Finite-size critical behavior in the Gibbs ensemble

A. D. Bruce
Department of Physics and Astronomy, The University of Edinburgh, Edinburgh EH9 3JZ, Scotland, United Kingdom
(Received 27 September 1996)

It is shown that the fluid density distribution measured in the Gibbs ensemble is related to the corresponding distribution measured within the grand canonical ensemble. The relationship leads directly to an explicit finite-size-scaling theory of critical behavior in the Gibbs ensemble, illuminates existing Monte Carlo data, and should provide the basis for high-precision determination of critical point parameters within the Gibbs ensemble framework. [S1063-651X(97)13602-9]

PACS number(s): 05.20.Gg, 02.70.Lq, 05.70.Jk, 05.70.Ce

I. INTRODUCTION

The past few years have seen significant advances in the application of Monte Carlo methods to the study of liquid-vapor phase coexistence. Two developments are relevant here. First, the *finite-sized behavior* observed near the liquid-vapor critical point, in the *grand canonical* ensemble (GCE), is now well-understood [1,2]: the behavior can be explicitly related to that of a near-critical Ising magnet, whose known universal signatures may be exploited to give high-precision estimates of the location of the liquid-vapor critical point, and to illuminate more subtle features of fluid critical behavior, such as scaling-field mixing. The second development is the *Gibbs ensemble* (GE) technique for the study of two-phase coexistence [3,4]. The GE comprises two subsystems of the fluid of interest, characterized by particle numbers N_i and volumes V_i $(i=1,2)$; the subsystems are free to exchange both particles and volume (and energy, with a common heat bath) subject to the constraints

$$N_1+N_2=N_0 \text{ and } V_1+V_2=V_0. \tag{1}$$

Given suitable choices of N_0 and V_0 the system displays phase-separation, with each subsystem housing one homogeneous phase. Problems associated with the formation of interfaces are avoided, as is the need to search for the value of the chemical potential locating coexistence [5]. The technique has been widely used in the study of both pure liquids and binary mixtures [4].

Notwithstanding its significant successes, key aspects of the Gibbs ensemble remain to be understood. Most notably, to date, the GE technique has lacked the support of a finite-size-scaling (FSS) theory, which is essential if one is to capitalize fully on Monte Carlo data gathered on systems of limited size, near criticality [6]. The need for such a theory has been recognized by others [7,8], and some steps in this direction have been taken [9,10] through the study of a ''restricted'' Gibbs ensemble (RGE) in which the subsystem volumes are *fixed* at $V_1=V_2=V_0/2$. These studies (based on a lattice gas representation of the fluid) provide evidence for Ising universality class scaling behavior, but with FSS functions that are ''different'' from that of the GCE. However the ''differences'' remain opaque and the implications (for FSS behavior) of volume fluctuations in the full GE remain unclear. Moreover, at a more basic qualitative level, the status of a third peak in the GE density distribution, observed in some simulations [7], has been questioned [9].

This paper addresses these issues. We show that the GE density distribution can be related to the corresponding GCE distribution; the relationship furnishes explicit predictions for the FSS form of the density distribution at criticality in terms of well-established functions; the predictions are in excellent accord with published RGE data; they also suggest that the third peak in the distribution is genuinely characteristic of the full GE, at criticality.

II. ANALYSIS

The analysis is straightforward. We denote by $E(\{\vec{r}\},N,V)$ the configurational energy of a fluid of N particles, of spatial coordinates $\{\vec{r}\}$, within volume V. The details of the interactions between the particles are irrelevant to the argument, except in as far as they are assumed to be short range (Lennard-Jones, for example). Periodic boundary conditions are to be understood. The equilibrium probability associated with a GE microstate, at temperature T, may then be written as [11]

$$P^{\mathrm{GE}}(\{\vec{r}\}^{(1)},\{\vec{r}\}^{(2)},N_1,V_1|N_0,V_0,T) = \frac{e^{-[E(\{\vec{r}\}^{(1)},N_1,V_1)+E(\{\vec{r}\}^{(2)},N_2,V_2)]/kT}}{Z^{\mathrm{GE}}(N_0,V_0,T)}, \tag{2}$$

where the remaining microstate coordinates, N_2 and V_2, are fixed (in terms of N_1 and V_1) by the constraint Eqs. (1), while Z^{GE} is a normalization constant. Integrating over the spatial coordinates we obtain

