

## Coexistence Curve Singularities at Critical End Points

Nigel B. Wilding

*Institut für Physik, Johannes Gutenberg Universität, Staudinger Weg 7, D-55099 Mainz, Germany*

(Received 21 October 1996)

We report an extensive Monte Carlo study of critical end point behavior in a symmetrical binary fluid mixture. On the basis of general scaling arguments, singular behavior is predicted in the diameter of the liquid-gas coexistence curve as the critical end point is approached. The simulation results show clear evidence for this singularity, as well as confirming a previously predicted singularity in the coexistence chemical potential. Both singularities should be detectable experimentally. [S0031-9007(97)02515-5]

PACS numbers: 64.60.Fr, 05.70.Jk, 64.70.Fx, 64.70.Ja

A critical end point occurs when a line of second order phase transitions intersects and is truncated by a first order phase boundary delimiting a new noncritical phase. Critical end points are common features in the phase diagrams of a diverse range of physical systems, notably binary fluid mixtures, superfluids, binary alloys, liquid crystals, certain ferromagnets, and ferroelectrics, etc. Perhaps the simplest of these is the binary fluid mixture, for which the phase diagram is spanned by three thermodynamic fields  $(T, \mu, h)$ , where  $T$  is the temperature,  $\mu$  is a chemical potential, and  $h$  is an ordering field coupling to the relative concentrations of the two fluid components. In the region  $h = 0$ , two fluid phases  $\beta$  and  $\gamma$  coexist. By tuning  $T$  and  $\mu$ , however, one finds a critical “ $\lambda$  line,”  $T_c(\mu)$ , where both phases merge into a single  $\beta\gamma$  phase. This  $\lambda$  line meets the first order line of liquid-gas transitions  $\mu_\sigma(T)$  at a critical end point  $(T_e, \mu_e)$ ; see Fig. 1. For  $T < T_e$ , the phase boundary  $\mu_\sigma(T)$  constitutes a triple line along which the fluid phases  $\beta$  and  $\gamma$  coexist with the gas phase  $\alpha$ , while for  $T > T_e$ ,  $\mu_\sigma(T)$  defines the region where the  $\beta\gamma$  and  $\alpha$  phases coexist. Precisely at the critical end point the critical mixture of  $\beta$  and  $\gamma$  phases coexists with the gas phase. Since the gas phase is noncritical, it is commonly referred to as a “spectator” phase.

Despite their ubiquity, it has only quite recently been pointed out that critical end points should exhibit novel properties beyond those observable on the critical line. Using phenomenological scaling and thermodynamic arguments, Fisher and co-workers [1] predicted that the singular behavior at the critical end point also engenders new singularities in the first order phase boundary itself. Additionally, new universal amplitude ratios were proposed for the shape of this boundary, as well as for the noncritical surface tensions near the critical end point [2]. These predictions were subsequently corroborated by analytical calculations on extended spherical models [3]. To date, however, empirical support from physically realistic systems has been scarce. While some experimental work on surface amplitude ratios has been reported [4], no attention seems to have been given to the bulk coexistence properties and the question of the predicted singularity in

the spectator phase boundary. There is a similar dearth of simulation work on the subject, and we know of no detailed numerical studies of critical end point behavior, either in lattice or continuum models.

In this Letter we move to remedy this situation by providing the first simulation evidence for singular behavior in the first order phase boundary close to a critical end point. The key features of our study are as follows. We consider a classical binary fluid within the grand canonical ensemble. We review the scaling arguments of Fisher and co-workers [1] and show that in addition to the previously predicted singularity in  $\mu_\sigma(T)$ , they also imply singular behavior in the diameter of the liquid-gas coexistence curve at the critical end point. We test these predictions using extensive Monte Carlo simulations of a symmetrical Lennard-Jones binary mixture, making full use of modern sampling methods, histogram extrapolation techniques, and finite-size scaling analyses. The results provide remarkably clear signatures of divergences in the appropriate temperature derivatives of the coexistence diameter and the phase boundary chemical potential.

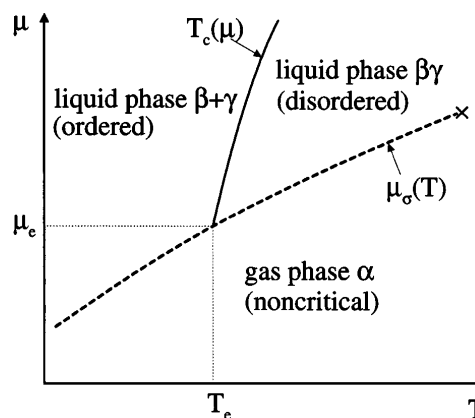


FIG. 1. Schematic phase diagram of a binary fluid in the coexistence surface  $h = 0$ . The broken line  $\mu_\sigma(T)$  is the first order liquid-gas phase boundary terminating at the critical point (cross). The full line is the critical line of second order transitions  $T_c(\mu)$  separating the demixed phases  $\beta + \gamma$ , from the mixed phase  $\beta\gamma$ . The two lines intersect at the critical end point.

