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THERMODYNAMIC INEQUALITY NEAR THE CRITICAL POINT FOR FERROMAGNETS AND FLUIDS*

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Measurements show that the specific heats at constant volume C_v for argon[1] and for oxygen[2] become very large near the critical point, apparently diverging as $|\log(T_c-T)|$ as T approaches the critical temperature T_c from below along the critical isochore. We have deduced a rigorous thermodynamic inequality [Eq. (3) below] which, when combined with previously published and analyzed data for the equations of state of xenon and carbon dioxide, indicates that the divergence of C_v for these materials should be even more rapid than logarithmic. The derivation of the inequality is carried out for the analogous problem of a ferromagnet near its Curie point, and the alterations required to obtain the same result for a fluid are indicated.

Let us assume that the spontaneous magnetization, zero-field specific heat, and initial susceptibility vary as (T_c-T) to the powers $\beta, -\alpha'$, and $-\gamma'$, respectively,[3] as T approaches T_c, the Curie temperature, from below. [For our purposes, a logarithmic divergence of the specific heat corresponds to[3] $\alpha' = 0$.]

Rushbrooke[4] has deduced the inequality

$$2\beta + \gamma' \geq 2-\alpha' \tag{1}$$

by thermodynamic arguments. If the magnetization M varies as

$$M \propto H^{1/\delta} \tag{2}$$

along the critical isotherm $T = T_c$ for small values of H, an analogous inequality

$$(1+\delta)\beta \geq 2-\alpha' \tag{3}$$

may be obtained as follows.

Let $A(T,M)$ be the thermodynamic potential or "free energy" for which

$$H = (\partial A/\partial M)_T; \quad S = -(\partial A/\partial T)_M, \tag{4}$$

where S is the entropy. For $T < T_c$ and M less than the spontaneous magnetization, H vanishes (by definition), and therefore both $A(T,M)$ and $S(T,M)$ are equal to $A(T), S(T)$, their respective values for zero magnetization.

Let M_1 be the spontaneous magnetization for some $T_1 < T_c$.

$$\begin{aligned} A(T_c, M_1) &= A(T_1, M_1) - \int_{T_1}^{T_c} S(T, M_1)dT \\ &\leq A(T_1, M_1) - S(T_1, M_1)(T_c - T_1) \\ &= A(T_1) - S(T_1)(T_c - T_1). \end{aligned} \tag{5}$$

The inequality follows from the fact that S is monotone increasing in T or, in other words, the specific heat at constant magnetization is positive. By the same reasoning,

$$A(T_1) \leq A(T_c) + (T_c - T_1)S(T_c), \tag{6}$$

and thus

$$A(T_c, M_1) - A(T_c) \leqslant (T_c - T_1)[S(T_c) - S(T_1)]. \quad (7)$$

From (2) and (4) it is evident that when T_1 approaches T_c, the left side of (7) behaves as

$$M_1^{1+\delta} \propto (T_c - T_1)^{\beta(1+\delta)}, \quad (8)$$

whereas the right side varies as $(T_c - T_1)$ to the power $2-\alpha'$. Thus (7) will be violated as $(T_c - T_1)$ goes to zero unless (3) is satisfied.[5]

For the two-dimensional Ising ferromagnet, Widom[5] has conjectured that $\delta = 15$, and Gaunt et al.[6] have obtained $\delta = 15.00 \pm 0.08$ by numerical extrapolation of the virial expansion. Inequality (3) combined with[3] $\alpha' = 0$ and $\beta = \frac{1}{8}$ yields the rigorous result $\delta \geqslant 15$. The estimates[6] $\alpha' \simeq \frac{1}{16}$, $\beta \simeq \frac{5}{16}$, $\delta \simeq 51/5$ for the three-dimensional Ising model are consistent with (3).

In the case of a fluid, let us assume that the specific volumes of vapor and liquid in equilibrium both approach the critical volume V_c as $(T_c - T)^\beta$, and C_v (on the critical isochore) and the second derivative of the vapor pressure[7] d^2P/dT^2 diverge as $(T_c - T)$ to the power $-\alpha'$ and $-\theta$, respectively. Further, assume the pressure and volume are related by

$$P - P_c \propto |V - V_c|^\delta \operatorname{sgn}(V_c - V) \quad (9)$$

along the critical isotherm when $|V - V_c|$ is small. An argument quite analogous to that used in the magnetic case, but employing the Helmholtz free energy[8] $A(T, V)$ in place of $A(T, M)$, again yields (3) and, in addition,

$$\theta \leqslant \alpha' + \beta. \quad (10)$$

For a simple Ising "lattice gas,"[9] $\theta = \alpha'$, and (10) is trivially satisfied.

The values $\alpha' \simeq 0$, $\beta \simeq 0.33$, $\delta \simeq 4.2$, tentatively suggested by Gaunt et al.[6] as appropriate exponents for a real fluid, on the basis of the meager experimental evidence now available, are inconsistent with (3) and hence cannot all be correct. (Of course, it is not impossible that different fluids have different exponents.) In particular, Widom and Rice[10] have estimated that $\delta \simeq 4.2$ for carbon dioxide and xenon, whereas β for these substances[3] appears to lie between 0.33 and 0.36. Hence by (3), we expect $\alpha' \gtrsim 0.13$ to 0.28, a deviation from a logarithmic divergence which may be observable in experiments. The C_v data for argon[1] seem not inconsistent[11] with a small positive value for α' (less than 0.1).

We may remark that in the derivation of (3) for a fluid it is assumed the parameter β is the same on both the liquid and vapor sides of the critical point. Should there be a small difference, the law of rectilinear diameter would be expected to fail for temperatures very near T_c, and both (3) and (1) would have to be modified.

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[2]A. V. Voronel' et al., Zh. Eksperim. i Teor. Fiz. 45, 828 (1963) [translation: Soviet Phys.-JETP 18, 568 (1964)].

[3]Notation as in M. E. Fisher, J. Math. Phys. 5, 944 (1964).

[4]G. S. Rushbrooke, J. Chem. Phys. 39, 842 (1963). The corresponding inequality for fluids is derived in reference 3.

[5]It is possible to obtain our inequality (3) if Rushbrooke's inequality (1) is combined with a relation $\gamma' = \beta(\delta - 1)$, suggested by B. Widom, J. Chem. Phys. 41, 1633 (1964). As Widom himself has emphasized, the relation is quite tentative, and his derivation is based on an assumption as to the behavior of the (P, T) isochores near the critical point, which is open to certain objections. Inequalities (1) and (3), on the other hand, are based on very general thermodynamic considerations.

[6]D. S. Gaunt, M. E. Fisher, M. F. Sykes, and J. W. Essam, Phys. Rev. Letters 13, 713 (1964).

[7]C. N. Yang and C. P. Yang, Phys. Rev. Letters 13, 303 (1964).

[8]In the two-phase region, both $A(T, V)$ and $S(T, V)$ are linear functions of V along the isotherms, with slopes given by $-P$ and dP/dT, respectively.

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[10]B. Widom and O. K. Rice, J. Chem. Phys. 23, 1250 (1955).

[11]M. E. Fisher, Phys. Rev. 136, A1599 (1964).