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Correlation Functions and the Critical Region of Simple Fluids

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The "classical" (e.g. van der Waals) theories of the gas-liquid critical point are reviewed briefly and the predictions concerning the nature of the singularities of the coexistence curve, the specific heat, and the compressibilities are compared critically with experiment and with the analytical and numerical results for lattice gas models.

The critical singularities are related to the behavior of the pair correlation function $G(r) = g(r) - 1$ and the Ornstein-Zernike theory of critical scattering is reviewed. Alternative derivations of the theory are discussed and its validity is assessed in relation to experiment and to more detailed theoretical calculations. The nature and magnitude of the expected deviations from the "classical" theory are described. The analogies with critical magnetic phenomena are mentioned briefly.

THIS is a review article about theories of the critical point and their experimental and theoretical validity. Recent work has revealed the shortcomings of the well-known approximate theories and it is hoped that this review, although in the main nonmathematical in character, will provide some stimulus to further theoretical (and experimental) work on this old, but still imperfectly understood problem.

1. THE CLASSICAL THEORY OF THE CRITICAL POINT

At temperatures below its critical temperature T_c a gas can be condensed by isothermal compression. At temperatures above T_c the transition from dense gas to liquid takes place without discontinuity of density or, as far as has been determined experimentally, without any higher-order singularities in the density or other variables. As the temperature increases to T_c the difference between the densities ρ_L and ρ_G of coexisting liquid and gas tends continuously to zero.¹ The limiting density ρ_c , and corresponding pressure p_c , define the *critical point* (see Fig. 1). In this article we shall be concerned with the properties of a simple fluid in the region of its critical point and in particular on the critical isochore $\rho = \rho_c$.

In many respects the behavior of binary fluid mixtures which undergo phase separation is closely analogous to the condensation of simple fluids and most of our remarks can be translated directly into

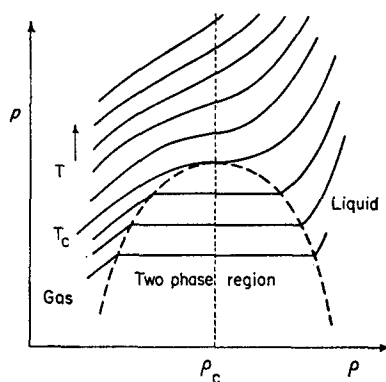


Fig. 1. Schematic isotherms for a simple fluid in the critical region.

such terms.² For simplicity, however, we refer in the main only to single-component systems.

As is well known, a qualitative account of condensation phenomena and the critical point is given by the classical equation of van der Waals

$$p/kT = \rho/(1 - b\rho) - a\rho^2/kT, \quad (1.1)$$

provided this is supplemented by the "equal area rule" of Maxwell which ensures that the density ρ is a single-valued function of the pressure p .³ The general appearance of the isotherms of a van der Waals gas in the critical region is similar to that of a real gas as shown in Fig. 1. In particular the p, ρ isotherms become flatter and flatter as T approaches T_c from above at the critical density and correspondingly the isothermal compressibility

$$K_T = -\frac{1}{V} \left(\frac{\partial V}{\partial p} \right)_T = \frac{1}{\rho} \left(\frac{\partial \rho}{\partial p} \right)_T \quad (1.2)$$

* J. S. Rowlinson, *Liquids and Liquid Mixtures* (Butterworths Scientific Publications, Ltd., London, 1959), Chap. 5.

³ Maxwell's thermodynamic derivation of the rule is unsatisfactory in that it is necessary to give thermodynamic significance to "unstable" (and "metastable") states on the original van der Waals isotherm. A formally equivalent but theoretically somewhat more convincing argument is to use the minimal properties of the Gibbs free energy (or chemical potential) to eliminate the unwanted parts of the van der Waals isotherm.

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¹ It now seems quite well established experimentally that for simple fluids, such as the noble gases, the coexistence curve does *not* have a significant "flat top." For a discussion of this suggestion see O. K. Rice, *J. Phys. & Colloid Chem.* **54**, 1293 (1950); and Ref. 60 below. See also D. R. Thompson and O. K. Rice, quoted in Ref. 11 below.

which is essentially the reciprocal of this slope, diverges to infinity at the critical point.

The derivation of the van der Waals equation given by Ornstein⁴ suggests that it should be a reasonably good approximation when the pair interaction potential $\phi(r)$ of the molecules of the fluid has a short-range strongly repulsive core and a very long-range weakly attractive tail. Indeed Kac, Uhlenbeck, and Hemmer⁵ have recently shown that the van der Waals isotherm (*with flat part*) follows rigorously for a one-dimensional gas of hard rods interacting with an attractive exponential potential *in the limit* that the exponential becomes infinitely long-ranged and infinitely weak [holding $\int_0^\infty \phi(r) dr$ constant]. It seems probable, however, that the behavior of a real gas *in its critical region* is crucially dependent on the finite or relatively short range of the attractive parts of more realistic potentials. This is supported by the comparison with real systems and exactly soluble models we present in the next section.

Three principal predictions concerning the critical region which follow from the van der Waals equation are:

(a) that the *coexistence curve* follows a square-root law, i.e., the difference between liquid and gaseous densities vanishes as

$$\rho_L - \rho_G \approx A(T_c - T)^{1/2} \quad (T \rightarrow T_c^-); \quad (1.3)$$

(b) that the *compressibility* along the critical isochore diverges as a simple pole,

$$K_T \approx B/|T - T_c| \quad (\rho = \rho_c, T \rightarrow T_c^+); \quad (1.4)$$

and

(c) that the *specific heat* (at constant volume) along the critical isochore rises to a maximum and then falls discontinuously as T increases through T_c , i.e.,

$$C_V(T) \approx C_c^+ - D^+ |T - T_c|, \quad T \geq T_c, \quad (1.5)$$

with $C_c^+ - C_c^- = \Delta C > 0$.

The compressibility of the gas and of the liquid

along the coexistence curve (i.e. at condensation) also diverges as a simple pole as $T \rightarrow T_c^-$ according to the van der Waals equation but the amplitude corresponding to B in (1.4) is smaller. (The constants A , B , C_c^+ and D^+ can of course be written explicitly in terms of the van der Waals parameters a and b .)

