[18]See, for example, Young and Crowell, Ref. 14, p. 190.

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QUANTUM CORRECTIONS TO CRITICAL-POINT BEHAVIOR

Michael E. Fisher

Wheatstone Physics Laboratory, King's College, London, England
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Recent experimental evidence[1-3] suggests that the behavior of He^3 and He^4 at their critical points deviates qualitatively from that observed with "classical" gases for which the de Boer parameter $\Lambda^* = h/(m\epsilon\sigma^2)^{1/2}$ is small. (m, ϵ, and σ measure the mass, potential well depth, and collision diameter, respectively.) In particular, while the coexistence curves of Xe and CO_2 may be described accurately over a wide range of T approaching T_c by

$$R(T) = (\rho_{\rm liq} - \rho_{\rm gas})/2\rho_c \approx D[1-(T/T_c)]^\beta \tag{1}$$

with β lying in the range 0.33 to 0.36,[4-6] the apparent value of β (e.g., on a log-log plot) for He^3 and He^4 seems to increase to values in the range 0.40-0.50 when $T/T_c \geqslant 0.98$.[1,2] Similar changes towards "Van der Waals-like" behavior appear to take place also in the other critical-point exponents (γ and γ' for the compressibility above and below T_c, etc.).[3,5,7]

Sherman and Hammel[7] have discussed these effects from the viewpoint of de Boer's theory of corresponding states. They implicitly suggested that the exponents $\beta(\Lambda^*)$, $\gamma(\Lambda^*)$, etc., are continuous smoothly varying functions of Λ^*. The purpose of this note is to argue, on the contrary, that the ideal critical-point exponents defined[5,8] in the limit $T \to T_c$ are probably discontinuous functions of Λ^* with, for example, $\beta = \beta_0$ for $\Lambda^* = 0$, $\beta = \beta_1$ for $0 < \Lambda^* < \Lambda^*_1$, and, possibly, $\beta = \beta_2$ for $\Lambda^* > \Lambda^*_1$. The implications of this conclusion for the shapes of coexistence curves, etc., will be discussed.

For pair interactions of the form $\varphi(r) = \epsilon f(r/\sigma)$, where $f(x)$ is a "universal" shape factor, the Hamiltonian of an N-body system may be written

$$\mathcal{H}_N = \epsilon(\mathcal{H}_0 + g\mathcal{H}_1), \tag{2}$$

where $\mathcal{H}_0$ is the reduced potential energy and $\mathcal{H}_1$ the reduced kinetic energy $-\frac{1}{2}\sum_i \partial^2/\partial x_i^2$, while the coupling constant is

$$g = (\Lambda^*/2\pi)^2 = (\lambda^*)^2. \tag{3}$$

For a classical gas ($g=0$), the analogy with a spin-$\frac{1}{2}$ Ising ferromagnet via the lattice-gas model is well known[8,9] and may be expressed by

$$\epsilon \equiv J^{\parallel}, \quad \varphi(0) = +\infty, \quad \varphi(r) \equiv -J(r),$$
$$\epsilon\mathcal{H}_0 + \mu N \equiv \mathcal{H}_{\rm Ising}, \quad \rho/\rho_c \equiv 1-(M/M_{\rm sat}),$$
$$\text{and } \mu_c - \mu \equiv 2H,$$

μ being the chemical potential and H the reduced magnetic field. As noticed by a number of authors,[10-15] there is a corresponding analogy between a quantum-mechanical Bose lattice gas and an anisotropic Heisenberg-Ising magnet. The reduced kinetic energy becomes the transverse interaction

$$\mathcal{H}_1 = \mathcal{H}^{\perp} = \sum_{ij}(S_i^x S_j^x + S_i^y S_j^y), \tag{4}$$

where the sum runs over nearest-neighbor pairs, and the coupling constant is

$$g = J^{\parallel}/J^{\perp} \equiv (2d\sigma^2/qa^2)(\lambda^*)^2, \tag{5}$$

where d is the dimensionality, q the coordination number, and a the lattice spacing. In the simplest ferromagnetic nearest-neighbor model,[15] $J(r)$ vanishes for $r > a$, and one may take $\sigma \simeq a$ so that the prefactor in (5) lies between $\frac{1}{2}$ and 1 for most lattices. The pure isotropic Heisenberg model then corresponds to $g=1$ or $\lambda^* = \lambda_1^* \simeq 1\text{-}\sqrt{2}$.

