CRITICAL ISOTHERM OF A FERROMAGNET AND OF A FLUID*

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The isotherms of Xe, CO_2, and H_2 near the gas-liquid critical point have been analyzed by Widom and Rice.[1] For $T=T_c$ their results close to the critical point[2] may be summarized as

$$p-p_c \approx \rho_c(\mu-\mu_c) \approx A|\rho-\rho_c|^{\delta} \operatorname{sgn}\{\rho-\rho_c\}, \quad (1)$$

where

$$\delta = 4.2 \pm 0.1. \quad (2)$$

[The symbols p, ρ, and μ denote pressure, density, and chemical potential, respectively. The first relation in (1) follows from the identity $\rho = (\partial p/\partial\mu)_T$.] The van der Waals equation, other approximate equations, and phenomenological theories[3] predict $\delta = 3$, in disagreement with (2).

Recently the magnetic isotherm of Ni at the Curie temperature was analyzed by Kouvel and Fisher[4] who found for small fields[5] that

$$M(H) \approx D|H|^{\epsilon} \operatorname{sgn}\{H\}, \quad (T=T_c,\ H\to 0), \quad (3)$$

with

$$\epsilon = 0.237 \pm 0.002 = 1/(4.22 \pm 0.05). \quad (4)$$

(M and H denote the magnetization and field.) Molecular-field theory, most approximate theories, and phenomenological treatments predict $\epsilon = \frac{1}{3}$.

The remarkable coincidence in the experimental values of δ and $1/\epsilon$ can be understood through the analogy between a ferromagnet and a fluid near their respective critical points. For an $S=\frac{1}{2}$ Ising ferromagnet and a simple, classical lattice gas the analogy is formally exact and is expressed most directly by[6]

$$M/M_{\rm sat} \equiv (\rho_c-\rho)/\rho_c, \quad 2mH \equiv \mu_c - \mu. \quad (5)$$

This immediately yields $\delta = 1/\epsilon$. The value of δ is not, however, known theoretically even in two dimensions. In this Letter we report calculations for the Ising model which lead to the estimates

$$\delta = 5.20 \pm 0.15 \quad \text{(three dimensions)}, \quad (6)$$

$$\delta = 15.00 \pm 0.08 \quad \text{(two dimensions)}, \quad (7)$$

and discuss the significance of these values. Full details of our work including calculations of the behavior away from T_c will be published in due course.

The analysis is based on the analog of Mayer's fugacity series

$$M/M_{\rm sat} = 1 - \sum_{l=1} l B_l(T) y^l, \quad (8)$$

where

$$y = \exp(-2mH/kT) \equiv z/z_c = \exp[(\mu-\mu_c)/kT]. \quad (9)$$

The cluster sums $B_l(T)$ are known up to $l=11$ for the bcc and sc, $l=13$ for the diamond, square, and honeycomb, and $l=8$ for the triangular lattices, respectively.[7] They were evaluated at the critical temperature using the exact values of T_c for the plane lattices and the best estimates in three dimensions.[8]

The nature of the singularity at the critical point ($y=1$, $M=0$) is determined by the behavior of the ratios $\lambda_n = nB_n/(n-1)B_{n-1}$ for large n.[9] Figure 1 shows a plot of the successive estimates

$$\epsilon_n = n(\lambda_n - 1), \quad \epsilon_n' = (n+\tfrac{1}{2})(\lambda_n - 1), \quad (10)$$

vs $1/n$ for the bcc and sc lattices. Extrapolation to $n=\infty$ indicates $\delta = 1/\epsilon = 5.17 \pm 0.12$ and 5.30 ± 0.20, respectively. The bcc ratios vary particularly smoothly. The ratios for the diamond and plane lattices behave less regularly (due evidently to the presence of other singularities on the circle of convergence $|y|=1$), but the former are consistent with $\delta \simeq 5.2$ and the latter indicate $\delta = 15 \pm 2$.

The critical exponent may also be estimated

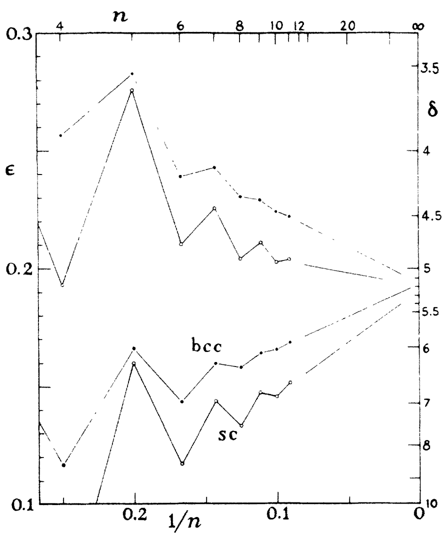

FIG. 1. Plot, versus $1/n$, of successive estimates for the exponent $\epsilon = 1/\delta$ based on the ratios λ_n of the cluster sums.

by forming the series for

$$\epsilon^*(H) = (1-y)(\partial/\partial y)\ln M(H, T_c), \tag{11}$$

and evaluating the Padé approximants to the truncated series[10,11] at $y = 1$ $(H = 0)$.

Successive estimates for δ using $n = 1 + L + M$ terms are presented in Table I for four lattices. The values for the sc and triangular lattices are particularly consistent, the last six lying in the ranges 5.19 to 5.28 and 15.02 to 15.08, respectively. The bcc and square lattice values agree rather closely. Estimates for the diamond and honeycomb lattices are consistent, but with a wider spread.

