Influence of quenched impurities on first-order phase transitions

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(Received 25 September 1978)

Microscopic random quenched impurities may or may not produce rounding of a first-order phase transition. We derive a criterion for the appearance of rounding due to local fluctuations in thermodynamic phase. Such fluctuations occur when the free-energy lowering due to taking advantage of local fluctuations in impurity density more than offsets the free-energy cost of the interface produced. The argument also predicts the spatial scale of such phase fluctuations, when they occur. In some situations this scale is just the coherence length ξ; in others, the inhomogeneity develops over "domains," which may be much larger than ξ. Near a second-order transition our criterion reduces to the one due to Harris. We specifically discuss what happens when a first-order transition becomes second order as an external parameter is varied.

I. INTRODUCTION

What effect do microscopic random quenched impurities (or other *local* defects) have on thermodynamic behavior near phase transitions? The central issue is whether, near the phase transition, the coherence length is sufficiently large effectively to "average out" the inhomogeneity, thus producing a sharp, pure-system-like transition, or whether, on the other hand, the growth of correlations is blocked by the impurities, effective inhomogeneity remains, and the transition becomes "smeared" or otherwise anomalous. Many authors have studied these questions in the context of second-order transitions.[1] First-order behavior has, by contrast, attracted much less attention.[2] This is probably due to the fact that the coherence length remains finite at a first-order transition, so "universal" behavior is not to be expected.

The question which we address in this paper is, does the presence of microscopic inhomogeneity produce *significant* rounding of a transition which is sharp and first order in the pure, homogeneous system? Our argument, which is heuristic but (we hope) physically correct, predicts that (a) there are several quite distinct types of behavior possible and (b) which one of these is observed in a particular sample depends in a specific way on sample parameters. We have not here attempted, comparison of the theory with experimental data: There are, in practice, severe difficulties to be overcome in preparing and characterizing microscopically random samples. Furthermore, first-order data are complicated by the presence of metastability and hysteresis.[3] Nevertheless, recent experimental developments are not unpromising.[4]

Our discussion is a simple generalization of an appealing argument used by Harris[5] to provide a *necessary* condition for the existence of a sharp *second*-order transition in an impure system: Suppose there is to be sharp, pure-system-like critical behavior at a temperature $T_c(p)$ (p is the fractional concentration of impurity sites). At a distance from criticality $\Delta T \equiv |T - T_c(p)|$, the size of a typical correlated region is measured by the coherence length $\xi \sim (\Delta T)^{-\nu}$. Each such "coherence volume" contains $n_I = p\xi^d + \Delta n_I$ impurities, where the typical fluctuation is $\Delta n_I \sim [p(1-p)\xi^d]^{1/2}$. The corresponding fluctuations in local impurity density, $\Delta p \sim [p(1-p)]^{1/2}\xi^{-d/2}$, produce local variations in T_c, $\Delta T_c \sim |dT_c(p)/dp|\Delta p$. Consistency then requires

$$\Delta T_c << \Delta T \tag{1}$$

for ΔT sufficiently small. [Scaling relations translate Eq. (1) into the condition that the specific-heat exponent α must be negative.] The corresponding argument for first-order transitions is closely related, as we shall see; however, additional (nonuniversal) parameters appear, which may represent experimentally useful degrees of freedom.

II. DERIVATION

Consider for specificity a magnetic lattice model in which each site has a probability p of being occupied by some impurity species. The system is assumed to have a transition at a temperature $T_f(p)$. When $p=0$, the system is pure and the transition is sharp and first order. We focus on the rounding of the transition caused by the introduction of impurities. The coherence length ξ (measured in lattice spacings) remains finite at $T_f(p)$ and provides a natural length scale. The dimensionless parameter $p\xi^d$ represents the average number of impurities in each coherence volume. When $p\xi^d \ll 1$, then all but a fraction $p\xi^d$ of the sample is effectively pure, so there is no significant deviation from pure-system thermodynamics. We treat the opposite limit $p\xi^d \gg 1$. Each coherence volume has its own impurity density $p+\Delta p$. The typical density fluctuation goes as $\Delta p \sim [p(1-p)]^{1/2}\xi^{-d/2}$, in precise parallel to Harris's argument. The corresponding spread in transition temperatures is

