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LETTERS

CRITICAL POINT IN LIQUID-GAS TRANSITIONS

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In two recent experiments,[1] the specific heats $C_V(T)$ of Ar and of O_2 near the critical temperature T_C have been measured at the critical volume. The measured specific heats display sharp peaks at T_C, suggesting logarithmic infinities. Rough fits of the experimental data yield, for Ar,

$$C_V/R = 1.8L + 13, \quad T < T_C,$$

$$C_V/R = 1.8L + 3, \quad T > T_C; \tag{1a}$$

for O_2,

$$C_V/R = 2.4L + 16, \quad T < T_C;$$

$$C_V/R = 2.4L + 4, \quad T > T_C, \tag{1b}$$

where

$$L = -\ln|T - T_C|, \quad T \text{ in } °C. \tag{2}$$

The singular behavior (1) is in sharp contrast with traditional views[2] about the behavior of thermodynamical functions near T_C. We make the following remarks on these very interesting data.

(A) Thermodynamical discussion of the two-phase region.—If μ is the chemical potential, it follows from

$$SdT = -Nd\mu + Vdp$$

that

$$C_V = -NT(d^2\mu/dT^2)_V + VT(d^2p/dT^2)_V. \tag{3}$$

Now (3) is applicable to the two-phase region as well as the one-phase region. In the two-phase region $d^2\mu/dT^2$ and d^2p/dT^2 are both functions of one variable only, T. Thus for a sample with fixed N (molar weight), $C_V(T, V)$ is <u>linear</u> in V and its measurement in the two-phase region can yield both $d^2\mu/dT^2$ and d^2p/dT^2 along the vapor-pressure curve. We urge that this be done.

(1) and (3) show that either $d^2\mu/dT^2$ or d^2p/dT^2 (at $T = T_C-$ along the vapor-pressure curve), or both, are ∞. It is important to find out which is the actual case. [For the lattice gas to be discussed under (D), $d^2\mu/dT^2 = 0$ along the vapor-pressure curve. For real gases, it is more reasonable to expect that both $d^2\mu/dT^2$ and d^2p/dT^2 become ∞.]

If d^2p/dT^2 along the vapor-pressure curve at $T = T_C-$ for He^4 is ∞ [see (C) below], corrections must be made in the vapor-pressure table[3] of He which serves as the international standard of temperature measurement at low temperatures. A logarithmic singularity of C_V would necessitate the addition of a term $K(T - T_C)^2 \ln|T - T_C|$ in the vapor pressure. (Unless the peak in C_V for He^4 is very large, this correction to p is expected to

be small, since the singularity occurs in the second derivative d^2p/dT^2. The correction to dp/dT is more important.)

(B) Thermodynamical discussion of the one-phase region.—Approaching the critical point from the one-phase region one obtains, from C_V $= T(E_{SS})^{-1}$ and (1),

$$E_{SS} \to \text{constant}(-\ln|T-T_C|)^{-1} \to 0, \qquad (4)$$

where E_{SS}, E_{SV}, and E_{VV} are the second derivatives of $E(S, V)$. Now along the vapor-pressure curve

$$(dp/dT) \to \alpha = \text{constant} \qquad (5)$$

at the critical point. We now assume, for $V = V_C$,

$$(\partial p/\partial T)_V = \text{continuous in } T \text{ at } T = T_C, \qquad (6)$$

which is experimentally[4] true [and is satisfied by the two-dimensional lattice gas to be discussed in (D)]. Similarly we assume, for $S = S_C$,

$$(\partial p/\partial T)_S = \text{continuous in } T \text{ at } T = T_C. \qquad (7)$$

If the second derivatives E_{SS}, E_{SV}, and E_{VV} approach limits as one approaches the critical point from the one-phase region, (4)-(7) require that they all approach zero in the following proportion;

$$E_{SS} : E_{SV} : E_{VV} = 1 : (-\alpha) : \alpha^2.$$

The velocity of sound is proportional to $(E_{VV})^{1/2}$. It therefore goes to zero as $(-\ln|T-T_C|)^{-1/2}$ near the critical point.

(C) Law of corresponding states.—de Boer[5] has pointed out that if the interatomic forces in noble gases follow a law with only two parameters, the equation of state of all noble gases in classical statistical mechanics would be the same when expressed in proper units. (The quantum correction is contained in the kinetic-energy term, which he showed was small except for He⁴.) The good agreement of his results with the critical data of noble gases shows that (in noble gases) the critical phenomenon in liquid-gas transitions is not a quantum effect. Accepting this conclusion one finds that all noble gases should have the same $C_V(T)$ singularity, of the same magnitude, as that exhibited in (1) for argon, except for He⁴.

Now the quantum effect is contained in the kinetic-energy term, which gives rise to a quantum dispersion of the positions of the molecules. If the peak in C_V is attributable [as will be argued in (D)] to a rapidly changing balance in the competition of holes and occupied volume, the quan-

tum dispersion (in smearing out the difference between holes and occupied volume) should be expected to diminish the peak. Thus we expect that for He⁴ the C_V peak would have a magnitude smaller than that for argon.