The evidence clearly supports the conjecture that δ depends on dimensionality but not on lattice structure and leads to the overall estimates (6) and (7), the indicated uncertainties being reasonable confidence limits.

It is natural to conjecture that the exact result in two dimensions is $\delta = 15$. To the extent that 15 is an odd integer this can be reconciled with a phenomenological treatment. The three-dimensional results seem, however, inconsistent with such an assumption, but support the conjecture $\delta = 5\frac{1}{5}$ which we now discuss.

Suppose that as $T \to T_c$ the specific heat, spontaneous magnetization, and initial susceptibility vary as $(T_c - T)$ to the powers $-\alpha'$, β, and $-\gamma'$, respectively.[12] On the basis of an extension of the droplet model of condensation

Table I. Successive estimates of δ formed from the $[L, M]$ Padé approximants to $\epsilon^*(0)$. An asterisk signifies the occurrence of a spurious intervening singularity.[a]

L,M	δ_{bcc}	L,M	δ_{sc}	L,M	δ_{tri}	L,M	δ_{sq}
2,2	5.267	2,3	5.413	2,2	15.027	3,3	15.428
2,3	5.159	3,2	5.426	2,3	15.067	3,4	15.222
3,2	5.169	3,3	4.590*	3,2	15.083	4,3	15.228
3,3	5.166	3,4	5.190	3,3	15.057	4,4	14.846
3,4	5.162	4,3	5.197	3,4	15.023	4,5	15.141
4,3	5.170	4,4	5.283	4,3	15.046	5,4	15.144
4,5	5.224	4,5	5.229			5,5	15.123
5,4	5.233	5,4	5.231			5,6	15.965*
5,5	5.379*	5,5	5.212			6,5	14.995
						6,6	15.070

[a]See reference 10.

it has been conjectured[13,11] that

$$\alpha' + 2\beta + \gamma' = 2, \tag{12}$$

and

$$\gamma' = \beta(\delta - 1). \tag{13}$$

For a ferromagnet Rushbrooke[14] has shown that

$$\alpha' + 2\beta + \gamma' \geq 2 \tag{14}$$

is a consequence of thermodynamics, and his argument has been extended to fluids[12] [where α', β, and γ' refer to the two-phase specific heat C_V, to $(\rho_L - \rho_G)$ at coexistence, and to the compressibility at condensation]. The relation (13) was first proposed by Widom,[15] who showed it followed from the assumption (A) that the (p, T) isochores near the critical point were effectively linear over a range from T_c to $T_0(\rho)$, where $T_0(\rho)$ is the coexistence curve (analogous to the spontaneous magnetization curve).

The relations (12) and (13) are certainly valid for a van der Waals or mean-field type of theory ($\alpha' = 0$, $\beta = \frac{1}{2}$, $\gamma' = 1$, $\delta = 3$). For the two-dimensional Ising model (12) is correct since $\alpha' = 0$, $\beta = \frac{1}{8}$, and $\gamma' = 1\frac{3}{4}$.[11,12] Relation (13) predicts[15] $\delta = 15$, in precise agreement with our estimate! This suggests (A) is correct for the plane lattices.

In three dimensions $\beta \simeq \frac{5}{16}$ is well established,[11] so that (14) yields $\alpha' + \gamma' \geq 1\frac{3}{8}$. The extrapolations of specific heat and susceptibility are less certain, but do indicate $0 \leq \alpha' \leq 0.1$ and $1.23 \leq \gamma' \leq 1.32$.[11,12,16] Accepting $\delta = 5\frac{1}{5}$ and

(13) yields $\gamma' = 1\frac{5}{16} = 1.312\,50$ so that, in turn, $\alpha' \geq \frac{1}{16} = 0.062\,50$.[17] These values are consistent with the previous estimates, which suggests that (A) is valid and that $\alpha' = \frac{1}{16}$, $\gamma' = 1\frac{5}{16}$, and $\delta = 5\frac{1}{5}$ might be exact.[18] (Note that $\delta = 5$ leads to $\gamma' = 1\frac{1}{4}$ and $\alpha' \geq \frac{1}{8}$, while $\delta = 5\frac{2}{5}$ yields $\gamma' = 1\frac{3}{8} = 1.375$, both of these results being inconsistent with the numerical extrapolations.[11,12,16]) For plane lattices the susceptibility exponent γ above T_c satisfies $\gamma = \gamma'$. In three dimensions $\gamma = 1\frac{1}{4}$,[8,9] so that the symmetry about T_c is apparently lost.

The discrepancy between $\delta = 5.2$ and the experimental value of 4.2 must, presumably, be attributed to the extreme anisotropy of the Ising spin interaction and to the artificial "rigidity" of a lattice gas with single-site hard cores.[18] The difference is appreciably larger than between $\beta = \frac{5}{16} = 0.3125$ and $\beta \simeq 0.33$ observed for fluids[12] and, recently, for a ferromagnet.[19]

Existing data for fluids seem inconsistent with relation (13), implying that real isochores break away from the vapor-pressure curve increasingly sharply as $T \to T_c$. This follows from $\beta \simeq 0.33$[12] and $\alpha' \simeq 0$ (logarithmic specific heats[18,20,21]), which by (14) imply $\gamma' \gtrsim 1.3$, whence (13) yields $\delta \gtrsim 5$, which contradicts (2). Experimental uncertainties might, however, just invalidate this conclusion and nothing can be said for ferromagnets since neither α' nor γ' is known. Further accurate measurements, preferably all on the same fluid or magnetic system, would be most valuable.

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