$$\Delta T_f = \left|\frac{dT_f(p)}{dp}\right| \Delta p \ . \tag{2}$$

It is tempting but wrong to argue now that each coherence volume undergoes a transition at its own $T_f(p+\Delta p)$, thus leaving the sample in an inhomogeneously mixed phase between $T_f(p)-\Delta T_f$ and $T_f(p)+\Delta T_f$, i.e., rounding or "smearing" the transition over a temperature range ΔT_f. The difficulty is that, when one coherence volume changes phase relative to its neighbors, an *interface* is created. In order for the phase change to take place, the lowering in volume free energy must more than compensate the cost in interfacial ("surface") free energy. This balance between volume and interfacial contributions[6] determines both the temperature range ΔT_r of the rounding and the spatial scale of phase inhomogeneity. Consider the situation depicted in Fig. 1. Phase 1 (the high-temperature phase) becomes more stable (lower free energy) relative to phase 2 (the low-temperature phase) as the impurity concentration is increased from p to $p+\Delta p$. The temperature $T_f(p)$ of the first-order phase transition is, therefore, lowered by the addition of impurities and it is easy to see that

$$\frac{dT_f(p)}{dp} = -\frac{\partial}{\partial p}(f_2-f_1)\Big/\frac{\partial}{\partial T}(f_2-f_1) \ . \tag{3}$$

Suppose the sample as a whole has impurity concentration p and is at a temperature $T=T_f(p)-\Delta T$ with $T_f(p+\Delta p) < T < T_f(p)$, i.e., nominally in phase 2 (see Fig. 1). Any coherence volume in the sample with *local* impurity concentration $p+\Delta p$ will actually prefer to be in phase 1, *provided* that the cost in interface energy is not too great. The condition that the cost in interfacial free energy be sufficient to stabilize the system against such a local phase fluctuation is

$$\xi^d[f_2(p+\Delta p, T_f(p)-\Delta T) - f_1(p+\Delta p, T_f(p)-\Delta T)] < C\sigma\xi^\lambda \ , \tag{4}$$

where σ is the interfacial tension and $C\xi^\lambda$ measures the amount of interface formed. Normally, $\lambda = d-1$; however, there are special situations involving coexistence between ordered phases of systems with continuous symmetries[2] where $\lambda = d-2$, as we shall comment on below. C is a geometrical factor. Dividing by ξ^d and using Eq. (3), we obtain for small ΔT and Δp the stability condition for an isolated coherence volume,[7]

$$\Delta T_f \equiv \left|\frac{dT_f(p)}{dp}\right| \Delta p < \frac{C\sigma T_f(p)}{L(p)\xi^{d-\lambda}} + \Delta T \ , \tag{5}$$

where we have noted that

$$\left[T\frac{\partial}{\partial T}(f_2-f_1)\right]_{p,T_f(p)} \equiv L(p) \ ,$$

the latent heat per site at the transition. Note already the close connection with the Harris criterion[5]: Near a *second*-order transition (and for $\lambda = d-1$)

$$\sigma \sim (\Delta T)^{2-\alpha-\nu} \ , \quad \xi^{d-\lambda} \sim (\Delta T)^{-\nu} \ ,$$