It is important to note that these predictions are not peculiar to the van der Waals equation but follow from almost *all* approximate equations of state. Indeed they are essentially a direct consequence of the implicit or explicit assumption that the free energy and the pressure can be expanded in a Taylor series in density and temperature *at the critical point*: in other words that the critical point is not a singular point of the free energy expressed as a function of ρ and T (except in as far as Maxwell's rule is utilized *below* $T = T_c$).⁶

To demonstrate this put

$$\Delta p = p - p_c, \quad \Delta \rho = \rho - \rho_c, \quad \Delta T = T - T_c. \quad (1.6)$$

and assume that

$$\Delta p = a(T) + b(T)\Delta\rho + c(T)\Delta\rho^2 + d(T)\Delta\rho^3 + \dots \quad (1.7)$$

By definition $a(T_c) = 0$ so we assume similarly that

$$a(T) = a_1\Delta T + a_2\Delta T^2 + \dots \quad (1.8)$$

Since the compressibility is infinite at the critical point, $b(T_c)$ must vanish so again we assume

$$b(T) = b_1\Delta T + b_2\Delta T^2 + \dots \quad (1.9)$$

Finally since $b(T_c) = 0$ and the pressure above T_c must be a monotonic increasing function of ρ we have $C(T_c) = 0$ and, presumably, $C(T)$ is small in the critical region. We thus obtain for small $\Delta\rho$ and ΔT the isotherms

$$\Delta p = a_1\Delta T + b_1\Delta T\Delta\rho + d_0\Delta\rho^3 + \dots \quad (1.10)$$

Near the critical point the compressibility is hence given by

$$K_T \simeq \frac{(b_1\rho_c)^{-1}}{\Delta T + (3d_0/b_1)\Delta\rho^2}, \quad (1.11)$$

from which the prediction (b) follows. Application of the equal area rule to the isotherms (1.10) with negative ΔT yields the coexistence curve

$$\Delta\rho^2 \simeq (b_1/d_0) |\Delta T| \quad (T \leq T_c), \quad (1.12)$$

which implies the square-root law (a). The divergence

⁴ L. S. Ornstein, Dissertation, Leiden 1908; see also Ref. 5.
⁵ M. Kac, G. E. Uhlenbeck, and P. C. Hemmer, J. Math. Phys. 4, 216 (1963). It should be noted that the correction to ideal gas behavior, arising from the hard core and represented by the parameter b , is exact in one dimension but only approximate in two or three dimensions. On the other hand the accuracy of the correction represented by the parameter a depends mainly on the long-range nature of the attractive tail of the potential and not so directly on dimensionality. Consequently, although the behavior of a three-dimensional model in the corresponding long-range limit should be van der Waals-like [in that Eqs. (1.3) to (1.5) should hold], one should still not expect van der Waals' equation (1.1) to hold precisely.

⁶ See, for example, Landau's theory of the critical point and second-order phase transitions [L. D. Landau and E. M. Lifshitz, *Statistical Physics* (Pergamon Press, Ltd., London, 1958), pp. 259-268 and pp. 434-439].

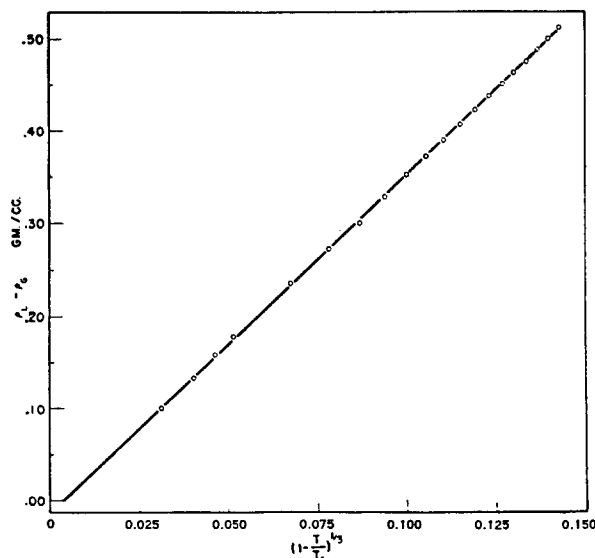


Fig. 2. Coexistence curve for xenon: plot of $(\rho_L - \rho_G)$ vs $[1 - (T/T_c)]^{1/3}$ (after Weinberger and Schneider⁹).

of the compressibility along the coexistence curve as $(T_c - T)^{-1}$ then follows from (1.10).

By integrating (1.9) with respect to Δp one finds the free energy $F(T, \rho)$. If one assumes that the additive constant of integration is also a nonsingular function of T and imposes the continuity of F on the coexistence curve (1.12) one finally derives the prediction (c) of the discontinuity in $C_V(T)$.

2. THE NATURE OF THE CRITICAL SINGULARITIES

Perhaps the most striking test of the predictions of the classical theories is provided by the data on the coexistence curves of simple gases. Some time ago Guggenheim⁷ showed that the gases Ne, Ar, Kr, Xe, N₂, and O₂ obey closely a law of corresponding states of the form

$$(\rho_L - \rho_G)/2\rho_c = A(1 - T/T_c)^\beta, \quad (T \rightarrow T_c), \quad (2.1)$$

with $\beta = \frac{1}{3}$. This relation was observed to hold with an accuracy of 0.5% (or better) in $\Delta\rho/\rho_c$ and in $\Delta T/T_c$ and over a range of temperatures from $T/T_c \simeq 0.6$ up to within $\frac{1}{2}\%$ of the critical temperature by when $(\rho_L - \rho_G)/2\rho_c$ had fallen to about 0.30. In earlier work on CO₂, Michels, Blaisse, and Michels⁸ found that the coexistence curve could be fitted over a similar range but with somewhat greater accuracy by (2.1) with the index $\beta = 0.357$.

These results seem to be in clear disagreement

with the classical prediction $\beta = \frac{1}{3}$ which should be applicable in range of $(T - T_c)$ and $(\rho - \rho_c)$ observed. They certainly show that the experimental coexistence curve is much flatter than the van der Waals curve. However, experiments near the critical region are very difficult to perform; a long time is needed to establish equilibrium and hysteresis phenomena are difficult to avoid; the system is very susceptible to minute amounts of impurities and, due to the large compressibility, highly sensitive to gravitational fields. Indeed as shown by Weinberger and Schneider⁹ it is important to take special precautions to reduce the effects of gravity if the true shape of the coexistence curve is to be measured close to T_c . In a very careful study of xenon (see Fig. 2) they extended the density measurements down to temperatures differing from T_c by only 1 part in 30 000 (i.e., $\Delta T/T_c \simeq 0.003\%$) and down to corresponding density differences of $(\rho - \rho_c)/2\rho_c \simeq 0.04$. [The temperature was controlled to within $\pm 0.001^\circ\text{C}$.] Their data accurately obey the relation (2.1) with a nonclassical value of the index β over about three decades in $(T - T_c)$. Analysis of their measurements indicates¹⁰ that

$$\beta = 0.345 \pm 0.015 \quad (2.2)$$

which is not inconsistent with a value of exactly $\frac{1}{3}$ as may be seen in Fig. 2.

While it is always possible that measurements taken much closer still to the critical point might yet yield the value $\beta = \frac{1}{3}$ it seems reasonable to conclude that the classical theory does *not* provide the correct description of reality. Furthermore measurements of the phase boundaries of binary fluid mixtures near both their upper and lower critical points are also fitted well by the same cube-root law.¹¹ This suggests that the behavior close to a critical point is insensitive to the detailed nature of the intermolecular forces. To check how far β is really independent of the interaction potentials it would be desirable to have measurements on other systems of an accuracy matching the experiments on xenon. One should note, however,

⁹ M. A. Weinberger and W. G. Schneider, *Can. J. Chem.* **30**, 422 (1952).

¹⁰ Note that the plot of $\rho_L - \rho_G$ versus $[1 - (T/T_c)]^{1/3}$ in Fig. 2 is a good straight line down to $(\rho_L - \rho_G)/2\rho_c = 0.04$ but does not extrapolate exactly to the origin [$\rho_L = \rho_G$ at $T = T_c$] as it should. This suggests that the index β is not precisely $\frac{1}{3}$ and a log-log plot leads to the value quoted. The uncertainty reflects the spread of the experimental points about the best straight line.