$$P^{\mathrm{GE}}(N_1,V_1|N_0,V_0,T) = Z^{\mathrm{GE}}(N_0,V_0,T)^{-1}Z(N_1,V_1,T)Z(N_2,V_2,T), \tag{3}$$

where

$$Z(N,V,T)=\frac{1}{N!}\int_V d\vec{r}_1\cdots d\vec{r}_N e^{-E(\{\vec{r}\},N,V)/kT} \tag{4}$$

is the canonical partition function for N particles within volume V. The associated grand canonical partition function can be written as [12]

$$\mathcal{Z}(\mu,V,T)=\sum_{N=0}^{\infty} e^{\mu N/kT}Z(N,V,T), \tag{5}$$

where μ is the chemical potential. The grand canonical distribution for particle number is then

$$P(N|\mu,V,T)=[\mathcal{Z}(\mu,V,T)]^{-1}e^{\mu N/kT}Z(N,V,T). \tag{6}$$

Utilizing this result in conjunction with Eq. (3) gives immediately

$$P^{\mathrm{GE}}(N_1,V_1|N_0,V_0,T) =A(V_1,V_2,N_0,\mu,T)P(N_1|\mu,V_1,T)P(N_2|\mu,V_2,T), \tag{7a}$$

where

$$A(V_1,V_2,N_0,\mu,T) =\mathcal{Z}(\mu,V_1,T)\mathcal{Z}(\mu,V_2,T)e^{-\mu N_0/kT}[Z^{\mathrm{GE}}(N_0,V_0,T)]^{-1} \tag{7b}$$

is independent of N_1. For some purposes (but not all) it is useful to rewrite Eq. (7a) in the form

$$P^{\mathrm{GE}}(N_1,V_1|N_0,V_0,T) =P^{\mathrm{GE}}(V_1|N_0,V_0,T)P^{\mathrm{RGE}}(N_1|V_1,N_0,V_0,T), \tag{8a}$$

where

$$P^{\mathrm{RGE}}(N_1|V_1,N_0,V_0,T) =\frac{P(N_1|\mu,V_1,T)P(N_2|\mu,V_2,T)}{\Sigma_{N_1=0}^{N_0}P(N_1|\mu,V_1,T)P(N_2|\mu,V_2,T)} \tag{8b}$$

is the restricted GE distribution. Equations (7) and (8) are our key results. They have one rather odd feature which deserves immediate comment: the left-hand side (lhs) [of Eqs. (7a) and (8b)] makes no reference to the chemical potential which appears on the right-hand side (rhs). The resolution lies in the fact that [as one sees from Eq. (6)] the GCE distributions associated with *different* chemical potentials are related by a simple reweighting [13]

$$P(N|\mu',V,T)\propto e^{(\mu'-\mu)N/kT}P(N|\mu,V,T) \tag{9}$$

for variations on N. It follows that

$$P(N_1|\mu',V_1,T)P(N_0-N_1|\mu',V_2,T) \propto P(N_1|\mu,V_1,T)P(N_0-N_1|\mu,V_2,T) \tag{10}$$

for variations on N_1. The rhs of Eq. (8b) is thus, in principle, invariant against the choice of μ. Nevertheless, in a practical sense, the choice of the value of μ to be utilized *is* significant: the mapping provided by Eqs. (7a) and (8b) is most immediately exploitable when the value of μ chosen leads to GCE distributions (on the rhs) whose weight lies predominantly in the region of interest, namely that in which the resultant distribution (the lhs) is concentrated.

The mapping from GE to GCE is quite general; we shall apply it only at the liquid-vapor critical temperature $T=T_c$. We shall make the *choice* $\mu=\mu_c$: we shall see that this choice allows us to deal with a *range* of possible values of the overall system density. With these parameter settings each of the GCE distributions on the rhs of Eq. (8b) describes an open system *at* criticality. For sufficiently large system size, such a GCE distribution has a universal scaling form (dependent upon space dimensionality d), characteristic of the Ising universality class [1,2]:

$$P(N|\mu,V,T_c)=V^{-1}P(\rho|\mu,V,T_c) \simeq a_{\mathcal{M}}^{-1}V^{-\delta/(1+\delta)}\tilde{p}^{\star}_{\mathcal{M}}\ (V^{1/(1+\delta)}a_{\mathcal{M}}^{-1}[\rho-\rho_c]), \tag{11}$$

where $a_{\mathcal{M}}$ is a nonuniversal scale factor, $\rho\equiv N/V$ is the number density, ρ_c is its critical value, δ is the equation of state exponent, and $\tilde{p}^{\star}_{\mathcal{M}}$ is a universal function, whose form is well established for both two and three dimensions [1,2]. Provided *both* the subsystems are sufficiently large (we shall return to this point) we may insert this result directly into Eq. (8b) and write the RGE density distribution in the form

$$P^{\mathrm{RGE}}(\rho_1|V_1,N_0,V_0,T_c)\simeq\mathcal{A}\tilde{p}^{\star}_{\mathcal{M}}\ (v_1^{1/(1+\delta)}x_1) \times\tilde{p}^{\star}_{\mathcal{M}}\ (v_2^{1/(1+\delta)}x_2), \tag{12}$$

where $\mathcal{A}$ is determined by normalization. We have introduced reduced volumes $v_i\equiv V_i/V_0$ and scaling variables

$$x_i\equiv(\rho_i-\rho_c)/\rho_u \quad i=1,2 \quad \text{with} \quad \rho_u\equiv a_{\mathcal{M}}V_0^{-1/(1+\delta)}, \tag{13}$$

where $\rho_i\equiv N_i/V_i$. Given the constraint Eqs. (1), the scaling variables are related by

$$x_1v_1+x_2v_2=\Delta x_0, \tag{14}$$

where

$$\Delta x_0=(\rho_0-\rho_c)/\rho_u \tag{15}$$

and $\rho_0=N_0/V_0$ is the *overall* system density. We proceed to explore Eq. (12) in a range of cases.

III. RESULTS AND DISCUSSION

Case A: $\rho_0=\rho_c$; $v_1\ll v_2$

Suppose that the overall system density coincides with its critical value, $\rho_0=\rho_c$, so that $\Delta x_0=0$ [Eq. (15)]. If $v_1\ll v_2$, Eq. (14) shows that the scaling variables satisfy $|x_2|\ll|x_1|$. Over the region in which the RGE density distribution (12) has significant weight it may then be approximated by

$$P^{\mathrm{RGE}}(\rho_1|V_1,N_0,V_0,T_c)\simeq\mathcal{A}\tilde{p}^{\star}_{\mathcal{M}}\ (v_1^{1/(1+\delta)}x_1)\tilde{p}^{\star}_{\mathcal{M}}\ (0). \tag{16}$$

In this case the (restricted) Gibbs density distribution is thus identical to the critical grand canonical density distribution. This is as it should be: in this regime the second subsystem acts as a particle reservoir for the first. This distribution is plotted in Figs. 1(a) and 2(a), for (respectively) the $d=2$ and $d=3$ realizations of the Ising-fluid universality class [1,2],