and

$$L \sim (\Delta T)^{1-\alpha} \ ,$$

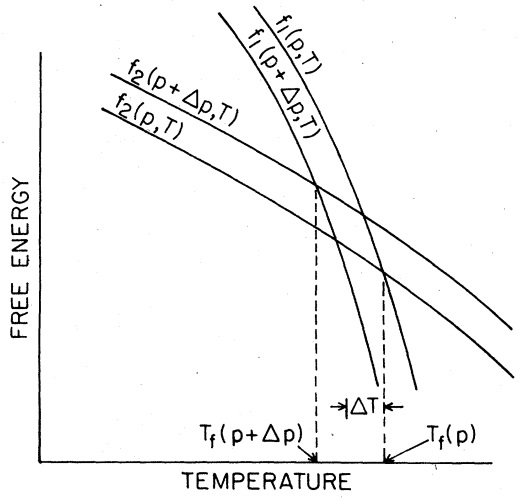

FIG. 1. Free energy per site as a function of temperature. $f_1(p,T)$ and $f_2(p,T)$ denote free energies of the high- and low-temperature phases, respectively. A first-order transition occurs at $T_f(p)$, where the two free energies are equal. Addition of impurities lowers the transition temperature.

so the whole right-hand side of Eq. (5) is proportional to ΔT and, as $\Delta T \to 0$, Eq. (5) reduces to Eq. (1).

In some situations it will pay to form a fluctuation involving a cluster of coherence volumes of linear dimension $l > \xi$, in order to lower the interfacial "barrier" by eliminating internal surfaces. Summing Eq. (4) over such a cluster generalizes Eq. (5) to[7]

$$\left|\frac{dT_f(p)}{dp}\right|\Delta p < \frac{C\sigma T_f(p)}{L(p)l^{d-\lambda}} + \Delta T \ , \quad l \geq \xi \ , \qquad (6)$$

where Δp now represents the local density fluctuation in the cluster of l^d sites.

In a quenched random system there is *some* probability for arbitrary local density fluctuations, limited only by $0 \leq p + \Delta p \leq 1$. Indeed, the probability of density fluctuation Δp in a region of N sites follows a binomial distribution,

$$\mathcal{P}_N(\Delta p) = N\frac{N!p^{N(p+\Delta p)}(1-p)^{N(1-p-\Delta p)}}{[N(p+\Delta p)]![N(1-p-\Delta p)]!}$$
$$\approx \left[\frac{N}{2\pi p(1-p)}\right]^{1/2} e^{-N(\Delta p)^2/2p(1-p)} \ , \qquad (7)$$

where the approximation is good provided[8]

$$N^{1/3}\Delta p < (p+\Delta p)^{1/6} \ , \quad (1-p-\Delta p)^{1/6} \ .$$

Because d exceeds λ, it is clear from Eq. (4) that, for arbitrary positive[7] Δp and ΔT clusters of sufficiently large size will always be unstable against phase fluctuation; however, if $\Delta p >> [p(1-p)]^{1/2}l^{-d/2}$, the probability of such clusters (and their influence on thermodynamic functions) will, from Eq. (7), be exponentially small. We distinguish these "precursor" effects, which are always present, from real "rounding," arising from Clusters with $\Delta p \sim [p(1-p)]^{1/2}l^{-d/2}$, which have probabilities of order unity. Equation (6) shows that these "probable" clusters will be unstable at $T_f(p) - \Delta T$, whenever

$$\Delta T < g(l) \equiv [p(1-p)]^{1/2}\left|\frac{dT_f(p)}{dp}\right| l^{-d/2}$$
$$- \frac{C\sigma T_f(p) l^{\lambda - d}}{L(p)} \ , \quad l \geq \xi \ . \qquad (8)$$

There is no "probable" instability for sufficiently large ΔT. Such instability first develops at a particular cluster size l^*, when

$$\Delta T = \Delta T_r \equiv g(l^*) \ , \qquad (9)$$

which determines the typical width ΔT_r of the rounding. For $0 < \Delta T < \Delta T_r$ a range of l's are unstable