¹¹ See Ref. 2, pp. 165-166 and especially the work of O. K. Rice referred to therein. See, also, D. R. Thompson and O. K. Rice, "Shape of the coexistence curve in the perfluoromethylcyclohexane-carbon tetrachloride system, II," *J. Am. Chem. Soc.* (1964) in press.

⁷ E. A. Guggenheim, *J. Chem. Phys.* **13**, 253 (1945).

⁸ A. Michels, B. Blaisse, and C. Michels, *Proc. Roy. Soc. (London)* **A160**, 358 (1937). More accurate measurements on CO₂ have since been made by H. L. Lorentzen, *Acta Chem. Scand.* **7**, 1335 (1953) and later work.

TABLE I. Critical indices.

Index	below T_c			above T_c ($\rho = \rho_c$)			
	α'	β	γ'	α	γ	ν	η
Defined in equations	(2.7, 2.12)	(2.1)	(2.8)	(2.7, 2.12)	(2.8)	(3.10, 5.6)	(4.7, 5.3)
Classical theory	$0_{\text{discon.}}$	$\frac{1}{8}$	1	$0_{\text{discon.}}$	1	$\frac{1}{2}$	0
Lattice gases $d = 2$	0_{log}	$\frac{1}{8}$	$1\frac{1}{2}$	0_{log}	$1\frac{1}{2}$	1	$\frac{1}{4}$
Lattice gases $d = 3$	≥ 0	$\approx \frac{5}{16}$	$\geq 1\frac{1}{4}$	$\geq 0, \leq 0.2$	$1\frac{1}{4}$	≈ 0.64	$\approx \frac{1}{16}$
Experiment	$\geq 0_{\text{log}}$	0.33–0.36	$\geq 1.27(?)$	$\geq 0.1 ?$	$> 1.1 ?$	$> 0.55 ?$	$> 0(?)$

Note: α' , β , and γ' are related by (2.20) and γ , ν , and η by (5.7). The queries, ? and (?), indicate greater and lesser degrees of experimental doubt.

that any value of β between $\frac{1}{2}$ and $\frac{1}{4}$ is inconsistent with the assumption that the critical point is a nonsingular point of the free energy in the sense discussed in the previous section.

The shape of the coexistence curve may also be studied theoretically for more-or-less idealized models of a fluid. The only model so far sufficiently tractable to yield significant predictions in the critical region is the very simplest lattice gas in which each molecule occupies a site of a lattice to the exclusion of other molecules and interacts, attractively, only with nearest-neighboring molecules. This model is equivalent to the well known Ising model of ferromagnetism which has been studied intensively.^{12,13}

The exact calculation of the free energy of the plane square lattice gas along its critical isochore (corresponding to zero magnetic field) was first achieved by Onsager.¹⁴ In addition, however, Onsager¹⁵ and Yang¹⁶ were able to find the coexistence curve (corresponding to the spontaneous magnetization). They found the relation (2.1) but with the index

$$\beta = \frac{1}{8}. \quad (2.3)$$

This result, which implies a very flat coexistence curve, is, of course, quite inconsistent with classical theory.¹⁷ It is important, furthermore, to note that the index β is independent of lattice structure for all soluble plane Ising lattices (including the triangular, honeycomb, kagomé, and checkerboard lattices^{12,13}).

For three-dimensional lattice gases no rigorous theoretical results are available. Nonetheless on the

basis of sufficiently long power-series expansions¹⁸ it has proved possible to draw quite accurate conclusions concerning the shape of the corresponding coexistence curves. [The coefficients are analyzed numerically with the aid of the recently introduced technique of Padé approximants.¹⁹]

The behavior again appears to be independent of lattice structure. [The simple, body-centered and face-centered cubic lattices^{20,21} and the tetrahedral (diamond) lattice²² have been studied; the latter on the basis of the more sensitive ratio method.²³] Dimensionality, however, is important since, in contrast to (2.3), the index β is found to lie in the range^{21,22}

$$0.303 \leq \beta \leq 0.318 \quad (2.4)$$

which is consistent with the conjecture $\beta = \frac{5}{16} = 0.31250$.

It is remarkable, and perhaps unexpected, that a model as simple as a lattice gas with only nearest-neighbor interactions should yield a result for the shape of the coexistence curve so close to the experimental results (2.1) and (2.2). The agreement suggests that in the critical region the lattice gas represents rather adequately the pertinent features of a real gas. It appears that only the grosser features of the model—in particular the dimensionality and the short range of the forces—are really essential for obtaining a good description of critical behavior.

It seems probable, nonetheless, that the difference of about 0.025 between the experimental and theoretical values of β is a real discrepancy due, presumably, to the more artificial aspects of the Ising Hamiltonian which, in particular, restricts the molecules to the lattice positions. There remains

¹² A. comprehensive review of the Ising model is C. Domb, *Advan. Phys.* 9, Nos. 34, 35 (1960), while Ref. 13 is a brief review of more recent results.

¹³ M. E. Fisher, *J. Math. Phys.* 4, 278 (1963).

¹⁴ L. Onsager, *Phys. Rev.* 65, 117 (1944).

¹⁵ L. Onsager, *Nuovo Cimento Suppl.* 6, 261 (1949); see also E. W. Montroll, R. B. Potts, and J. C. Ward, *J. Math. Phys.* 4, 308 (1963).

¹⁶ C. N. Yang, *Phys. Rev.* 85, 808 (1952); T. D. Lee and C. N. Yang, *Phys. Rev.* 87, 410 (1952).

¹⁷ Since β is the inverse of an integer it could still be possible for the free energy to be an analytic function of ρ at the critical point. In view of the logarithmic singularity in the specific heat, however (Ref. 14 and the discussion below), this possibility seems rather remote.

¹⁸ The expansion variable is $\exp[-V_0/kT]$ where V_0 is the depth of the well in the pair interaction potential. Details of the expansions are given in Ref. 11.

¹⁹ G. A. Baker, Jr., J. L. Gammel, and J. G. Wills, *J. Math. Anal. Appl.* 2, 405 (1961).

²⁰ G. A. Baker, Jr., *Phys. Rev.* 124, 768 (1961).

²¹ J. W. Essam and M. E. Fisher, *J. Chem. Phys.* 38, 802 (1963).

²² J. W. Essam and M. F. Sykes, *Physica* 29, 378 (1963).

²³ C. Domb and M. F. Sykes, *J. Math. Phys.* 2, 63 (1961).

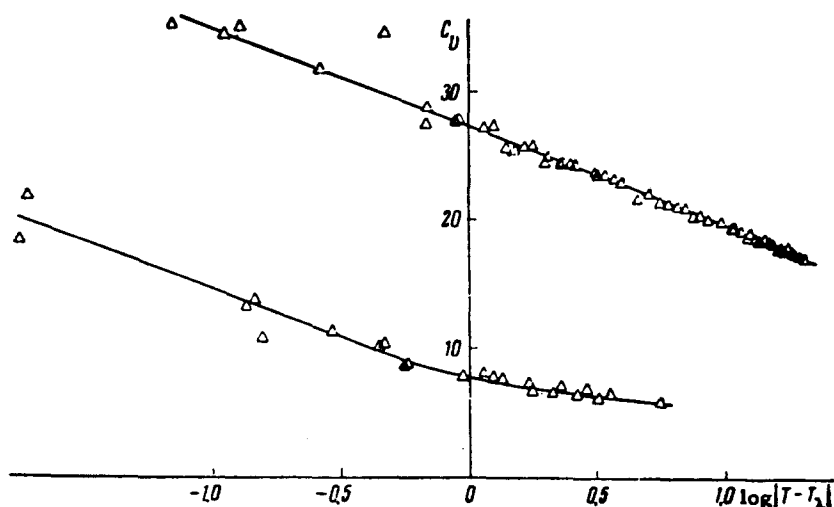


FIG. 3. Variation of the constant-volume specific heat of argon along the critical isochore (after Bagatskii *et al.*²⁵). (Note that the logarithm to the base ten of $|T - T_c|$ in $^{\circ}\text{K}$ is plotted.)