(D) Model of lattice gas.—The model of a lattice gas[6] was discussed more than ten years ago. It is a classical "gas" moving on discrete lattice points, with an infinite repulsive force preventing two molecules from occupying the same site, and other interactions outside of this infinite core. For the special case in which all these other interactions are attractive, the system[6] can have at most one phase transition. It was shown in reference 6 that the thermodynamics of the model can be obtained from that of an Ising model in an external magnetic field H. In this correspondence, one has the $H = 0$ region of the Ising model transformed into the two-phase region plus the $V = V_C$ line of the lattice gas, as exhibited in Table I.

Now the Ising model with nearest-neighbor interaction, with $H = 0$, has been solved in two dimensions[7] for various lattices.[8] In three dimensions many approximate methods have been devised[8,9] for locating the singularities, and for finding the thermodynamical functions. Applying the transformation of reference 6 to these results we obtained various quantities for various lattice gases. These quantities are tabulated in Table II. The results for the two-dimensional lattice gases are exact. Those for the three-dimensional ones are computed from the Ising-model approximate computations of Baker.[9] The rest of the Table lists the experimental data of references 1, 2, and 4, the values of the parameter β given by Fisher,[10] and of standard critical measurements.

It is seen that qualitatively the three-dimensional lattice gas with nearest-neighbor interaction gives a fair description of the critical phenomenon. Now the critical phenomenon of a lattice gas originates from a rapidly changing balance in the competition between the occupied and unoccupied sites. One is thus led to the suggestion that in real gases, the critical phenomenon originates from a rapidly changing balance in the competition between holes and occupied volume.[11]

Table I. Correspondence between lattice gas and Ising model.

Lattice gas	Ising model
Two-phase region	$H = 0$, $\quad T \leq T_C$
$V = V_C$, $\quad T \geq T_C$	$H = 0$, $\quad T \geq T_C$

Table II. Critical data of lattice gases and of some real gases. L is defined in (2). $\beta = d \ln(V_G - V_L)/d \ln(T_C - T)$ at $T = T_C$.[a] V_{LO} = liquid volume at low T in equilibrium with vapor.

Lattice	C_V/RL $(T = T_C - 0)$	C_V/RL $(T = T_C + 0)$	$\left(\dfrac{pV}{RT}\right)$	$\left(\dfrac{d \ln p}{d \ln T}\right)$	V_C/V_{LO}	β
Hexagonal	0.9562	0.9562	0.076	7.0	2	$\tfrac{1}{8}$ [b]
Square	0.9890	0.9890	0.096	6.3	2	$\tfrac{1}{8}$
Triangular	0.9982	0.9982	0.110	6.0	2	$\tfrac{1}{8}$
Simple cubic	1.18	~0.4	0.226	4.8	2	~0.31 [a]
Bcc	0.98	~0.3	0.252	4.65	2	
Fcc	0.90	~0.3	0.268	4.4	2	
He			0.305	3.83	1.8	~0.33 [a]
Ne			0.296		2.3	
Ar	1.8	1.8	0.292	5.82	2.6	
Kr			0.333		2.8	
Xe			0.288		2.6	
O_2	2.4	2.4	0.293		3.3	

[a]See reference 10.
[b]See reference 6.

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[1]M. I. Bagatskii, A. V. Voronel, and V. G. Gusak, Zh. Eksperim. i Teor. Fiz. 43, 728 (1962) [translation: Soviet Phys.—JETP 16, 517 (1963)]; A. V. Voronel, Yu. R. Chashkin, V. A. Popov, and V. G. Simkin, Zh. Eksperim. i Teor. Fiz. 45, 828 (1963) [translation: Soviet Phys.—JETP 18, 568 (1964).

[2]See, e.g., L. D. Landau and E. M. Lifshitz, Statistical Physics (Addison-Wesley Press, Reading, Massachusetts, 1958), pp. 21, 79, 80, 81. See also p. 262, last paragraph.

[3]See, e.g., F. G. Brickwedde, H. van Dijk, M. Durieux, J. R. Clement, and J. K. Logan, The "1958 He⁴ Scale of Temperatures," National Bureau of Standards Monograph 10 (U. S. Dept. of Commerce, Washington, D. C., 1960).

[4]See, e.g., A. Michels, J. M. Levelt, and W. de Graaff, Physica 24, 659 (1958).

[5]J. de Boer, Physica 14, 139, 149 (1948).

[6]T. D. Lee and C. N. Yang, Phys. Rev. 87, 410 (1952).

[7]L. Onsager, Phys. Rev. 65, 117 (1944).

[8]See, e.g., the review article of C. Domb, Advan. Phys. 9, 149 (1960).

[9]G. A. Baker, Phys. Rev. 129, 99 (1963).

[10]M. E. Fisher, to be published.

[11]For other recent discussions of the critical phenomena, see P. C. Hemmer, M. Kac, and G. E. Uhlenbeck, J. Math. Phys. 5, 60 (1964), and reference 10.

[12]C. N. Yang, Bull. Am. Phys. Soc. 9, 276 (1964).