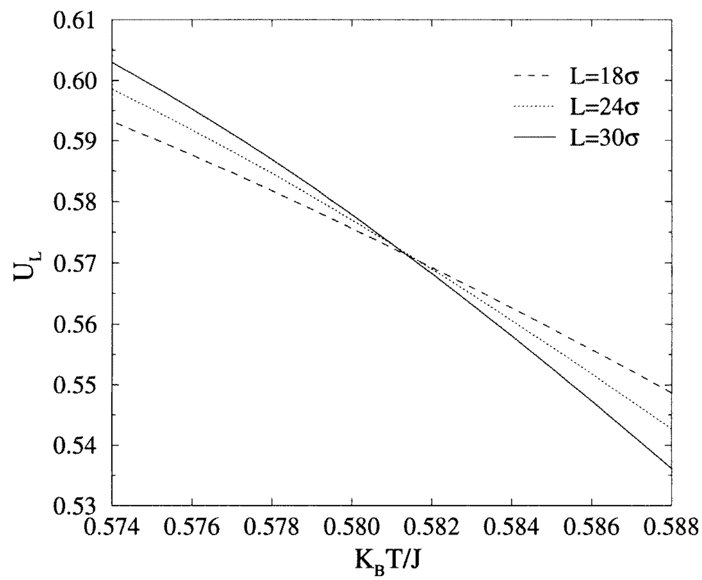

Figure 2. The measured cumulant ratio $U_L^{\mathcal{D}}$ for each of the three system sizes $L = 18\sigma$, 24σ and 30σ along the first-order line and its analytic extension.

The distributions $p_L(\mathcal{D})$ and $p_L(\mathcal{M})$, at the designated values of the tricritical parameters, are shown in figure 3. Also shown are the corresponding tricritical distributions of the 2D spin-1 Blume–Capel model (obtained in a separate study [8]), to whose universality class the 2D binary fluid is expect to belong. Clearly, in each instance and for each system size, the operator distributions collapse extremely well onto one another as well as onto those of the tricritical Blume–Capel model. This data collapse therefore constitutes strong evidence for fluid-magnet universality. The values of the tricritical exponents can also be extracted from the FSS properties of the operator distributions, and are found to agree well with the exact values known from conformal invariance calculations [8].

The forms of the scaling operator distributions also convey insight into the nature of the tricritical fluctuations. In particular, it is noteworthy that the *three-peaked* form of $p_L(\mathcal{M})$ differs from the universal magnetization distribution of the 2D critical Ising model, which is strongly *double*-peaked in two dimensions [11, 12]. The existence of a three-peaked structure for tricritical phenomena reflects the additional coupling that arises between

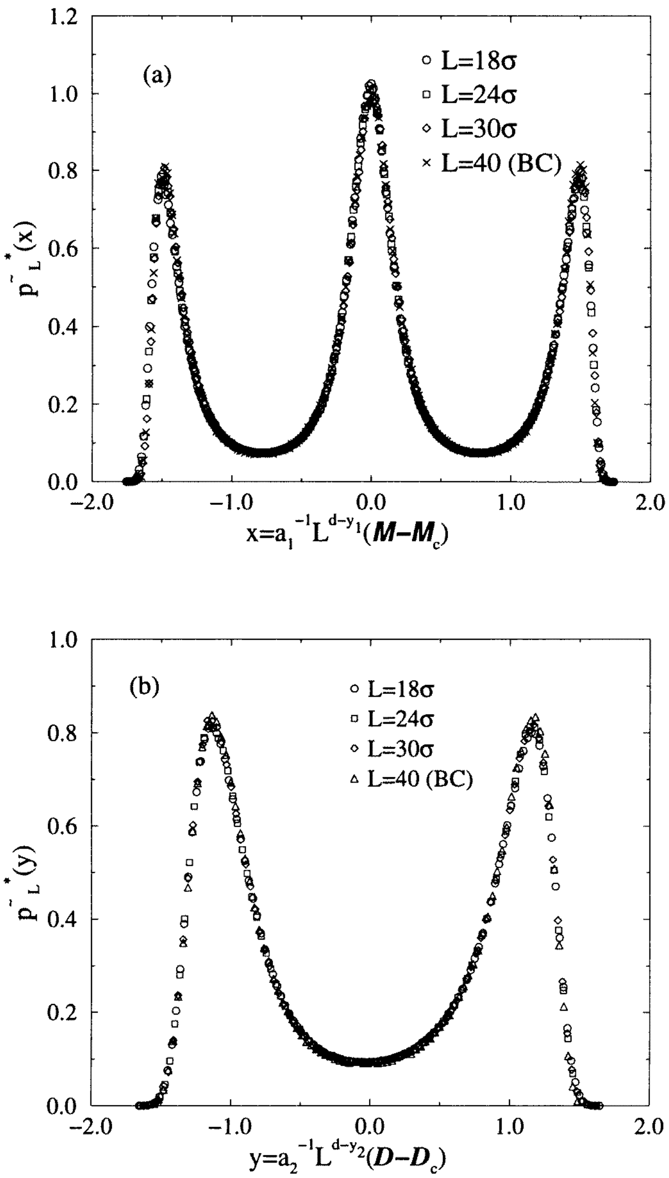

Figure 3. The tricritical scaling operator distributions for the three system sizes $L = 18\sigma$, 24σ and 30σ. (*a*) $\tilde{p}^\star_L(\mathcal{M})$, (*b*) $\tilde{p}^\star_L(\mathcal{D})$. Also shown for comparison are the corresponding tricritical distributions for the 2D Blume–Capel (BC) model. All distributions are expressed in terms of the scaling variable $a_i^{-1}L^{d-y_i}(\mathcal{O}-\mathcal{O}_c)$ and are scaled to unit norm and variance. Statistical errors do not exceed the symbol sizes.

the density and concentration fluctuations. Specifically, the central peak corresponds to fluctuations to small density which are concomitant with an overall reduction in the magnitude of the excess concentration. Were one, however, to depart from the tricritical point along the critical demixing line, these density fluctuations would gradually die out and a crossover to a distribution having the double-peaked Ising form would be expected.

In conclusion, we have seen that the simulation and FSS framework together enables the accurate determination of both the universal and non-universal critical point properties for model fluids. It would now be interesting to try to apply similar techniques to investigate some of the many outstanding questions concerning fluid universality in more complex fluid systems such as ionic or polymeric liquids.

Acknowledgments

Part of the work reported here evolved from fruitful collaboration with A D Bruce, M Müller and P Nielaba. The author acknowledges the financial support of the European community (ERB CHRX CT-930 351) and the Max Planck Institute für Polymerforschung, Mainz.

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