Variation of C_v of argon with $\log |T - T_c|$.

($T_c = 150.5^{\circ}\text{K}$).

the theoretical problem of calculating β for more realistic continuum models. (For convenience the various results for β are collected in Table I.)

Turning now to the question of the specific heats, it has long been known that real gases exhibit a large "anomalous" specific-heat maximum above T_c which lies near the critical isochore and which is not expected on classical theory.²⁴ Similarly in the two-phase region below the critical point specific heats rise much more rapidly than expected as T approaches T_c . From the earlier measurements one could not conclude with certainty that the specific heat actually became infinite at T_c , but recent measurements by Bagatskii, Voronel', and Gusak²⁵ of $C_v(T)$ for argon along the critical isochore (see Fig. 3) suggest strongly that

$$C_v(T) \rightarrow \infty \quad \text{as } T \rightarrow T_c \pm. \quad (2.5)$$

Such a result is again inconsistent with classical theory.

The measurements covered a range from 15% below to 5% above T_c at temperature intervals of 0.04 to 0.05 $^{\circ}\text{C}$ (corresponding to $\Delta T/T_c \simeq 0.03\%$). Over a range of one or two decades in $|T - T_c|$ the specific heat could be fitted quite well²⁵ by a logarithmic singularity of the form

$$C_v(T) \simeq -A^+ \log |1 - (T/T_c)| + B^+ \quad (T \geq T_c), \quad (2.6)$$

where the marked asymmetry of the curve (see

Fig. 3) indicates that $B^+ \ll B^-$ and possibly that $A^+ < A^-$. The specific-heat curve in fact resembles quite closely the famous lambda anomaly displayed by liquid helium at its transition to the superfluid state.²⁶ [In this case the formula (2.6) is followed very accurately over four or more decades.²⁶ It should be noted, however, that the lambda point of helium has a quantum-mechanical origin and is not a critical point in the usual sense.]

The data for argon are not at present, accurate enough to confirm (2.6) as closely as might be wished.^{26a} To avoid prejudicing the conclusions one should preferably consider a singularity of a form such as

$$C_v(T) \simeq (A^+/\alpha) \{ |1 - (T/T_c)|^{-\alpha} - 1 \} + B^+ \quad (T \geq T_c), \quad (2.7)$$

and ask for the experimental value (and uncertainty) of the index α . [When $\alpha \rightarrow 0$ this expression reduces to the logarithmic singularity (2.6).] In particular the definite curvature of the plot of $C_v(T)$ versus $\log |T - T_c|$ for $T > T_c$ (see Fig. 3) suggests that the true value of α might be greater than say 0.1. If this is so it seems probable that below T_c the index has a somewhat different value, α' which is probably less than 0.1. It would be valuable to have similar and more extensive measurements on the other noble gases in order to test the relation

²⁴ M. J. Buckingham and W. M. Fairbank, in *Progress in Low Temperature Physics III*, edited by C. J. Gorter (North-Holland Publishing Company, Amsterdam, 1961), Chap. 3.

²⁵ See Ref. 2, pp. 100-101; Ref. 8; and A. Michels, J. M. H. Levelt, and W. de Graaff, *Physica* 24, 769 (1958).

²⁶ M. I. Bagatskii, A. V. Voronel', and B. G. Gusak, *Zh. Eksperim. i Teor. Fiz.* 43, 728 (1962) [English transl.: *Soviet Phys.—JETP* 16, 517 (1963)].

^{26a} More recent experiments on oxygen have given very similar results: A. V. Voronel', Yu. R. Chasshkin, V. A. Popov, and V. G. Simkin, *Zh. Eksperim. i Teor. Fiz.* 45, 828 (1963) [English transl.: *Soviet Phys.—JETP* 18, 568 (1964)].

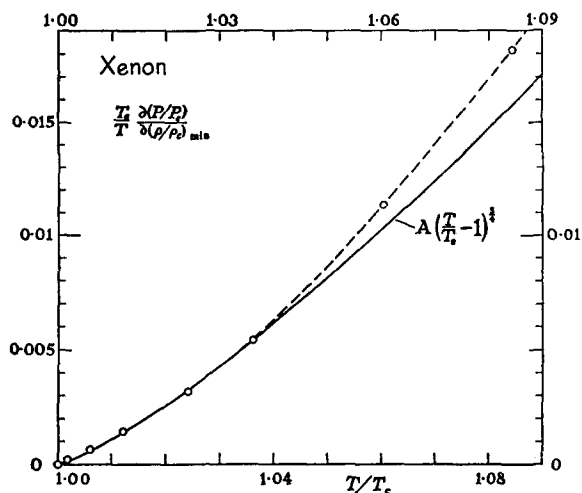


FIG. 4. Variation of the inverse of the maximum isothermal compressibility of xenon (based on the experiments of Habgood and Schneider³⁰).

(2.7) more critically and to decide how far a logarithmic singularity might be truly "universal."^{26a}

Significant theoretical predictions are again available only for the simple lattice gas models. Onsager's rigorous solution¹⁴ for the plane square lattice (and subsequent results for all other soluble plane lattices^{12,13}) yielded a *symmetric* logarithmic specific heat singularity, i.e., $\alpha = \alpha' = 0$ and $A^+ = A^-$, $B^+ = B^-$. Although this famous result demonstrates conclusively the weakness of the classical theory and is very suggestive in view of the experimental results it is, unfortunately, restricted to two-dimensional systems.

For three-dimensional Ising lattices the specific-heat series expansions have been calculated both above and below T_c . Numerical analysis of these series indicates that $C_V(T)$ is almost certainly infinite at T_c but the precise nature of the divergence is more difficult to ascertain. Below the critical point the series can be fitted well by a logarithmic singularity (i.e., $\alpha' = 0$).^{13,22,27,28} As with the experimental results, however, it is not easy to exclude the possibility of a slightly sharper singularity corresponding in (2.7) to, say, $\alpha' = 0.06$. On the high-temperature side of the transition the series may be fitted moderately well by a logarithmic singularity if $A^+/A^- \simeq \frac{1}{2}$.^{27,13} However, careful analysis of the ratios of coefficients definitely suggests a sharper singularity of the form (2.7) with $\alpha \simeq 0.2$.^{29,13} This would lead to a shallow parabolic curve for $C_V(T)$ versus $\log|T - T_c|$ not inconsistent with the corresponding (lower) experimental curve in Fig. 3.

One may hope that with further work based on longer series or on more rigorous arguments the theoretical conclusions will be drawn more firmly. The present results are summarized in Table I.