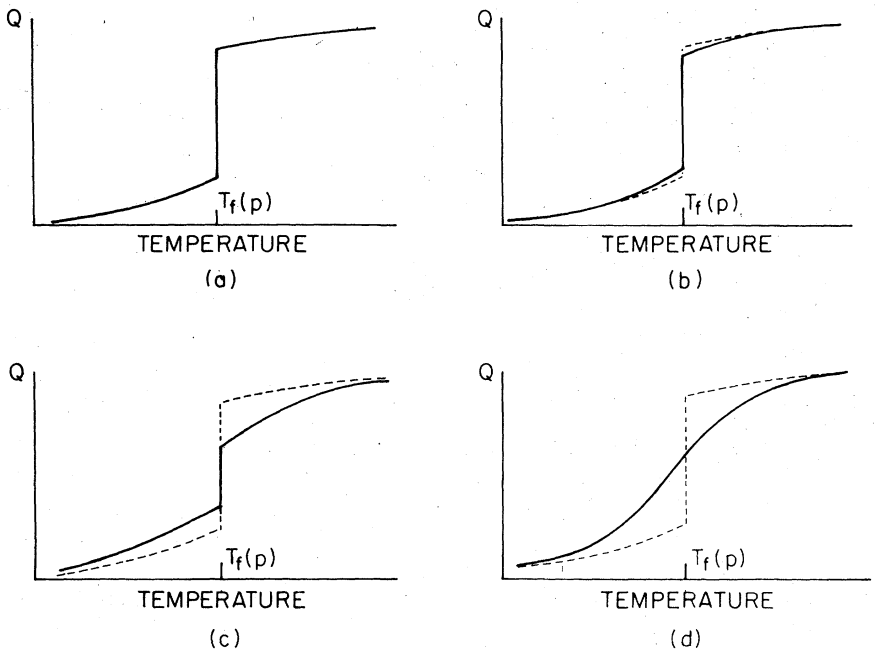

FIG. 2. Schematic behavior of a typical first derivative of the free energy at a first-order transition. (a) Characteristic sharp discontinuity of pure-system behavior. (b) Exponentially small precursor effects, which are always present in the impure system. (c) Partial rounding due to impurities (discontinuity reduced by a fraction of order unity). (d) Complete rounding due to impurities (discontinutiy eliminated).

and some fraction of the sample of order unity is already in the "wrong" phase. This will reduce by a fraction of order unity the characteristic first-order discontinutities at $T_f(p)$. Our argument is not sufficiently powerful to predict whether such discontinuities are entirely eliminated ("complete rounding") or only reduced ("partial rounding"). The various possibilities are illustrated in Fig. 2. Physical behavior depends crucially on the shape of the function $g(l)$ and is discussed in detail in Sec. III. Figure 2 might represent the possible behavior of the bulk entropy, for example. Behavior of the order parameter (magnetization), itself, may be especially delicate: For $\Delta T < \Delta T_r$ there will certainly be local regions of effective ferromagnetic alignment. However, if these regions are sufficiently separated by regions of disordered material, it seems likely that their moments will remain uncorrelated, so no bulk magnetization will be observable. Only when the ordered regions are sufficiently close to one another to communicate through the intervening disordered material will a transition occur to a state with bulk magnetization.

So far our attention has focused on a thermally-driven first-order transition. Generalization to transitions driven by other fields is straightforward. Consider, for example, a magnetic system below T_c which undergoes a first-order transition from "up" to "down" as the external magnetic field passes through $H=0$. Suppose that a random distribution of randomly directed local moments is introduced, exchange-coupled to the neighboring magnetic ions. This is equivalent to introducing at a fraction p of lattice sites a magnetic field of some fixed strength H_0 but randomly directed such that its average vanishes. A typical coherence volume contains $p\xi^d$ such sites and, thus, feels an extra local magnetic field per site $|H_{\rm loc}| \sim H_0 p^{1/2}\xi^{-d/2}$. Because of this, the transition is shifted locally to $H=-H_{\rm loc}$. Thus, even though the external field is up, there may be local regions where the total field is down. These regions will remain stable only if the cost in interfacial free energy of flipping them is sufficiently large. A development entirely parallel to that leading to Eq. (6) gives as the condition for stability of a cluster of l^d sites at external field ΔH,

