Renormalized Critical Behavior or First-Order Phase Transitions?

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The exactly solvable Baker-Essam model for a compressible Ising lattice is re-examined. We find that, depending on the type of constraint imposed upon the system, the second-order phase transition either gets renormalized or is changed into a first-order transition. We resolve the apparent disagreement of this result with Fisher's renormalization theory by showing that, in fact, our result is typical of the correct state of affairs to be expected on the basis of the general theory of critical points in systems with hidden variables.

A great deal of controversy has occurred over the effects of lattice compressibility on the critical point of a magnetic phase transition. Early efforts at solving the case of a compressible Ising model seemed to indicate that the magnetoelastic interactions would invariably change the second-order transition, observed at zero field in the rigid Ising model, to a first-order transition.[1-5] All these calculations are based on approximations and are thus open to serious doubts for the reason that all known methods of approximation break down in the vicinity of the Ising phase transition. Using a completely different approach, Fisher[6] has treated rigorously the general problem of hidden variables and their effects on a second-order phase transition. The compressible Ising model is a special case of this —the volume or pressure being the hidden variable. His conclusion for this case is that for one and only one type of constraint on the hidden variable is the ideal Ising behavior retained, whereas for all others it is "renormalized," i.e., the critical-point exponents are changed in a specified way. In no case does he obtain a first-order phase transition. Following this, Essam and Baker[7] succeeded in solving an exactly solvable special case of the compressible Ising model which appeared to verify some of Fisher's general conclusions. In particular, no first-order transition was found to occur. In contrast to this we will first show that there exists a simple constraint on the system under which the transition does become first order.[8] Furthermore we will show that rather than being in disagreement with Fisher's general theory,[6] this behavior is, in fact, to be expected and that Fisher's conclusions arose from an implicit assumption regarding the type of constraints.

The suspicion that there might occur a first-order transition in the Baker-Essam (BE) model[7] arises from observing that the compressibility that they calculate for it [Eq. (11) of BE] becomes negative when the pressure is negative and when the system is sufficiently close to the point of the Ising phase transition.[9,10]

To verify this suspicion we present an explicit calculation as it appears for the two-dimensional variant of BE. We perform our calculations in the "λ ensemble," in which the partition sum is given by[11]

$$Z = \int \prod_{i=1}^{N} d^3r_i d^3p_i \exp\left\{-\beta \sum_{i=1}^{N} \frac{\vec{p}_i^{\,2}}{2m} - \beta \sum_{\text{bonds}} [\varphi(\vec{e}_{ij}\cdot\vec{r}_{ij}) + J(\vec{e}_{ij}\cdot\vec{r}_{ij})\sigma_i\sigma_j + \lambda\vec{e}_{ij}\cdot\vec{r}_{ij}]\right\}, \tag{1}$$

where, similar to BE,

$$\varphi(x) \equiv \varphi_0 + \tfrac{1}{2}\varphi_2(x-a_0)^2, \quad J(x) \equiv J_0 + J_1(x-a_0),$$

and λ is a Lagrange multiplier introduced to determine the average interparticle separation $a \equiv \langle x \rangle$. The sum over bonds includes all nearest-neighbor pairs of a two-dimensional square lattice.

By using the methods of BE, this can be calculated explicitly. The result is

$$\ln Z = N \ln\left(\frac{2\pi m}{\beta}\frac{2\pi}{\beta\varphi_2}\right) - 2\beta N\left(\varphi_0 + \lambda a_0 - \frac{\lambda^2 + J_1^{\,2}}{2\varphi_2}\right) + \ln Z_{\mathrm{I}}(\beta J_{\mathrm{eff}}), \tag{2}$$

where $Z_I(\beta J_{\text{eff}})$ is the usual Ising partition sum and

$$J_{\text{eff}} \equiv J_0 - J_1\lambda/\varphi_2. \tag{3}$$

The average interparticle distance is given by

$$a \equiv -\frac{1}{2N\beta}\frac{\partial \ln Z}{\partial \lambda} = a_0 - \frac{\lambda}{\varphi_2} - \frac{J_1}{\varphi_2}\langle \sigma_i \sigma_j \rangle. \tag{4}$$