The accurate experimental measurement of the isothermal compressibility of a gas near its critical point is not easy and the classical prediction (1.4) that K_T should diverge as $(T - T_c)^{-1}$ along the isochore does not seem to have been properly tested. In practice plots of $1/K_T$ versus temperature are distinctly concave upwards in the critical region which suggests that the compressibility might diverge more sharply than a simple pole, i.e., as

$$K_T(T) \approx \frac{B}{|(T/T_c) - 1|^\gamma} \quad (\rho = \rho_c, T \rightarrow T_c) \quad (2.8)$$

with $\gamma > 1$. By way of illustration a plot of $1/K_T$ (suitably normalized) versus T/T_c for xenon is shown in Fig. 4.³⁰ The experimental results indicated by circles and the broken line, were obtained by differentiation of the experimental isotherms, a procedure which is necessarily subject to appreciable uncertainty when K_T is large. The solid curve in Fig. 4 corresponds to the nonclassical prediction (2.8) with $\gamma = 1.25$ (see below) and is evidently quite consistent with the experimental points near T_c . This fit cannot be considered very significant, however, since estimates of γ based on the data alone are rather indefinite, although they do seem to indicate that γ is greater than 1.1.

More extensive and accurate experimental data would be extremely valuable since the compressibility is an important theoretical parameter and one which is usually somewhat easier to calculate than the specific heat or the coexistence curve. Indeed the theoretical situation for the simple lattice gases is quite unequivocal (see Table I). On the basis of Onsager and Kaufman's exact calculations³¹ of the correlation functions it can be shown³² that the compressibility of the plane square lattice gas (which is isomorphic to the magnetic susceptibility) should diverge as (2.8) with

$$\gamma = 1\frac{3}{4}. \quad (2.9)$$

This represents a very large deviation from the classical prediction $\gamma = 1$. Numerical examination of the corresponding series expansions confirms (2.9) in two dimensions for all other lattices and leads,

³⁰ Figure 4 is based on the measurements of H. W. Habgood and W. G. Schneider, Can. J. Chem. 32, 98 (1954) as presented in their Fig. 4.

²⁷ M. E. Fisher and M. F. Sykes, Physica 28, 939 (1962).

²⁸ G. A. Baker, Jr., Phys. Rev. 129, 99 (1963).

²⁹ C. Domb and M. F. Sykes, Phys. Rev. 108, 1415 (1957).

³¹ B. Kaufman and L. Onsager, Phys. Rev. 76, 1244 (1949).

³² See Sec. 5 and M. E. Fisher, Physica 25, 521 (1959).

in three dimensions, to the estimate

$$\gamma = 1.250, \quad (2.10)$$

which is again independent of lattice structure and accurate to ± 0.001 or better.^{12,20,23}

The compressibility of the simple lattice gases can also be studied on the coexistence curve below T_c .²¹ In two dimensions it is found that (2.8) holds with the index $\gamma' = \frac{1}{4}$ so that $\gamma' = \gamma$ although the amplitude B^- is much smaller than B^+ . In three dimensions the analysis yields $\gamma' \simeq 1.25 = \gamma$ but cannot at present exclude the possibility that γ' exceeds γ (by perhaps 0.05).

On the basis of heuristic arguments related to the Frenkel-Bijl-Band picture of condensation³³ Essam and Fisher^{21,34} conjectured that the indices for the specific heat, coexistence curve and compressibility below T_c were in general related by

$$\alpha' + 2\beta + \gamma' = 2, \quad (2.11)$$

where the index α' is defined, more precisely, by

$$\alpha' = \lim_{T \rightarrow T_c^-} [\log C_v(T) / |\log (T_c - T)|], \quad (2.12)$$

and similarly for β and γ' . A logarithmic specific heat still corresponds to $\alpha' = 0$ so that the relation (2.11) is certainly verified for the two-dimensional lattice gases (see Table I). The formula remains true even for a van der Waals gas since a discontinuity in specific heat is now also equivalent to $\alpha' = 0$ [assuming only $C_v(T_c^-) > 0$].

Rushbrooke³⁵ has shown that the relation (2.11) can be proved as an inequality (with \geq replacing $=$) by purely thermodynamic reasoning. His argument as presented applies only to a ferromagnetic system but it may be adapted for a fluid as follows.

Firstly recall that in the two-phase region the specific heat at constant *total* volume is related to the properties of the system in its liquid and gaseous phases separately by³⁶

$$C_v = x_L C_v^L + x_G C_v^G - T \left(\frac{\partial p}{\partial T} \right)_\sigma \left[x_L \left(\frac{\partial V_L}{\partial T} \right)_\sigma + x_G \left(\frac{\partial V_G}{\partial T} \right)_\sigma \right], \quad (2.13)$$

where the subscript σ denotes properties along the coexistence curve and where the mole fractions are given by

$$x_L = \frac{V_G - V}{V_G - V_L}, \quad x_G = \frac{V - V_L}{V_G - V_L}. \quad (2.14)$$

Now by the standard argument used to relate C_p and C_v one may show that in a single phase

$$C_\sigma = C_v - T \left(\frac{\partial p}{\partial V} \right)_T \left(\frac{\partial V}{\partial T} \right)_\sigma \left(\frac{\partial V}{\partial T} \right)_\sigma. \quad (2.15)$$

On eliminating the factor $(\partial V / \partial T)_\sigma$ through

$$\left(\frac{\partial V}{\partial T} \right)_\sigma = \left(\frac{\partial V}{\partial T} \right)_p + \left(\frac{\partial V}{\partial p} \right)_T \left(\frac{\partial p}{\partial T} \right)_\sigma, \quad (2.16)$$

and substituting for C_σ^L and C_σ^G separately in (2.12) one expresses C_v in terms of C_v^L and C_v^G . Finally on introducing the coexisting densities ρ_L and ρ_G and the corresponding isothermal compressibilities K_T^L and K_T^G , one gets

$$C_v(T) = x_L C_v^L + x_G C_v^G + \frac{x_L T}{\rho_L^3 K_T^L} \left(\frac{\partial \rho_L}{\partial T} \right)^2 + \frac{x_G T}{\rho_G^3 K_T^G} \left(\frac{\partial \rho_G}{\partial T} \right)^2. \quad (2.17)$$

Now C_v^L and C_v^G are necessarily positive since they are essentially mean square energy fluctuations. Consequently all terms on the right of (2.17) are positive and by dropping the first three we obtain the inequality

$$C_v(T) \geq \frac{x_G T}{\rho_G^3 K_T^G} \left(\frac{\partial \rho_G}{\partial T} \right)^2. \quad (2.18)$$

As the critical point is approached at constant density x_G (and x_L) approaches the value $\frac{1}{2}$, ρ_G (and ρ_L) tends to ρ_c and $(\partial \rho_G / \partial T)$ diverges as $(T_c - T)^{-1+\beta}$.³⁷ If K_T^G , the compressibility at condensation, diverges as $(T_c - T)^{-\gamma'}$ we obtain

$$\log C_v(T) \geq (2 - 2\beta - \gamma') |\log (T_c - T)| + \dots \quad (2.19)$$

The higher-order terms vanish on dividing by $|\log (T_c - T)|$ and taking the limit $T \rightarrow T_c^-$ which, by (2.12), yields the index α' . We have thus proved quite generally

$$\alpha' + 2\beta + \gamma' \geq 2. \quad (2.20)$$

Various consequences follow from this inequality. For the two-dimensional lattice gases the rigorous results¹⁴⁻¹⁶ $\alpha' = 0$ and $\beta = \frac{1}{8}$ show that $\gamma' \geq \frac{1}{4}$ thereby confirming the numerical estimates. [As before, the van der Waals gas corresponds to the case of equality.] If, for a three-dimensional lattice gas, the values $\beta = 0.3125$ and $\gamma' = 1.25$ are

³⁷ We assume (as is true in reality and for the models considered) that as $T \rightarrow T_c$ $[\frac{1}{2}(\rho_L + \rho_G) - \rho_c]$ does not vanish as rapidly as does $(\rho_L - \rho_G)$.