We shall focus attention on the liquid-gas coexistence region in the vicinity of a critical end point. Following Fisher and Barbosa [1], coexistence is prescribed by the equality of the Gibbs free energy  $G = -k_B T \ln Z$  in the gas and liquid phases, i.e.,  $G_g(\mu_\sigma(T), T, h) = G_l(\mu_\sigma(T), T, h)$ . Since the gas spectator phase is non-critical, its free energy is analytic at the end point and thus may be expanded as

$$G_g(\mu, T, h) = G_e + G_1^g \Delta\mu + G_2^g t + G_3^g h + G_4^g \Delta\mu^2 + \dots, \quad (1)$$

where  $t \equiv (T - T_e)/T_e$ ,  $\Delta\mu \equiv \mu - \mu_e < 0$ . The liquid phase on the other hand is critical and therefore contains both an analytic (background) and a singular contribution to the free energy

$$G_l(\mu, T, h) = G_0(\mu, T, h) - |\tau|^{2-\alpha} \mathcal{G}_\pm(\hat{h}|\tau|^{-\Delta}), \quad (2)$$

where  $G_0$  is the analytic part, while  $\mathcal{G}_\pm(y)$  is a universal scaling function whose two branches  $\pm$  must satisfy matching conditions as  $y \rightarrow \pm\infty$ . The quantities  $\tau(\mu, T, h)$  and  $\hat{h}(\mu, T, h)$  are both scaling fields that measure deviations from criticality, and comprise linear combinations of  $\Delta\mu$ ,  $t$  and  $h$ .  $\alpha$  and  $\Delta$  are, respectively, the specific heat and gap exponents associated with the  $\lambda$  line.

Expanding the critical free energy in  $\Delta\mu$ ,  $t$  and  $h$ , and setting  $G_g(\mu_\sigma(T), T, h) = G_l(\mu_\sigma(T), T, h)$ , then yields [1] in the region  $h = 0$

$$\mu_\sigma(T) - \mu_o(T) \approx -X_\pm |t|^{2-\alpha}, \quad T \rightarrow T_e \pm, \quad (3)$$

with  $\mu_o(T) = \mu_e + g_1 t + \dots$ , analytic,  $X_\pm > 0$ . If  $\alpha > 0$ , this in turn implies a divergence in the curvature of the spectator phase boundary

$$\frac{d^2 \mu_\sigma}{dT^2} \approx -\tilde{X}_\pm |t|^{-\alpha}, \quad (4)$$

where the amplitude ratio  $\tilde{X}_+/\tilde{X}_-$  is expected to be universal [1].

Let us now consider the behavior of the coexistence density in the neighborhood of the critical end point. Specifically, we shall examine the temperature dependence of the coexistence diameter in the symmetry plane  $h = 0$ , defined by

$$\rho_d(T) \equiv \frac{1}{2}[\rho_g(\mu_\sigma(T)) + \rho_l(\mu_\sigma(T))], \quad (5)$$

which is simply obtained from the coexistence free energy as

$$\rho_d(T) = -\frac{1}{V} \left( \frac{\partial G(\mu_\sigma(T), T)}{\partial \mu} \right), \quad (6)$$

where  $G(\mu_\sigma(T), T) = [G_g(\mu_\sigma(T), T) + G_l(\mu_\sigma(T), T)]/2$ . Appealing to Eqs. (1) and (2), one then finds

$$\rho_d(T) = -U_\pm |\tau|^{1-\alpha} - V_\pm |\tau|^\beta + \text{terms analytic at } T_e. \quad (7)$$

This singularity is of the same form as the overall density singularity [5] on the critical line  $T_c(\mu)$ , which for

binary fluids with short ranged interactions is expected to be Ising-like. For the symmetrical binary fluid studied in the present work, one finds that the amplitude  $V_\pm = 0$  in Eq. (7). The diameter derivative then exhibits a specific heatlike divergence

$$\frac{d\rho_d(T)}{dT} \approx -\tilde{U}_\pm |t|^{-\alpha}, \quad (8)$$

where we have used  $|\tau| = |t|[1 + O(|t|^{1-\alpha})]$  along the coexistence curve. Since this divergence occurs in the first derivative of  $\rho_d(T)$ , it is in principle more readily visible than that in the second derivative of  $\mu_\sigma(T)$ ; cf. Eq. (4). As we shall now show, however, clear signatures of both divergences are readily demonstrable by Monte Carlo simulation [6].