Numerical evidence for the simple $d=3$ Ising model[16] shows that $\beta(0) = 0.31 \simeq 5/16$ and $\gamma(0) = 1.25 \simeq 5/4$, whereas for the Heisenberg model $T_c(1) < T_c(0)$ and $\gamma(g=1) = 1.33 \simeq \frac{4}{3}$ is indicated.[17] These changes are actually away from Van der Waals-like behavior ($\gamma = 1$). On the other hand, the critical ratio $p_C v_C / kT_C$ increases, from 0.258 to 0.262 for the fcc lattice,[18] which is in the direction found experimentally (0.290 for Xe to 0.305 for He^4). Furthermore, the value of γ for intermediate g or Λ^* has not yet been estimated and it is not certain that it need lie between 5/4 and $\frac{4}{3}$. (It has been conjectured that $\beta(1) = 0.33$ but this has not been tested numerically close to T_C.)

If the anisotropic magnetic Hamiltonian is treated by the method of truncated Green functions,[19] one finds[20] (A) $\gamma(g) = 0$ for $0 \leqslant g < 1$ but $\gamma(1) = 2$. This result cannot, of course, be trusted quantitatively, but there is further theoretical evidence which suggests that the isotropic Heisenberg model represents a singular limit where analytic behavior changes discontinuously.[21] Possibly, therefore, $\Lambda^* = \Lambda_1^* \simeq 2\pi - 2^{3/2}\pi$ might similarly be a "transition" value for the fluid problem in the Bose case. It seems unlikely, however, that this is attained in the real world, since $\Lambda^*(He^4) \simeq 2.67$ [while $\Lambda^*(He^3) \simeq 3.08$].

In further support for the discontinuity of the exponents $\beta(g)$, $\gamma(g)$, etc., we describe three "soluble" problems where the Hamiltonian is split in analogy to (3). Consider the spherical model for $d = 3$ with an interaction potential

$$\varphi(r) = \epsilon[f(r/\sigma) + g(\sigma/r)^{3+\zeta}], \qquad (5)$$

where $f(x)$ is of finite range and $\frac{3}{2} < \zeta < 2$. One finds[22] (B) $\gamma(g = 0) = 2$ but $\gamma(g) = \zeta/(3-\zeta) < 2$ for $g > 0$.

Secondly, consider the two-dimensional Ising model with, in addition to normal nearest-neighbor interactions, a "Kac potential" $\epsilon g \kappa^2 \times \exp[-\kappa(r/\sigma)]$ in which the limit $\kappa \to 0$ is taken after the thermodynamic limit.[23,24] For this model it follows[24] that (C) $\beta(0) = \frac{1}{8}$, $\gamma(0) = 7/4$ but $\beta(g) = \frac{1}{2}$, $\gamma(g) = 1$ for $g > 0$. A similar result would hold when $d = 3$.

Finally, as a very simple illustrative example, consider the matrix "Hamiltonian" $\mathsf{A}(t) + g\mathsf{B}(t)$ when

$$\mathsf{A} = \begin{bmatrix} 1 & 0 \\ 0 & 1+t^2 \end{bmatrix}, \quad \mathsf{B} = \begin{bmatrix} 0 & t \\ t & 0 \end{bmatrix}. \qquad (6)$$

For small t, the energy gap $\Delta(t) = E_1 - E_0$ behaves as $|t|^\delta$ with (D) $\delta(g = 0) = 2$ but $\delta(g) = 1$ for $g > 0$. From the exact result, $\Delta(t) = |t|(t^2 + \frac{1}{4}g^2)^{1/2}$, one sees that a plot of $\Delta(t)$ for small g would appear quadratic down to $t = O(\frac{1}{2}g)$ but would become linear for smaller t.

Similar "nonuniformity" must occur in the coexistence curves and plots of compressibilities in the examples (A), (B), and (C).[25] A simple formula for the coexistence curve with this property[25] is

$$R(T) = (\rho_L - \rho_G)/2\rho_c \approx D(\lambda^*)t^{\beta_1}[t + b(\lambda^*)^2]^{\beta_0 - \beta_1}, \qquad (7)$$

where $t = 1 - [T/T_c(\lambda^*)]$. The power of λ^* in the last factor is suggested by dimensional considerations [kT, kT_c, ϵ, and $\hbar^2 m\sigma^2 = (\lambda^*)^2\epsilon$ being the fundamental energies]. First-order perturbation theory would be expected to yield $T_c(\lambda^*) \simeq T_c(0)[1 - c(\lambda^*)^2]$ and $D(\lambda^*) \simeq D(0)[1 - d(\lambda^*)^2]$ and hence suggests the linearity in t of the last factor. [Other powers could, however, be accommodated by changing this factor to $t^n + b(\lambda^*)^{n'}$ and its exponent to $(\beta_0 - \beta_1)n$ although at present there seems no justification for this.]