³³ J. Frenkel, *Kinetic Theory of Liquids* (Oxford University Press, London, 1946), Chap. VII; J. Chem. Phys. **7**, 200, 538 (1939); A. Bijl, Doctoral Dissertation, Leiden, 1938; W. Band, J. Chem. Phys. **7**, 324, 927 (1939).

³⁴ Other conjectures relating the indices γ and β have been made by B. Widom [J. Chem. Phys. **37**, 2703 (1962)].

³⁵ G. S. Rushbrooke, J. Chem. Phys. **39**, 842 (1963).

³⁶ See, for example, Ref. 2, p. 41.

accepted one must conclude that $\alpha' \simeq 0.125$. Conversely for a logarithmic specific heat singularity the compressibility index γ' would have to exceed 1.25 by about 0.1. At present it is difficult to judge between these alternatives.^{21,35}

For a real gas the evidence of Fig. 3 suggests $0.1 > \alpha' \geq 0$ and the coexistence data indicate $\beta < 0.36$. Consequently we should certainly have

$$\gamma' \geq 1.27, \quad (2.21)$$

and probably $\gamma' \geq 2 - 2(0.345) = 1.31$. It would be most interesting to have an experimental test of this prediction since it differs appreciably from the classical result.

It should be mentioned that Widom and Rice³⁸ have observed that the critical isotherms of real gases also deviate significantly from the classical prediction being much flatter than the cubic (p, ρ) curve which follows from the van der Waals equation. As yet however, this feature has not been investigated theoretically for lattice gases.

3. PAIR CORRELATION FUNCTION AND CRITICAL SCATTERING

To obtain insight into the microscopic nature of a fluid in the critical region it is natural to consider the many-particle distribution functions $n_s(\mathbf{r}_1, \dots, \mathbf{r}_s)$ which describe the correlations between the constituent molecules. In particular the pair correlation function defined, for a uniform system, by

$$g(\mathbf{r}_{12}) = n_2(\mathbf{r}_1, \mathbf{r}_2)/n_1(\mathbf{r}_1)n_1(\mathbf{r}_2) = n_2(\mathbf{r}_{12})/\rho^2 \quad (3.1)$$

is of central importance. When the system is in one phase $g(r) \rightarrow 1$ as $r \rightarrow \infty$ and one may introduce the net correlation function

$$G(\mathbf{r}) = g(\mathbf{r}) - 1 \quad (3.2)$$

which decays to zero as $r \rightarrow \infty$. The deviation of $G(\mathbf{r})$ from zero is a direct measure of the influence of one molecule on another.

As is well known $G(\mathbf{r})$ is rather directly related to the thermodynamic variables of the system. For our purposes the most important result is the so called fluctuation theorem for the isothermal compressibility,

$$k_B T \left(\frac{\partial \rho}{\partial p} \right)_T = k_B T \rho K_T = 1 + \rho \int G(\mathbf{r}) d\mathbf{r}, \quad (3.3)$$

which is a quite general consequence of the laws of statistical mechanics. [For a two-dimensional system the integral in (3.3) is restricted appro-

priately while for a lattice system it is replaced by a sum.]

Now $G(\mathbf{r})$ is essentially a bounded function (more precisely its integral over a finite region is bounded in virtue of the existence of a maximum density arising from the incompressibility of real molecules.) Hence the fact that K_T becomes infinite at the critical point can only be understood if the integral over $G(\mathbf{r})$ diverges at its upper limits. This means that at the critical point the net correlation function becomes *long-range* in the sense that it decays to zero more slowly than $1/r^3$ (or in d -dimensions than $1/r^d$). It is clearly of interest to know the precise nature of this critical decay and to understand the rate of approach of $G(\mathbf{r})$ to its long-range behavior as $T \rightarrow T_c$.

Fortunately the pair correlation function can also be studied directly by scattering waves off the system. In practice experiments are usually performed with light or with x rays but thermal neutrons may also be used.³⁹ The observed angular dissymmetry is then a direct measure of the degree of correlation. To the extent that multiple scattering may be neglected (first Born approximation) we have for the scattering intensity

$$I(\mathbf{k})/I_0(\mathbf{k}) = \chi(\mathbf{k}) = 1 + \rho \hat{G}(\mathbf{k}), \quad (3.4)$$

where $I_0(\mathbf{k})$ is the scattering intensity in the absence of correlation (the molecular form factor), \mathbf{k} is the wave vector, $k = (4\pi/\lambda) \sin \frac{1}{2}\theta$, and where

$$\hat{G}(\mathbf{k}) = \int e^{i\mathbf{k} \cdot \mathbf{r}} G(\mathbf{r}) d\mathbf{r} \quad (3.5)$$

is the Fourier transform of $G(\mathbf{r})$; for an isotropic three-dimensional system

$$\hat{G}(k) = 4\pi \int_0^\infty \frac{\sin kr}{kr} G(r) r^2 dr. \quad (3.6)$$

The ratio $\chi(k)$ may be regarded as a generalized "susceptibility" since it measures the response of the fluid to an impressed periodic potential of wave number k .⁴⁰

Comparison of (3.5) and (3.4) with the fluctuation relation (3.3) shows that

$$\chi(0) = \lim_{k \rightarrow 0} I(k)/I_0(k) = 1 + \rho \hat{G}(0) = k_B T \rho K_T, \quad (3.7)$$

so that the scattering intensity extrapolated to zero angle is proportional to the isothermal compress-

³⁸ B. Widom and O. K. Rice, J. Chem. Phys. 23, 1250 (1955).

³⁹ L. Van Hove, Phys. Rev. 95, 249 (1954). To discuss neutron scattering fully one must also consider the time dependence of the pair correlation function. Near the critical point, however, the decay of fluctuations probably becomes slower and it is reasonable to neglect this aspect of the problem in first approximation.