In order to determine the pressure, we first calculate the Helmholtz free energy $F(T, V)$. To do this we note that $F(T, V)$ is numerically equal to the thermodynamic potential for T and a, $\tilde{F}(T, a)$. This in turn is obtained from the thermodynamic potential for T and λ, namely, $-kT\ln Z$, by a Legendre transformation. We can thus write

$$F(T, V) = \tilde{F}(T, a) = -kT\ln Z - 2Na\lambda. \tag{4a}$$

From this, remembering that $V = Na^2$, we immediately find that

$$P = \frac{\partial F(T, V)}{\partial V} = -\frac{\partial \tilde{F}(T, a)}{\partial a}\frac{1}{2Na} = \frac{\lambda}{a}. \tag{5}$$

It is easy to see from (4) that a is alwasy a monotonic decreasing function of λ. Therefore a given value of a uniquely determines λ and vice versa. This is not so when P is given. The equation for λ in that case is obtained by substituting (4) into (5) to get

$$-\frac{J_1}{\varphi_2}\langle \sigma_i \sigma_j \rangle = \lambda\left(\frac{1}{P} + \frac{1}{\varphi_2}\right) - a_0. \tag{6}$$

In Fig. 1 we show schematic graphs of the two sides of this equation plotted as functions of λ: The left-hand side LHS is drawn for βJ_0 small and positive. (Other values would cause a sideways shift of the graph of the LHS.) The RHS is a straight line with a slope determined by $1/P$ for small P. Several appropriate straight lines are shown, and it is evident that for $P > 0$ we can get only one solution to Eq. (6). For $P < 0$, we also ordinarily get only one solution, except when the intersection is close to one of the Ising phase transition points—λ_{c1} or λ_{c2}—in which case there are three solutions. To find the stable one we should examine the Gibbs free energy,

$$G(T,P) = F(T, V) + PV = -kT\ln Z(\beta, \lambda) - 2Na\lambda + PV = -kT\ln Z(\beta, \lambda) - N\lambda^2/P, \tag{7}$$

in order to determine when its value is smallest for given T and P.

Ordinarily, the Gibbs free-energy function is obtained when everywhere in this equation we substitute $\lambda = \lambda(\beta, P)$ as determined by Eq. (6). Since, however, P does not determine λ uniquely, we will continue to keep λ on the RHS of (7) as a free parameter and use the new function thus obtained,

$$\Gamma(T, P, \lambda) \equiv -kT\ln Z(\beta, \lambda) - N\lambda^2/P, \tag{8}$$

to compare the values of $G(T,P)$ obtained for the three solutions of Eq. (6). To this end we first calculate the following derivative of Γ:

$$\partial\Gamma(T, P, \lambda)/\partial\lambda = 2N(a - \lambda/P). \tag{9}$$

The difference in $G(T,P)$ between any two solutions of Eq. (6) that correspond to identical values of P can now be obtained by integrating Eq. (9):

$$\Delta G(T,P) = \Gamma(T, P, \lambda_2) - \Gamma(T, P, \lambda_1) = 2N\int_{\lambda_1}^{\lambda_2} d\lambda\,(a - \lambda/P), \tag{10}$$

where λ_1, λ_2 are two solutions corresponding to the same P. The integral which appears in this equation is equal to the area in Fig. 1 that is bounded from below by the straight line, from above by the wiggly line, and on the left and right by the points of intersection $\lambda = \lambda_1$ and $\lambda = \lambda_2$. From this it is immediately clear that whenever there are three intersections in the graph, the middle one always corresponds to a value of G that is greater than the other two; in fact, it is not even a local minimum of G. Of the remaining two intersections, the one that is near the larger area enclosed between the two lines has the lower G. This means that as we vary the pressure, thus varying the slope of the straight line, the