If (7) is valid, a plot of R^{1/β_0} vs T should be linear for $t \gg b(\lambda^*)^2$ with slope D^{1/β_0} and with an intercept extrapolated linearly to $R = 0$ falling short of the true critical temperature (if $\beta_1 > \beta_0$) by a shift

$$\delta T/T_c \simeq b[(\beta_1/\beta_0) - 1](\lambda^*)^2. \qquad (8)$$

This behavior may be seen in Fig. 1 where the

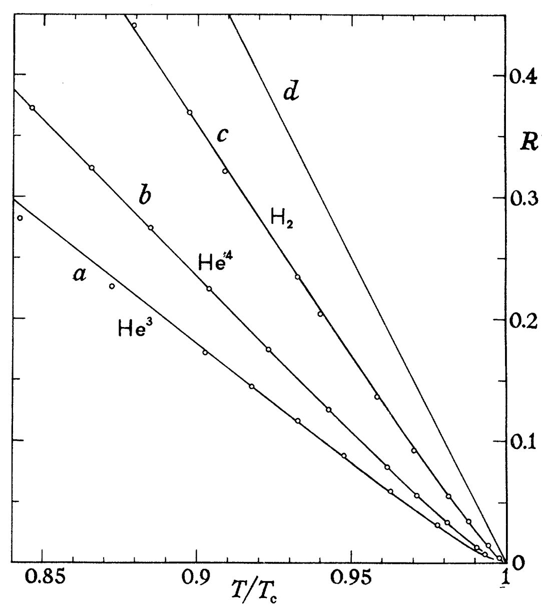

FIG. 1. Plots of $R^3 = [(\rho_L - \rho_G)/2\rho_c]^3$ vs T/T_c from Eqs. (7) and (9) with $\beta_0 = \frac{1}{3}$, $\beta_1 = \frac{1}{2}$, and $b = 0.12$ for (a) He^3, (b) He^4, (c) parahydrogen, and (d) the classical limit $\Lambda^* = 0$ which is approximated by xenon. The data points are from Refs. 1, 27, and 26, respectively.

relation (7) is tested against the data for He^3, He^4, and parahydrogen.[26] For simplicity we have assumed that $\beta_0 = \frac{1}{3}$ and $\beta_1 = \frac{1}{2}$. The values $b = 0.12$ ($\delta T/T_c = 0.011$) and $D = 1.373$ then provide an excellent fit to the data for He^4.[27] For H_2 and He^3 the same value of b was taken together with

$$D(\bar{\lambda}^*) = 1.71[1 - 1.09(\bar{\lambda}^*)^2]. \tag{9}$$

This relation yields the quoted value for He^4 and is also consistent with data for Ne ($D \simeq 1.69$, $\Lambda^* = 0.595$) and Xe.[28] The fits for H_2 and He^3 are not quite as good as for He^4; this may be due to defects of (7), to a breakdown of a corresponding-states representation, to He^3 being a Fermi fluid,[29] or to the experimental difficulties of obtaining the coexistence curve precisely from PVT measurements.[29,30] [Of course deviations from (7) must be expected at temperatures sufficiently far removed from T_c.]

The fractional shifts $\delta T/T_c$ predicted by (8) for other gases are

Xe	Ar	Ne	D_2	HD
6×10^{-6}	6×10^{-5}	5×10^{-4}	2×10^{-3}	3×10^{-3}

Thus deviations from a simple power law should be observable for HD, D_2, and Ne although probably not for Ar and Xe. [A first power for $\bar{\lambda}^*$ in (7) (or $n' = n$) would predict deviations for Xe at temperatures where they seem experimentally to be absent.] Finally, in contrast to (9), we note the following relations which hold with surprising accuracy from Xe to He^3:

$$p_c v_c / k T_c = 2.875 \pm 0.275(\bar{\lambda}^*)^{1/2}, \tag{10}$$

$$C(\bar{\lambda}^*) = 0.80(1 - 2.05\bar{\lambda}^*), \tag{11}$$

where $C = (\Delta\bar{\rho}/\rho_c)/(\Delta T/T_c)$ is the reduced mean slope of the rectilinear diameter of the coexistence curve taken over the range 0.75 T_0 to T_c.

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