⁴⁰ P. G. de Gennes, Nuovo Cimento 9, Suppl. 1, 240 (1958).

ibility. By virtue of the divergence of K_T at the critical point the low-angle scattering must thus become very large as the critical point is approached in the one-phase region. This is the "anomalous" critical scattering long known with visible light as *critical opalescence*. In physical terms one may say that the large compressibility near the critical point allows long-wavelength density fluctuations to grow to large amplitude and these produce visible diffraction.³⁹

The classical theory of critical scattering is that developed by Ornstein and Zernike.^{41,42} Their results have since been rederived many times and in various ways. In order to discuss the validity of their conclusions we will outline two approaches which characterize most of the derivations: on the one hand the original method of Ornstein and Zernike^{41,43} which is perhaps the more mathematical, and on the other hand a semithermodynamic method which concentrates attention on the fluctuations of the free energy and their relation to the gradients of the density deviations. This latter approach was initiated by Rocard⁴⁴⁻⁴⁶ in the spirit of Einstein's semiphenomenological ideas, but we will follow the presentation of Landau.⁴⁶

Ornstein and Zernike⁴¹ argue on a heuristic basis that the correlation $G(\mathbf{r}_1 - \mathbf{r}_2)$ between molecules 1 and 2 can be regarded as caused by (i) a *direct* influence of 1 on 2 described by the so-called "direct correlation function" $C(\mathbf{r}_1 - \mathbf{r}_2)$ which should be short-ranged [essentially having the range of the pair potential $\phi(r)$], and (ii) an indirect influence propagated directly from 1 to a third molecule at \mathbf{r}_3 which in turn exerts its total influence on molecule 2. Integrating over \mathbf{r}_3 they thus write the relation

$$G(\mathbf{r}_1 - \mathbf{r}_2) = C(\mathbf{r}_1 - \mathbf{r}_2) + \rho \int C(\mathbf{r}_1 - \mathbf{r}_3) G(\mathbf{r}_3 - \mathbf{r}_2) d\mathbf{r}_3. \quad (3.8)$$

In the absence of an independent theory enabling one to calculate $C(r)$ in terms of the molecular parameters this relation is really only a *definition* of the direct correlation function: we will, in the main, adopt this attitude. However, Ornstein and Zernike regarded $C(r)$ as the more basic function

(in its, presumably, closer relation to the intermolecular forces) and they contemplated the possibility of calculating $C(r)$ directly.

On introducing the Fourier transform of $C(r)$ the relation (3.8) (which states that $G(\mathbf{r}_1 - \mathbf{r}_2)$ and $C(\mathbf{r}_1 - \mathbf{r}_2)$ are reciprocal kernels in the sense of the theory of integral equations) can be solved to yield

$$1 + \rho \hat{G}(\mathbf{k}) = 1/[1 - \rho \hat{C}(\mathbf{k})]. \quad (3.9)$$

On substituting in (3.4) one finds for the inverse scattering intensity

$$1/\chi(\mathbf{k}) = 1 - \rho \hat{C}(\mathbf{k}). \quad (3.10)$$

Consequently the divergence of the compressibility $K_T = \chi(0)/k_B T \rho$ at the critical point is associated with the equation

$$1 - \rho \hat{C}(0) = 1 - \rho \int C(r) dr = 0. \quad (3.11)$$

This shows that the integral of $C(r)$ (i.e., its zeroth moment) remains finite at the critical point. Thus $C(r)$ certainly decays to zero more rapidly than $G(r)$ thereby confirming the expectation that it should be relatively short-ranged. To develop the theory further, however, one makes the central assumption that $C(r)$ is strictly short-ranged *at* (and near) the critical point in the sense that its transform $\hat{C}(\mathbf{k})$ has a Taylor series expansion in powers of k^2 . In particular, one assumes that the second moment

$$R^2 = \frac{1}{2} \rho \langle \cos^2 \theta \rangle \int r^2 C(r) dr, \quad (3.12)$$

exists at the critical point and does not vary rapidly in the vicinity. [In three dimensions the average over angles yields $\langle \cos^2 \theta \rangle = \frac{1}{3}$.]

We note again that unless $C(r)$ can be calculated in an independent way R^2 will have the status only of a semiphenomenological parameter. The short-range character of $C(r)$ and the existence of R^2 at the critical point constitute a major problem of the theory and we will return to it. We remark here, however, that the virial expansion of $C(r)$ may be obtained quite easily from that for $G(r)$ ^{43,42} and indicates for low densities at least, that $C(r)$ is, in a definite sense, shorter ranged than $G(r)$.

This may be seen in terms of the graphical representations of the respective expansions. All the graphs required^{47,48} are connected and have two

⁴¹ L. S. Ornstein and F. Zernike, Proc. Acad. Sci. Amsterdam 17, 793 (1914); Physik. Z. 19, 134 (1918); *ibid.* 27, 761 (1926).

⁴² F. Zernike, Proc. Acad. Sci. Amsterdam 18, 1520 (1916).

⁴³ See also J. Yvon, Nuovo Cimento 9, Suppl. 1, 144 (1958) and Ref. 40.

⁴⁴ Y. Rocard, J. Phys. Radium 4, 165 (1933).

⁴⁵ See also: M. Fierz in *Theoretical Physics in the Twentieth Century*, edited by M. Fierz and V. F. Weisskopf (Interscience Publishers, Inc., New York, 1960), pp. 175 *et seq.*; M. J. Klein and L. Tisza, Phys. Rev. 76, 1861 (1949).

⁴⁶ L. D. Landau and E. M. Lifshitz, *Statistical Physics* (Pergamon Press, Ltd., London, 1958), Sec. 116.

⁴⁷ See, for example, E. Meeron, J. Math. Phys. 1, 192 (1960); J. M. J. Van Leeuwen, J. Groeneveld, and J. De Boer, Physica 25, 792 (1959); T. Morita and K. Hiroike, Progr. Theoret. Phys. (Kyoto) 23, 1003 (1960).

⁴⁸ G. E. Uhlenbeck and G. W. Ford, in *Studies in Statistical Mechanics, I*, edited by J. De Boer and G. E. Uhlenbeck, (North-Holland Publishing Company, Amsterdam, 1962), Chap. B.III 4.

fixed points (corresponding to the two molecules fixed at distance r apart) and $n = 0, 1, 2, \dots$ field points. Each point is associated with a power of the density ρ while the bonds are, as usual, associated with the Mayer f factors $f_{ij} = \exp[-\phi(r_{ij})/kT] - 1$. If the potential is of strictly finite range b [in the sense that $\phi(r) = 0$ for $r > b$] the factor f_{ij} vanishes unless $r_{ij} \leq b$. This fact restricts the distance up to which a graph of given type can "stretch." Thus in the expansion of $G(r)$ the longest-ranged term in a given order, say ρ^{2m+1} , comes from the open chain of $2m$ bonds which contributes up to distances $r = 2mb$ but not beyond. The graphs entering the expansion of $C(r)$, however, are restricted to be "nonnodal", i.e., none of the field points may be cutting points whose removal would separate the graph into two parts.⁴⁷ The open chain of bonds is thus excluded and the longest-ranged contribution to $C(r)$ in order ρ^{2m+1} comes from the graph consisting of two parallel chains of m bonds each. This graph, however, will make no contribution for $r > mb$.