$$\frac{H_0[p(1-p)]^{1/2}}{l^{d/2}} < \frac{C\sigma}{Ml^{d-\lambda}} + \Delta H \ , \tag{10}$$

where M is the magnetization per site. For an Ising magnet ($n=1$) $\lambda = d-1$; however, for XY or Heisenberg models ($n>1$) the direction of local magnetization can vary continuously, so the "surface" free energy is distributed over the whole cluster[2] and $\lambda = d-2$. The structures of Eqs. (10) and (6) are identical, so discussion of the first-order magnetic-field-driven transition parallels that given in Sec. III for the thermally-driven transition. Terms similar to those appearing in Eq. (10) have been discussed in connection with the critical behavior of systems with random fields.[2,9] The random-field model has been applied to charge-density-wave transitions.[10]

III. APPLICATIONS

In this section we discuss the physical behavior expected on the basis of Eqs. (6), (8), and (9). The shape of the function $g(l)$ [Eq. (8)] depends crucially on d and λ. The l dependence of the two terms is the same at $d=d_c=2$ (for $\lambda=d-1$) or 4 (for $\lambda=d-2$). When $d>d_c$, the second (surface) term dominates at large l, while the first (ΔT_f) term dominates at small l. When $d<d_c$, the situation is reversed, as illustrated in Fig. 3. The zero of $g(l)$ occurs at

$$l_0 = \left[\frac{[p(1-p)]^{1/2}L\,|dT_f/dp|}{C\sigma T_f}\right]^{1/(\lambda-d/2)} \tag{11a}$$

and its extremum takes place at

$$l_x = l_0\left[\frac{d}{2(d-\lambda)}\right]^{1/(\lambda-d/2)} > l_0 \ . \tag{11b}$$

The relative magnitudes of ξ, l_0, and l_x will be important in what follows. When $g(l)$ exceeds ΔT for a range of l's, so instability can occur on a variety of length scales, the dominant configurations of phase inhomogeneity will be those that maximize the free-energy benefit per site, i.e., those which maximize $g(l)$ subject to $l \geq \xi$. We now examine some different physical situations.

A. $d > d_c$, inhomogeneity on the scale of the coherence length

This case applies, e.g., to normal thermal first-order transitions in $d=3$. When $\xi > l_0$, then there is no significant rounding over any temperature range $\Delta T > 0$, although precursor effects will as always be present [Fig. 2(b)]. When $\xi < l_0$, then there is significant rounding at $\Delta T_r = g(\xi)$ [Figs. 2(c) or 2(d)]. As ΔT decreases, the phase inhomogeneity remains on the scale of ξ but there is increasing probability of "wrong-phase" coherence volumes. Precisely what occurs as $\Delta T \to 0$ is beyond our argument. Perhaps all discontinuities are wiped out, leaving only some weaker singularity associated with the percolation of wrong-phase coherence volumes. Note that the condition $\xi < l_0$ can be expressed as

$$\frac{L}{T_f}\left|\frac{dT_f}{dp}\right|\frac{[p(1-p)]^{1/2}}{C\sigma} > \xi^{\lambda-d/2} \ , \tag{12}$$

so small σ, large L, and large $T_f^{-1}|dT_f/dp|$ all enhance smearing, as is physically reasonable.

B. $d < d_c$, domain formation

This case applies, e.g., to the magnetic transition [Eq. (10)] for $n > 1$. If $\xi > l_x$, then $\Delta T_r = g(\xi)$ and inhomogeneity occurs on the scale of the coherence length, as above. However, if $\xi < l_x$, then the rounding width is $\Delta T_r = g(l_x)$. The thermodynamic situation is again as shown in Figs. 2(c) or 2(d); however, microscopically the situation is quite different. The scale of phase inhomogeneity is now l_x, which can be much greater than ξ, depending on the parameters (e.g., σ) appearing in Eq. (11). We refer to such regions as "domains."