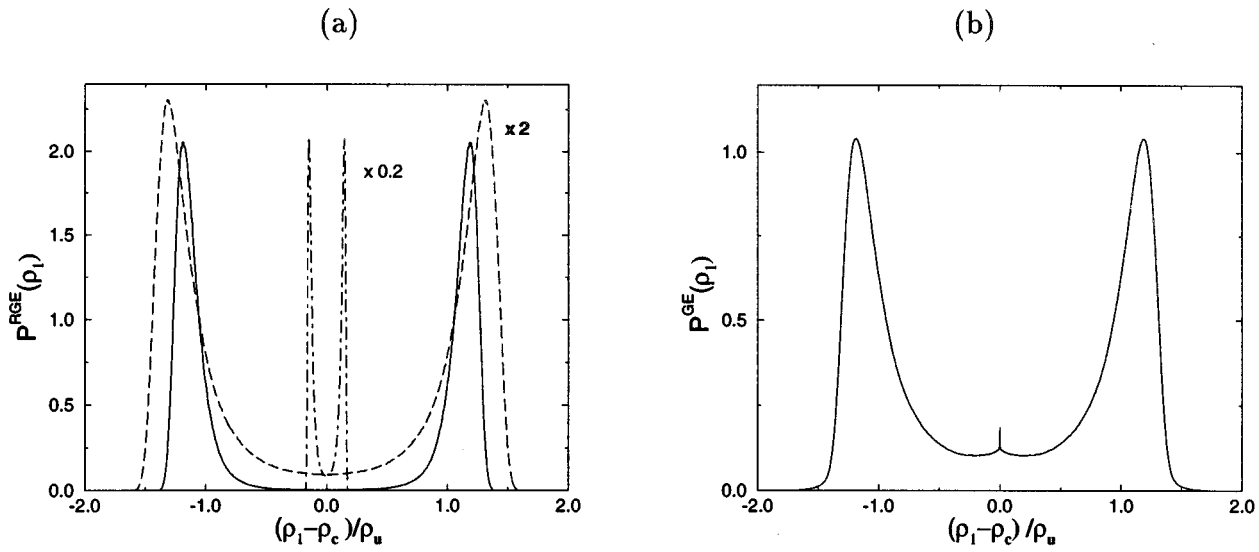

FIG. 1. Various realizations of critical Gibbs ensemble distributions for the density $\rho_1 = N_1/V_1$ for a two-dimensional fluid. The density scale is the same for each graph with units ρ_u defined in Eq. (13) [14]. (a) $v_1 = 0.1$ (dashed line; has been multiplied by 2) and $v_1 = 0.9$ (dot-dashed line; has been multiplied by 0.2), for both of which the RGE approaches the grand canonical distribution; and $v_1 = v_2$ (solid line) giving the symmetric RGE studied in Refs. [9,10]. (b) the full (idealized) GE distribution determined on the basis of assumptions detailed in the text.

for $v = 0.1$. The shape of such distributions can be conveniently characterized by the cumulant ratio [15]

$$G \equiv \frac{3\langle \Delta\rho_1^2\rangle^2 - \langle \Delta\rho_1^4\rangle}{2\langle \Delta\rho_1^2\rangle^2} = \frac{3\langle x_1^2\rangle^2 - \langle x_1^4\rangle}{2\langle x_1^2\rangle^2}, \tag{17}$$

where $\Delta\rho_1 \equiv \rho_1 - \rho_c$. For the $d = 2$ GCE limit the value of G is well established: $G^{\mathrm{GCE}}(d=2) = 0.9154(10)$ [16].

Case B: $\rho_0 = \rho_c$; $v_1 = v_2$

Consider now the symmetrical version of the restricted Gibbs ensemble (SRGE) where $v_1 = v_2$; this is the case studied by Mon and Binder [9,10]. The density distribution is of the form

$$P^{\mathrm{RGE}}(\rho_1 | V_1, N_0, V_0, T_c) \simeq \mathcal{A}[\tilde{p}^{\star}_{\mathcal{M}}(\tilde{x}_1)]^2,$$