The simulations described here were performed for a symmetrical binary fluid model using a Metropolis algorithm within the grand-canonical ensemble (GCE) [7]. The fluid is assumed to be contained in (periodic) volume  $V = L^3$ , with grand-canonical partition function

$$Z_L = \sum_{N_1=0}^{\infty} \sum_{N_2=0}^{\infty} \prod_{i=1}^N \left\{ \int d\vec{r}_i \right\} e^{[\mu N - \Phi(\{\vec{r}\}) + h(N_1 - N_2)],} \quad (9)$$

where  $\Phi = \sum_{i<j} \phi(r_{ij})$  is the total configurational energy,  $\mu$  is the chemical potential, and  $h$  is the ordering field (all in units of  $k_B T$ ).  $N = N_1 + N_2$  is the total number of particles of types 1 and 2. The interaction potential between particles  $i$  and  $j$  was assigned the familiar Lennard-Jones (LJ) form

$$\phi(r_{ij}) = 4\epsilon_{mn}[(\sigma/r_{ij})^{12} - (\sigma/r_{ij})^6], \quad (10)$$

where  $\sigma$  is a parameter which serves to set the interaction range, while  $\epsilon_{mn}$  measures the well depth for interactions between particles of types  $m$  and  $n$ . In common with most other simulations of LJ systems, the potential was cut off at a radius  $r_c = 2.5\sigma$  to reduce the computational effort.

An Ising model type symmetry was imposed on the model by choosing  $\epsilon_{11} = \epsilon_{22} = \epsilon > 0$ . This choice endows the system with energetic invariance under  $h \rightarrow -h$  and ensures that the critical end point lies in the symmetry plane  $h = 0$ . A further parameter  $\epsilon_{12} = \delta$  was used to control interactions between unlike particles. The phase diagram of the model in the surface  $h = 0$  is then uniquely parametrized by the ratio  $\delta/\epsilon$ . Choosing  $\delta/\epsilon \leq 1$  yields a phase diagram having a critical end point temperature  $T_e \ll T_c^{lg}$  and density  $\rho_e \gg \rho_c^{lg}$ , where  $T_c^{lg}$  and  $\rho_c^{lg}$  are the liquid-gas critical temperature and density, respectively. Choosing a smaller value of  $\delta/\epsilon$ , however, moves the end point towards the liquid-gas critical point, into which it merges for a certain sufficiently small  $\delta/\epsilon$ , forming a tricritical point. Empirically we find that the phase diagram is rather sensitive to the choice of  $\delta/\epsilon$ . Thus for  $\delta/\epsilon \approx 0.6$ , we find a tricritical point, while for  $\delta/\epsilon = 0.75$  there is a critical end point having  $\rho_e \approx 2.3\rho_c^{lg}$ . In the present work, all simulations were

performed with  $\delta/\epsilon = 0.7$ , which yields critical end point parameters  $T_e \approx 0.93T_c^{lg}$ ,  $\rho_e \approx 1.75\rho_c^{lg}$ . This temperature is sufficiently small compared to  $T_c^{lg}$  that critical density fluctuations (which might otherwise obscure the end point behavior) may safely be neglected, while at the same time  $\rho_e$  is not so large as to hinder particle insertions.

Although use of conventional GCE simulations to study liquid-gas phase coexistence presents no great practical difficulties when  $T \lesssim T_c^{lg}$  [8], investigations of the strongly first order regime  $T \ll T_c^{lg}$  are rendered extremely problematic by the large free energy barrier separating the coexisting phases. This leads to metastability effects and protracted correlation times. To circumvent this difficulty we employed the multicanonical preweighting method [9], which encourages the simulation to sample the interfacial configurations of intrinsically low probability. This is achieved by incorporating a suitably chosen weight function in the Monte Carlo update probabilities. The weights are subsequently folded out from the sampled distributions to yield the correct Boltzmann distributed quantities. Further details of the implementation of this technique as well as a method for determining a suitable preweighting function are given elsewhere [6,8].