C. $d = d_c$, the marginal dimension

Our example here is a thermally-driven first-order transition in a two-dimensional Ising-like system such as the Blume-Emery-Griffiths (BEG) model.[11] At the marginal dimension the magnitude of the constants in Eq. (8) becomes crucial. If

$$\frac{C\sigma T_f(p)}{L(p)} \geqslant [p(1-p)]^{1/2}\left|\frac{dT_f}{dp}\right| ,$$

then $g(l)$ is never positive and only precursor effects occur [Fig. 2(b)]. Otherwise, $\Delta T_r = g(\xi)$ and rounding takes place with phase inhomogeneity on the scale of ξ.

D. Behavior near criticality

An interesting situation occurs when variation of some external parameter μ (e.g., pressure) transforms a second-order transition into one which is (weakly) first-order, as, for example, near a tricritical point. Suppose μ is a nonordering field and $\mu = \mu_c$ defines the limit of criticality. We expect that for $\mu = \mu_c + \Delta\mu$, L and σ are small, while ξ is large, i.e.,

$$L \approx L_0(\Delta\mu)^{1-\alpha} , \quad \sigma = \sigma_0(\Delta\mu)^{2-\alpha-\nu} ,$$
$$\xi = \xi_0(\Delta\mu)^{-\nu} . \tag{13}$$

For $\lambda = d - 1$ and $d > d_c = 2$,

$$\left(\frac{l_0}{\xi}\right)^{d/2-1} = \frac{[p(1-p)]^{1/2}L_0}{C\sigma_0 T_f \xi^{d/2-1}}\left|\frac{dT_f}{dp}\right|(\Delta\mu)^{-\alpha/2} . \tag{14}$$

The argument of Sec. III A shows that for[12] $\alpha < 0$ there is no smearing near enough μ_c, in accordance with the Harris criterion.[5] It would be interesting to find a system with $\alpha < 0$ but exhibiting a large prefactor in Eq. (14). Thus, the first-order transition would be sharp near $\mu = \mu_c$ but would smear strongly with increasing $\Delta\mu$. Observation of such systematically variable smearing would constitute clear evidence of an intrinsic microscopic effect (the type discussed by theorists!) as opposed to one due to macroscopic sample inhomogeneities.

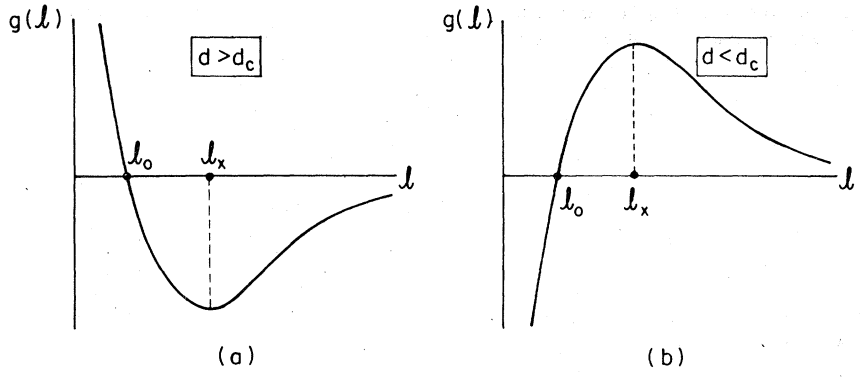

FIG. 3. Sketch of the function $g(l)$ defined in Eq. (8). $g(l_0) = 0$. The extremum takes places at $l = l_x$. The magnitude of ξ relative to that of l_0 and l_x is crucial in determining the presence and type of rounding.