with

$$\tilde{x}_1 = 2^{-1/(1+\delta)} x_1, \tag{18}$$

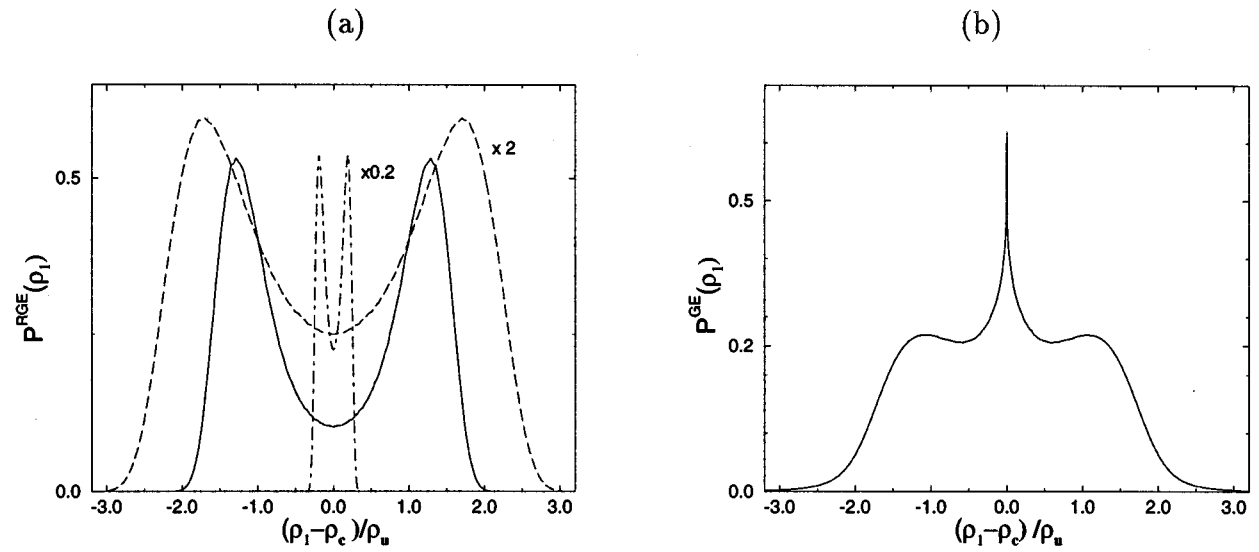

FIG. 2. Critical Gibbs ensemble distributions for the density $\rho_1 = N_1/V_1$ for a three-dimensional fluid. For details see the caption to Fig. 1.

where we have used the fact that $\tilde{p}^{\star}_{\mathcal{M}}$ is *even* [1]. This distribution again follows from knowledge of the universal grand canonical form; it is also shown in Figs. 1(a) and 2(a). Again it may be characterized by the value of the cumulant ratio G, Eq. (17). For this case we find, in $d=2$, $G=G^{\mathrm{SRGE}}(d=2)\simeq 0.976$, in excellent agreement with the result $G^{\mathrm{SRGE}}(d=2)=0.977(2)$ obtained in Mon's Monte Carlo study of the two-dimensional lattice gas representation of the SRGE [10,15], providing strong corroboration of our basic equations.

Case C: $\rho_0=\rho_c$; $v_1 \gg v_2$

This is the complement of case A. Now the scaling variables satisfy $|x_1| \ll |x_2|$ and the RGE density distribution may be approximated by

$$\begin{aligned} P^{\mathrm{RGE}}(\rho_1|V_1,N_0,V_0,T_c) &\simeq \mathcal{A}\tilde{p}^{\star}_{\mathcal{M}}(0)\tilde{p}^{\star}_{\mathcal{M}}(v_2^{1/(1+\delta)}x_2) \\ &= \mathcal{A}\tilde{p}^{\star}_{\mathcal{M}}(0)\tilde{p}^{\star}_{\mathcal{M}}([v_1/v_2]^{\delta/(1+\delta)}v_1^{1/(1+\delta)}x_1). \end{aligned} \tag{19}$$

The RGE distribution is thus again effectively grand canonical, but now by virtue of the fact that subsystem 1 acts as a particle reservoir for subsystem 2. While the *form* of the density distribution is the same as in case A, its *scale* (the typical size of the fluctuations) is reduced with respect to case A, as exemplified in the results (for $v_1=0.9$) shown in Figs. 1(a) and 2(a).

Case D: $\rho_0 \neq \rho_c$; $v_1 \simeq v_2$

Suppose now that, while $T=T_c$ (as throughout this argument), the overall system density does *not* coincide with ρ_c. We may continue to use the mapping onto the *critical* grand canonical distribution (recall that μ is at our discretion) but must do so carefully in the light of the constraint on the scaling variables expressed in Eq. (14), where, now, $\Delta x_0 \neq 0$. Given the rapid decay of the function $\tilde{p}^{\star}_{\mathcal{M}}$ [see Eq. (20) below], for large enough Δx_0 (in principle for *any* nonzero value of $\rho_0-\rho_c$, at large enough N_0 and V_0) the dominant contributions to P^{RGE} will arise when the arguments of *both* the functions appearing on the rhs of Eq. (12) are large compared to unity (in fact, close to Δx_0). In this regime it has been conjectured [17], and subsequently confirmed by Monte Carlo studies [18], that

$$\ln\tilde{p}^{\star}_{\mathcal{M}}(x) \simeq -a_{\infty}|x|^{\delta+1}+O(\ln x), \tag{20}$$

where a_{∞} is a constant, implicit in the form of the universal function $\tilde{p}^{\star}_{\mathcal{M}}$. Feeding this expansion back into Eq. (12) we find that the competition between the two grand canonical distributions produces a turning point at $x_1=x_2=\Delta x_0$. Expanding around this turning point shows that the RGE distribution for the density ρ_1 is Gaussian with mean and variance

$$\begin{aligned} \overline{\rho_1} &= \rho_0, \\ \overline{[(\rho_1-\rho_0)/\rho_u]^2} &= [a_{\infty}\delta(\delta+1)v_1(1+v_1/v_2) \\ &\quad \times |(\rho_0-\rho_c)/\rho_u|^{\delta-1}]^{-1}. \end{aligned} \tag{21}$$