In the course of the simulations, three systems sizes of volume  $V = (7.5\sigma)^3$ ,  $(10\sigma)^3$ , and  $(12.5\sigma)^3$  were studied, corresponding to average particle numbers of  $N \approx 250$ , 600, and 1200, respectively, at the critical end point (whose location we discuss below). Following equilibration, runs comprising up to  $6 \times 10^9$  MCS (Monte Carlo step) [10] were performed and the density  $\rho = N/V$ , energy density  $u = \Phi/V$ , and number difference order parameter  $m = (N_1 - N_2)/V$  were sampled approximately every  $10^4$  MCS. Attention was focused on the finite-size distributions  $p_L(\rho)$  and  $p_L(m)$ . Precisely on the liquid-gas coexistence curve, the density distribution  $p_L(\rho)$  is (to within corrections exponentially small in  $L$ ) double peaked with equal weight in both peaks [11]. For a given simulation temperature, this "equal weight" criterion can be used to determine the coexistence chemical potential to high accuracy. Simulations were carried out for each  $L$  at several (typically five) temperatures along the coexistence curve, and histogram reweighting [12] was used to interpolate between simulation points and to aid the precise location of the coexistence chemical potential [8]. The position of the critical end point itself was estimated using finite-size scaling techniques in the standard manner [13], by studying the scaling of the fourth order cumulant ratio  $U_L = 1 - 3\langle m^4 \rangle / \langle m^2 \rangle^2$  for  $p_L(m)$  as a function of  $T$  and  $L$  along the liquid branch of the coexistence curve. A cumulant intersection [6] implying critical scale invariance was obtained at  $\tilde{T}_e = 0.958(2)$ ,  $\rho_e = 0.587(5)$ , where  $\tilde{T} = k_B T / \epsilon$ . Further points on the  $\lambda$  line away from the critical end point were also determined using the same method. Related finite-size scaling techniques, this time focusing on the densitylike ordering

operator [8,14] were utilized to locate the liquid-gas critical point. This yielded the estimates  $\tilde{T}_e^{lg} = 1.024(2)$ ,  $\rho_c^{lg} = 0.327(2)$ .

Figure 2 shows the estimated coexistence liquid and gas densities as a function of temperature, determined as the peak densities of  $p_L(\rho)$ . Also shown is the measured locus of the  $\lambda$  line and the position of the liquid-gas critical point. Clearly a pronounced "kink" is discernible in the liquid-branch density in the vicinity of the critical end point. The gas branch, on the other hand, displays no such kink due to the analyticity of  $G_g(\mu, T)$  at  $T_e$ . To probe more closely the behavior of the coexistence density, we plot in Fig. 3(a) the diameter derivative  $-d\rho_d/dT$ , for the three system sizes studied. The data exhibit a clear peak close to  $T_e$ , which grows with increasing system size. Very similar behavior is also observed in the curvature of the spectator phase boundary  $-d^2\mu_\sigma/dT^2$ ; see Fig. 3(b). These peaks constitute, we believe, the finite-size-rounded forms of the divergences Eqs. (8) and (4). On the basis of finite-size scaling theory [13], the peaks are expected to grow in height like  $L^{\alpha/\nu}$ , with  $\nu$  the correlation length exponent. Unfortunately it is not generally feasible to extract estimates of  $\alpha/\nu$  in this way (even for simulations of lattice Ising models), because to do so necessitates an accurate measurement of the analytic background, for which the present system sizes are much too small. Nevertheless, the correspondence of the peak position with the independently estimated value of  $\tilde{T}_e$ , as well as the growth of the peak with increasing  $L$ , constitutes strong evidence supporting the existence of the predicted singularities.

In summary we have employed advanced Monte Carlo simulation techniques to study the first order phase boundary near the critical end point of a continuum binary fluid model. The results provide the first empirical evidence for singularities in the phase boundary and

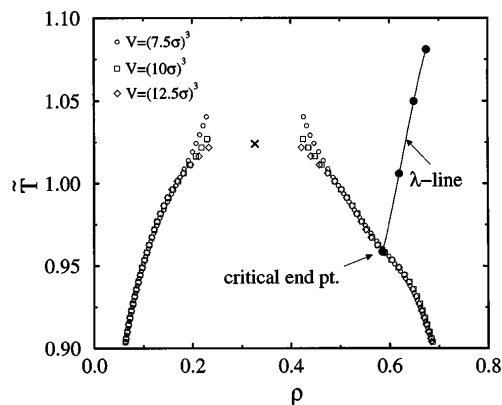


FIG. 2. The peak densities corresponding to the coexistence form of  $p_L(\rho)$  for the three systems sizes studied, plotted as a function of the temperature. Also shown is the estimated locus of the  $\lambda$  line (circles) and the liquid-gas critical point (cross). Statistical errors do not exceed the symbol sizes.