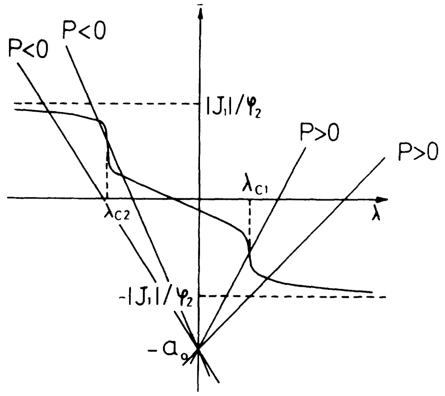

FIG. 1. Schematic drawing of the two sides of Eq. (6) as functions of λ. The wiggly line represents the LHS. Each straight line represents the RHS for a definite value of P. $\lambda_{c1}, \lambda_{c2}$ are the two transition points of the ideal Ising lattice, the ferromagnetic transition and the antiferromagnetic transition. (Which is which depends on the sign of J_1.)

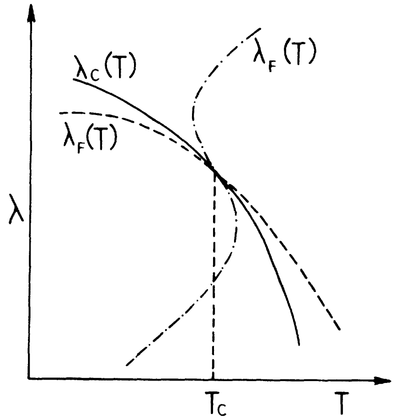

FIG. 2. Schematic drawing of the line of unconstrained critical points $\lambda_c(T)$ (solid line), the constrained equation of state $\lambda_F(T)$ for the constraint $a=c$ (dashed line), and the constrained equation of state $\lambda_F(T)$ for the constraint $a=\lambda c$ (dotted-dashed line). At the crossing point of $\lambda_c(T)$ and $\lambda_F(T)$ the curves have a common tangent.

value of λ that characterizes the stable equilibrium state makes a discontinuous jump when the two enclosed areas become equal. A similar phenomenon occurs if the temperature is varied —this time because of a sideways shifting of the wiggly graph.

We see that for $P<0$, the BE model has a first-order transition with a discontinuous volume, while for $P>0$, the second-order renormalized transition is obtained as derived by BE.

These results appear to be consistent with a recently published experimental result[12] in which it was discovered that the so-called "λ transition" of NH_4Cl is in fact a first-order transition at low pressures, but then changes to a second-order transition at high pressures.

We would like to note that the fate of the second-order transition in the compressible lattice depends crucially on the type of constraint that is imposed upon it[13]: At fixed P we have seen that both renormalization and a first-order transition are possible results, depending on whether $P>0$ or $P<0$.[14] At fixed a, which also means fixed volume, we always get renormalization. At fixed λ, as well as at $P=0$, the system retains its ideal behavior.

Since these results seem to disagree with Fisher's renormalization theory,[6] and might be criticized for pertaining to a very unphysical model where negative P is possible, we will reconsider that part of Fisher's arguments that is based on Fig. 2 of his paper.[6] The general constraint, which we write in the form $F(\lambda, a, T)=c$, is replaced in that figure by $a=c$, where a is a hidden extensive variable (corresponding to Fisher's variable x), λ is the conjugate force (corresponding to Fisher's variable ξ), c is a constant, and F is a regular function. When that constraint is substituted into the equation of state, $a=a(\lambda, T)$, the solution $\lambda=\lambda_F(T)$ that is obtained is single valued and has a unique intersection T_c with the line of critical points $\lambda_c(T)$. But, contrary to what Fisher implicitly assumes, this does not always occur. A case in point, suggested by our treatment of the BE model, is the constraint $a=\lambda c$. (There the constraint was $a=\lambda/P$, but here we are speaking in more general terms.) In this case, as well as in many others, the constrained equation of state $\lambda_F(T)$ is not single valued, but has the s-shaped form shown schematically in Fig. 2. It is possible to show that a first-order transition then follows with a general equal-area rule.