The mean is the constrained density of the whole system. As one might anticipate, the variance diverges, as ρ_0 approaches ρ_c, with a power that matches that characterizing the divergence of the compressibility (as $\mu \to \mu_c$, at $T=T_c$) in the GCE.

Case E: The GE density distribution

Thus far we have considered only various realizations of the RGE in which the subsystem volumes are fixed. In most GE studies the subvolumes are allowed to vary; the subsystem density distribution established is then an average of RGE distributions. To evaluate this average we need to know the form of the distribution $P^{\mathrm{GE}}(V_1)$ appearing in Eq. (8a); equivalently we need the subvolume dependence of the function A featured in Eq. (7a), which, in turn, reflects the volume dependence of the grand canonical partition function [Eq. (7b)]. In the thermodynamic limit, at least, we may make the identification [12]

$$\lim_{V\to\infty}\frac{\ln\mathcal{Z}(\mu,V,T)}{V}=\frac{\tilde{p}(\mu,T)}{kT}, \tag{22}$$

where $\tilde{p}(\mu,T)$ is the pressure. It follows that

$$\begin{aligned} \ln A(V_1,V_2,N_0,\mu,T) &= \frac{\tilde{p}(\mu,T)(V_1+V_2)}{kT} - \ln[e^{\mu N_0/kT}Z^{\mathrm{GE}}(N_0,V_0,T)] \\ &\quad + (\text{corrections}) \\ &= \ln B(V_0,N_0,\mu,T) + (\text{corrections}), \end{aligned} \tag{23}$$

where B is independent of both subsystem particle numbers N_i, *and* volumes V_i. The unspecified remainder in this equation represents the contributions arising from the finite-size corrections to the thermodynamic limit in Eq. (22). For the periodic boundary conditions supposed here we would expect [19] that the leading corrections to Eq. (22) at μ_c, T_c are $O(1/V)$ [rather than $O([\ln V]/V)$], so that the neglect of the corrections to Eq. (23) may not be unreasonable for finite-sized systems. We explore the implications of this assumption. Taking care to pick up other volume-dependent factors [which disappear from the restricted distribution, Eqs. (8b) and (12), courtesy of normalization conditions] we find

$$\begin{aligned} P^{\mathrm{GE}}(\rho_1,V_1|N_0,V_0,T_c) &\simeq \mathcal{B}v_1^{1/(1+\delta)}v_2^{-\delta/(1+\delta)}\tilde{p}^{\star}_{\mathcal{M}} \\ &\quad \times (v_1^{1/(1+\delta)}x_1)\tilde{p}^{\star}_{\mathcal{M}}([v_1/v_2]^{\delta/(1+\delta)}v_1^{1/(1+\delta)}x_1), \end{aligned} \tag{24}$$

where $\mathcal{B}$ is determined by normalization. One can then integrate numerically [20] over the subvolume of system 1 to obtain the full Gibbs ensemble density distribution

$$P^{\mathrm{GE}}(\rho_1|N_0,V_0,T_c)=\int_0^{V_0}dV_1P^{\mathrm{GE}}(\rho_1,V_1|N_0,V_0,T_c). \tag{25}$$

The resulting distributions are shown in Fig. 1(b) (for $d=2$) and Fig. 2(b) (for $d=3$); they have three notable features.

First, the two distinct peaks (the precursors of the peaks that can be associated, unambiguously, with liquid and vapor phases, further down the coexistence curve) are present in

the GE distribution *at* criticality. Thus the suggestion in [7] that the peaks associated with the coexisting phases disappear from the GE density distribution *below* the critical temperature is almost certainly incorrect [21].