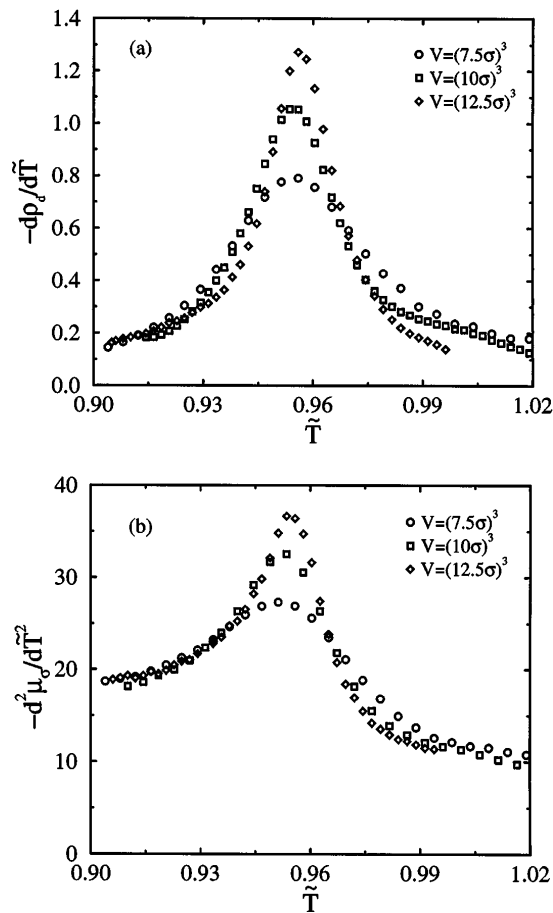


FIG. 3. (a) The numerical temperature derivative of the measured coexistence diameter  $-\rho_d/dT$  in the vicinity of the critical end point temperature. (b) The measured curvature of the phase boundary,  $-d^2\mu_\sigma/dT^2$ , in the vicinity of the critical end point temperature.

the coexistence curve diameter. We expect that similar effects should be experimentally observable (not only in binary fluids), and that due to the absence of finite-size rounding they should be even more marked than observed

here. Moreover, as we have shown, for asymmetrical systems such as real binary mixtures, the coexistence diameter is expected to exhibit a much stronger singularity than occurs in the present symmetrical model. This should therefore be particularly conspicuous.

The author thanks K. Binder and D.P. Landau for stimulating discussions. Helpful correspondence with A.D. Bruce, M.E. Fisher, M. Krech, and M. Müller is also gratefully acknowledged. This work was supported by BMBF Project No. 03N8008 C.

- [1] M.E. Fisher and P.J. Upton, Phys. Rev. Lett. **65**, 2402 (1990); M.E. Fisher and M.C. Barbosa, Phys. Rev. B **43**, 11 177 (1991).
- [2] M.E. Fisher and P.J. Upton, Phys. Rev. Lett. **65**, 3405 (1990).
- [3] M.C. Barbosa and M.E. Fisher, Phys. Rev. B **43**, 10 635 (1991); M.C. Barbosa, Phys. Rev. B **45**, 5199 (1992).
- [4] B.M. Law, Phys. Rev. Lett. **67**, 1555 (1991).
- [5] M.A. Anisimov, E.E. Gorodetskii, V.D. Kulikov, and J.V. Sengers, Phys. Rev. E **51**, 1199 (1995).
- [6] N.B. Wilding (unpublished).
- [7] M.P. Allen and D.J. Tildesley, *Computer Simulation of Liquids* (Oxford University Press, New York, 1987).
- [8] N.B. Wilding, Phys. Rev. E **52**, 602 (1995).
- [9] B. Berg and T. Neuhaus, Phys. Rev. Lett. **68**, 9 (1992).
- [10] We define a Monte Carlo step to comprise a particle transfer attempt (insertion or deletion) *and* a particle identity change (type  $1 \rightarrow 2$  or  $2 \rightarrow 1$ ) attempt.
- [11] C. Borgs and R. Kotecký, Phys. Rev. Lett. **68**, 1734 (1992).
- [12] A.M. Ferrenberg and R.H. Swendsen, Phys. Rev. Lett. **61**, 2635 (1988); **63**, 1195 (1989).
- [13] See, e.g., K. Binder, in *Computational Methods in Field Theory*, edited by H. Gausterer and C.B. Lang (Springer-Verlag, Berlin, Heidelberg, 1992), pp. 59–125.
- [14] A.D. Bruce and N.B. Wilding, Phys. Rev. Lett. **68**, 193 (1992).