IV. SUMMARY

We propose a criterion based on measurable parameters which predicts whether or not a first-order transition will be smeared by the presence of quenched random microscopic impurities. Above a critical dimensionality d_c, a system with sufficiently large coherence length [$\xi > l_0$, see Eq. (11a)] will not exhibit smearing, while one with sufficiently small coherence length ($\xi < l_0$) will smear by developing inhomogeneity on the scale of ξ. When $d < d_c$, we predict that smearing is always present; however, for large coherence length [$\xi > l_x$, see Eq. (11b)] phase inhomogeneity is on the scale of ξ, while for small coherence length ($\xi < l_x$) phase inhomogeneity occurs over domains of size l_x, which may be much larger than ξ.

ACKNOWLEDGMENTS

We wish to acknowledge the hospitality of the physics departments of Tel-Aviv University, where this paper was begun, NORDITA and the IBM Zurich Research Laboratory, where it was continued, and the BNL, where it was concluded. We are grateful to A. Aharony, M. Azbel, D. J. Bergman, D. Mukamel, and A. Mueller for useful discussions. This research was supported in part by NSF Grant No. DMR 75-22241.

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[1]G. Grinstein and A. Luther, Phys. Rev. B 13, 1329 (1976); A. B. Harris and T. C. Lubensky, Phys. Rev. Lett. 33, 1540 (1974); T. C. Lubensky, Phys. Rev. B 11, 3573 (1975); D. E. Khmel'nitsky, Zh. Eksp. Teor. Fiz. 68, 1960 (1975), [Sov. Phys. JETP 41, 981 (1976)].

[2]Y. Imry and S.-k. Ma, Phys. Rev. Lett. 35, 1399 (1975), have studied the critical behavior of systems subject to a random magnetic field. They find that the low-temperature phase has domain structure below a certain critical dimensionality, in correspondence with our results.

[3]Although this paper concerns equilibrium properties only, the picture which emerges has obvious relevance to questions of metastability and nucleation.

[4]For example, N. N. Krainik, G. A. Smolensky, L. S. Kamzina, V. A. Trepakov, and A. A. Berezhnoi, Ferroelectrics (GB) 12, 169 (1976), which contains previous references.

[5]A. B. Harris, J. Phys. C 7, 1671 (1974).

[6]See, for example, the discussion of heterophase fluctuations and pretransitional effects in pure systems by J. Frenkel, *Kinetic Theory of Liquids* (Dover, New York, 1955), p. 382 ff.

[7]In the specific example given here (Fig. 1) Δp and ΔT are positive and dT_f/dp is negative. Absolute values have been inserted into Eqs. (5) and (6) to cover other cases. Δp and ΔT are always to be understood as the magnitude of the appropriate deviation from p and $T_f(p)$, respectively.

[8]H. Jeffreys, *Theory of Probability* (Oxford, London, 1967), p. 61.

[9]G. Grinstein, Phys. Rev. Lett. 37, 944 (1976); A. Aharony, Y. Imry, and S.-k. Ma, Phys. Rev. Lett. 37, 1364 (1976).

[10]H. Fukuyama and P. A. Lee, Phys. Rev. B 17, 535 (1978); J. A. Wilson, L. J. di Salvo, and S. Mahajan, Adv. Phys. 24, 117 (1975).

[11]M. Blume, V. J. Emery, and R. B. Griffiths, Phys. Rev. A 4, 1071 (1971).

[12]A sharp transition with $\alpha > 0$ must, of course, be inconsistent. If Eq. (13) is assumed with $\alpha > 0$, then l_0 exceeds ξ as $\Delta\mu \to 0$, so smearing is predicted. However, Eq. (9) gives $\Delta T_r \sim (\Delta\mu)^{1-\alpha/2}$, appearing to allow a sharp transition at $\mu = \mu_c$. The resolution of this difficulty is that, precisely because $\alpha > 0$, the apparent boundary of smearing approaches the limit of criticality through a second-order region, where Eq. (1) applies, preventing a sharp transition.