Second, while the GCE distribution decays *exponentially* at large density fluctuations [cf. Eq. (20)], the GE distribution shows *power-law* decay [22], which is reflected in the wings visible in Figs. 1(b) and 2(b). This behavior can be traced to the contributions made by systems (corresponding to case A, above) with $v_2 \gg v_1$. One can, perhaps, see traces of this behavior in Fig. 1 of Ref. [7].

Third, the GE distribution displays further structure at intermediate densities, in the form of a cusp at ρ_c. The origin of this structure is easily identified: it reflects the behavior of systems with $v_1 \gg v_2$ (case C, above) whose densities are more tightly confined to the region $\rho \simeq \rho_c$, and whose contributions to the GE average are accentuated by the prefactor in Eq. (24). A ''third peak'' in such a region of ρ values was observed in Monte Carlo studies by Smit *et al.* [7,23]. These authors also provide phenomenological arguments, taking account of mixed phase configurations, which show how such structure may come about. The appropriateness of such an analysis in the vicinity of the critical point has been questioned by Mon and Binder [9], who suggest that the additional structure observed in the simulations is just a small-system artifact. The results here suggest that, although the phenomenological arguments of [7] are indeed untrustworthy in detail near criticality, the structure in question may well be an authentic feature of the GE critical behavior. We must note, however, that the results of Figs. 1(b) and 2(b) are, in a sense, also ''untrustworthy in detail.'' They describe an idealized experiment in which one realizes subvolumes covering the *entire* range $0<v_1<1$, *all* of which are assumed to satisfy the conditions for the use of a scaling theory. In practice, of course, realizations of the extreme cases (where $v_1 \to 0$ or $v_1 \to 1$) will always violate these conditions. The cusp (originating, as it does, in the $v_1 \to 1$ regime) is certainly idealized in this sense. But the *principle*—that the contributions arising from this regime are concentrated towards the center of the distribution—appears more secure, and it seems reasonable to interpret the observed ''third peak'' as a manifestation of this effect [24].

Although the results in Figs. 1(b) and 2(b) do, then, represent an unrealizable ideal, the predictions made here *are* testable and exploitable. In particular, the structure of the RGE distribution for *every* pair of subvolumes which *do* satisfy the scaling conditions should be given by Eq. (12), with the relative scales of the distributions for different subvolume pairs fully prescribed. If one utilizes *only* data drawn from such members of the ensemble, it should thus be possible to draw on established forms of the relevant distributions (incorporating the effects of field mixing) [1,2] to refine the location of critical point parameters, for realistically modeled systems, within the GE framework. Certainly one should be able to improve upon the precision and confidence levels of strategies which rely on fitting a power law to the behavior of the order parameter, for which the separation of the two peaks in the density distribution is typically taken as a finite-size estimator: such strategies fail to capitalize fully on the wealth of information available in the full *distribution.*

Finally we note that the results presented here may cast some light on the observation that, empirically, power-law-fitting strategies—whatever their limitations—seem to provide better estimators of critical-point parameters in the GE than in either the GCE [7] or the RGE [25]. If this observation is interpreted as meaning that finite-size effects are ''smaller'' in the GE than in either of the other ensembles, it is somewhat paradoxical: it is hard to see how one could *reduce* finite-size effects by folding in data gathered on systems substantially *smaller* than the largest studied. The interpretation is, probably, more subtle. It rests on the fact that the power-law-fitting strategies implicitly take the coalescence of the two distinct peaks in the measured density distribution as the signature of criticality. In all three ensembles this will lead to an overestimate of the critical temperature, since in all three cases it appears [21] that the observed distribution, in any system of finite size, will retain distinct peaks *at* the bulk system critical point, and coalescence will occur at an effective critical temperature lying *above* the bulk value [26]. But, in the case of the GE, the additional weight in the center of the distribution associated with the ''third peak'' presumably makes this effect (the difference between bulk and effective values) smaller, for any given system size. The observed ''improvement'' of GE estimates can thus be traced to the partial [27] cancellation of one finite-size effect (the two-peaked structure, *at* criticality) by another (the contributions made by the *smallest* volumes visited in the ensemble).

ACKNOWLEDGMENTS

I am most grateful to Nigel Wilding for helpful correspondence, drawing my attention to Ref. [25] in particular, and for allowing me to use the data of Ref. [2].