We can summarize these considerations by saying that the correct conclusion which should be drawn from Fisher's very general and very beautiful analysis is that when there is an extensive hidden variable a and a conjugate force λ, and if under the constraint $\lambda=\text{const}$ there exists an ideal second-order phase transition (i.e., one with an infinite specific-heat anomaly), then under any other constraint either the transition remains second order but with renormalized critical exponents, or else it is changed into a first-order phase transition.

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Luban for letting us know the results of his work prior to publication. This helped to stimulate our interest in the problems dealt with in this paper. We would also like to thank Professor S. Alexander and Dr. J. Grunzweig-Genossar for helpful discussions. We would like to thank Dr. E. Litov for bringing to our attention the recent results of Garland and Weiner.[12]

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[8] We have been recently informed by Essam (to whom we are very grateful for his communication to us) that he and Baker have solved exactly a compressible Ising model with infinite shear forces which exhibits a first-order transition at all pressures. (See Ref. 14 for related comments.) The latest BE work will be published in Proceedings of the International Conference on Magnetism, Grenoble, France, September 1970 [J. Phys. (Paris) Suppl., to be published].

[9] This fact, though completely obvious from Eq. (11) of BE, was first noted by L. A. Coplan and M. Dresden, Phys. Rev. Lett. 25, 785 (1970). They realized that "the thermodynamic instability... might well have observable consequences." We have confirmed this conjecture, demonstrating moreover that the system undergoes a first-order phase transition. Coplan and Dresden also dealt with the effect of "boundary conditions" and quadratic $J(x)$.

[10] While negative pressure cannot occur in equilibrium states of real systems, in this model it is perfectly all right because of the peculiar and nonphysical property of the interparticle forces, namely, that they become more and more attractive and grow without limit as the interparticle distance increases.

[11] The results we find are essentially the same for the BE model in three dimensions and when $\varphi(x)$ and $J(x)$ are arbitrary functions. This generalization as well as the independence of our results on the ensemble will be discussed elsewhere.

[12] C. W. Garland and B. B. Weiner, Phys. Rev. B 3, 1634 (1971).

[13] We would like to emphasize that this conclusion differs entirely from what was obtained in Refs. 1–5 by approximate methods.

[14] We expect that the special role played by $P=0$ as the dividing point between the region of renormalization and the region of the first-order transition is an artifact of the special model we have treated. Use of a more realistic model, including, for example, shear forces between the lattice points, would hopefully move this point to some positive value of the pressure.

Birefringence of Nematogenic Liquids Caused by Electrical Conduction

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Experiments are reported which show that the electrical birefringence of the isotropic phase of two nematic liquid crystals depends on electrical conductivity. It is argued that the conduction-induced alignment is due to local conduction anisotropy.

The alignment of nematic liquid crystals in electric fields is known to be strongly influenced by electrical conduction. Simple dielectric alignment is often prevented by electrohydrodynamic flow if the conductance of the sample is large enough. There seems to be essentially two mechanisms of such flow. One operates in isotropic and anisotropic liquids and requires injected space charge.[1] The other is based on conduction anisotropy and is usually ascribed to an intrinsic conductivity (but may also work with injected charge).[2] The second mechanism seems by definition restricted to liquid crystals. However, a similar aligning effect appears possible in the isotropic phase of nematogenic liquids at temperatures not too far above the clearing point.

If a liquid crystal is heated into the isotropic state, the long-range order breaks down, but the parallel ordering of the rodlike molecules is preserved on a smaller scale. The existence of "swarms"[3] of parallel molecules may be inferred, for instance, from measurements of the bire-