[1] A.D. Bruce and N.B. Wilding, Phys. Rev. Lett. **68**, 193 (1992); N.B. Wilding and A.D. Bruce, J. Phys. Condens. Matter **4**, 3087 (1992).

[2] N.B. Wilding, Phys. Rev. E **52**, 602 (1995).

[3] A.Z. Panagiotopoulos, Mol. Phys. **61**, 813 (1987); A.Z. Panagiotopoulos, N. Quirke, M. Stapeleton, and D.J. Tildesley, *ibid.* **63**, 527 (1988).

[4] For a review see A.Z. Panagiotopoulos, in *Observation and Prediction of Phase Transitions in Complex Fluids*, edited by M. Baus, R.F. Rull, and J.P. Ryckaert (Kluwer, Dordrecht, 1995), p. 463.

[5] In the GE one needs only to ensure that the overall density lies somewhere in the range between those of the coexisting phases; this constraint sharpens with the approach to the critical point.

[6] For a review of FSS, see *Finite Size Scaling and Numerical Simulation of Statistical Systems,* edited by V. Privman (World Scientific, Singapore, 1990).

[7] B. Smit, Ph. de Smedt, and D. Frenkel, Mol. Phys. **68**, 931 (1989).
[8] A.Z. Panagiotopoulos, Int. J. Thermophys. **15**, 1057 (1994).
[9] K.K. Mon and K. Binder, J. Chem. Phys. **96**, 6989 (1992).
[10] K.K. Mon, Phys. Rev. B **47**, 5497 (1993).
[11] We make no notational distinction between the probability distributions of discrete variables and the probability densities of continuous variables.
[12] See, e.g., T.L. Hill, *Statistical Mechanics* (McGraw-Hill, New York, 1956).
[13] See, e.g., A.M. Ferrenberg and R.H. Swendsen, Phys. Rev. Lett. **61**, 2635 (1988).
[14] With this choice of units, and with the conventions implicit in the definition of the scaling function $\tilde{p}^{\star}_{\mathcal{M}}$ [1], the variance of the density in the grand canonical limit described by Eq. (16) is given by $\langle \Delta\rho_1^2 \rangle / {\rho_u}^2 = {v_1}^{-2/(1+\delta)}$.
[15] Some authors prefer to use the cumulant ratio U introduced by K. Binder, Z. Phys. B **43**, 119 (1981); the relationship between the two cumulant ratios is $G = -U/2$.
[16] D. Nicolaides and A.D. Bruce, J. Phys. A **21**, 233 (1988); T.W. Burkhardt and B. Derrida, Phys. Rev. B **32**, 7273 (1985).
[17] A.D. Bruce, J. Phys. A **28**, 3345 (1995); R. Hilfer, Z. Phys. B **96**, 63 (1994); R. Hilfer and N.B. Wilding, J. Phys. A **28**, L281 (1995).
[18] G.R. Smith and A.D. Bruce, J. Phys. A **28**, 6623 (1995).
[19] V. Privman and M.E. Fisher, Phys. Rev. B **30**, 322 (1984); see also Ref. [6].
[20] Some care is needed to deal with the $v_1 \to 1$ and $v_1 \to 0$ limits.
[21] The note of reserve reflects the fact that the predictions for the full GE (i.e., the average over volumes) rest on the assumptions, detailed in the text, about the corrections featuring in Eq. (23).
[22] Appealing to Eqs. (11) and (25) it is not hard to show that, for large $|\rho_1 - \rho_c|$, $P^{\rm GE}$ must fall off as $|\rho_1 - \rho_c|^{-(\delta+2)}$ (given $\rho_0 = \rho_c$, and $T = T_c$).
[23] There are also some indications of structure of this kind in Fig. 5 of Ref. [4].
[24] The peak observed does not have the sharpness of the cusp apparent in Figs. 1(b) and 2(b), but this is to be expected, since, as noted, the universal scaling form 11 will not describe the smallest systems visited in the simulations.
[25] J.R. Recht and A.Z. Panagiotopoulos, Mol. Phys. **80**, 843 (1993); D.G. Green, G. Jackson, E. de Miguel, and L.F. Rull, J. Chem. Phys. **101**, 3190 (1994).
[26] See also the discussion in Ref. [9].
[27] And nonuniversal, in view of the remarks in [24].