We see therefore that in a given order the range of $C(r)$ is only half that of $G(r)$. It is clear, nevertheless, that one should not expect the virial series to converge well in the critical region (if it converges at all) so that the assumed short-range nature of $C(r)$ cannot be established in this way. For the present, however, we follow Ornstein and Zernike and accept the existence of the second moment R^2 and the possibility of a Taylor series expansion of $\hat{C}(k)$. From (3.10) and (3.12) we then obtain on neglecting terms of order k^4 , the scattering formula

$$\chi(k) = 1 + \rho \hat{G}(k) \simeq R^{-2}/(\kappa^2 + k^2), \quad (k^2 \rightarrow 0), \quad (3.13)$$

where κ , which has the dimensions of an inverse length, is defined by

$$\kappa^2 = [1 - \rho \hat{C}(0)]/R^2. \quad (3.14)$$

Fourier inversion of the simple Lorentzian scattering curve (3.13) shows that the behavior of $G(r)$ for large r is given in three dimensions by the famous result

$$G(r) \simeq \frac{1}{4\pi\rho R^2} \frac{e^{-\kappa r}}{r} \quad (r \rightarrow \infty). \quad (3.15)$$

From this one concludes that the correlations decay exponentially with an inverse range κ which, via the fluctuation theorem (3.3), should be related to the compressibility by

$$K_T = A/\kappa^2 \quad (T \rightarrow T_c). \quad (3.16)$$

The constant of proportionality is $A = 1/k_B T \rho R^2$

and is expected to be only slowly varying in the critical region. The divergence of K_T at the critical point thus implies

$$\kappa(T) \rightarrow 0 \quad \text{as} \quad T \rightarrow T_c, \quad (3.17)$$

so that the critical point correlation function is no longer exponentially damped but is predicted to follow the law

$$G_o(r) \simeq D/r \quad (r \rightarrow \infty, T = T_c). \quad (3.18)$$

In as far as the relation $K_T \sim 1/\kappa^2$ is valid and the classical variation of $K_T(T)$ is accepted, the inverse range will go to zero along the critical isochore as

$$\kappa(T) \simeq \kappa^0 |1 - (T/T_c)|^\nu \quad (T \rightarrow T_c), \quad (3.19)$$

with $\nu = \frac{1}{2}$. This conclusion was mentioned by Zernike⁴² and is accepted by other authors.⁴⁹⁻⁵² More generally, however, if one recognizes deviations of the isothermal compressibility from van der Waals behavior one would get the "nonclassical" result $\nu = \frac{1}{2}\gamma > \frac{1}{2}$ [see Eq. (2.8)].

The principal alternative approach to the Ornstein-Zernike theory is based on considering the thermodynamic work, or change in free energy, required to establish a density fluctuation in the system,^{44-46,49-52} i.e., a local inhomogeneity. One supposes that a local free-energy density $F(\mathbf{r})$ can be defined for an inhomogeneous system and considers the expansion of F (or its integral over a small but macroscopic volume) about its homogeneous mean value \bar{F} in terms of the local deviation $\delta\rho(\mathbf{r})$ of the density from its mean value ρ . In the spirit of the classical theory of the equation of state one assumes that a Taylor series exists even at the critical point. The first power of $\delta\rho$ may be dropped by virtue of the conservation of particles. The coefficient of $\delta\rho^2$ is, thermodynamically, proportional to $1/K_T$ and so this term must be retained.

Since the state of the system will be inhomogeneous, however, one must also expect terms dependent on $\nabla\rho$ the gradient of the density deviation, and on higher derivatives. The necessity for such terms can indeed be seen rather generally from the existence of surface tension which represents, of course, an additive contribution to the free energy directly associated with the density inhomogeneities at an interface. On the grounds of symmetry the leading term will be proportional to $(\nabla\rho)^2$. [The terms $\nabla^2\rho$ and $\rho\nabla^2\rho$ add nothing further after

⁴⁹ P. Debye, J. Chem. Phys. **31**, 680 (1959).

⁵⁰ E. W. Hart, J. Chem. Phys. **34**, 1471 (1961).

⁵¹ M. Fixman, J. Chem. Phys. **33**, 1357 (1960).

⁵² M. Fixman, J. Chem. Phys. **36**, 1965 (1962).

integrating over a small volume.^{46]} Consequently, one writes the expansion

$$\Delta F(\mathbf{r}) = \frac{1}{2}c\delta\rho^2 + \frac{1}{2}d(\nabla\rho)^2 + \dots \quad (3.20)$$

and assumes that at least for small slowly varying deviations (i.e., small k), the higher-order terms may be neglected to a good approximation even at the critical point. By stability considerations c and d must be positive. Although c will vanish at the critical point d remains nonzero.

On introducing the Fourier components of the density deviation

$$\delta\hat{\rho}_{\mathbf{k}} = V^{-1} \int e^{i\mathbf{k}\cdot\mathbf{r}} \delta\rho(\mathbf{r}) d\mathbf{r}, \quad (3.21)$$

substituting in (3.20) and integrating over the volume of the system one obtains for the total free energy fluctuation

$$\Delta F_{\text{total}} = \frac{1}{2}V \sum_{\mathbf{k}} (c + dk^2) |\delta\hat{\rho}_{\mathbf{k}}|^2. \quad (3.22)$$

We notice that each density mode contributes additively to the free energy so that the modes are statistically independent or, in other words, effectively noninteracting. This conclusion is, of course, a direct consequence of the truncation of (3.20) although it also has an immediate physical appeal for long wavelength modes.

Now the Boltzmann factor for a fluctuation $\delta\hat{\rho}_{\mathbf{k}}$ is $\exp[-\Delta F_{\mathbf{k}}/k_B T]$ and consequently the mean square fluctuation is predicted, at least for small k , to be

$$\langle |\delta\hat{\rho}_{\mathbf{k}}|^2 \rangle = k_B T / V(c + dk^2). \quad (3.23)$$

Now by the definition (3.21) of the Fourier coefficients we have

$$\langle |\delta\hat{\rho}_{\mathbf{k}}|^2 \rangle = \langle \delta\hat{\rho}_{\mathbf{k}} \delta\hat{\rho}_{-\mathbf{k}} \rangle = V^{-1} \int e^{i\mathbf{k}\cdot\mathbf{r}} \langle \delta\rho(0) \delta\rho(\mathbf{r}) \rangle d\mathbf{r},$$

where one integration over \mathbf{r} space has been performed using the (approximate) translational invariance of the system. Since the mean-density fluctuation is zero

$$\begin{aligned} \langle \delta\rho(0) \delta\rho(\mathbf{r}) \rangle / \rho &= \langle [\rho + \delta\rho(0)][\rho + \delta\rho(\mathbf{r})] \rangle / \rho - \rho, \\ &= \rho g(\mathbf{r}) + \delta(\mathbf{r}) - \rho, \end{aligned}$$

where the second line follows from the definition (3.1) of $g(\mathbf{r})$, the delta function being added to allow for the identity of the correlated particles [which was implicitly excluded in (3.1)]. Substitution shows that

$$\begin{aligned} (V/\rho) \langle |\delta\hat{\rho}_{\mathbf{k}}|^2 \rangle &= 1 + \rho \hat{G}(\mathbf{k}) \\ &\simeq \frac{(k_B T / \rho)}{c + dk^2}, \end{aligned} \quad (3.24)$$

which is clearly equivalent to the Ornstein-Zernike result (3.13).⁵³

The relationship between the two approaches to critical scattering theory is revealed by the more recent development of a complete formal theory of the statistical mechanics of nonuniform systems which shows the significance of the direct correlation function in constructing expansions of the thermodynamic variables of inhomogeneous systems.⁵⁴⁻⁵⁶ In particular the existence of local thermodynamic variables and the convergence of the corresponding expansions turns out to be dependent on the short range nature of $C(r)$.

A fruitful method developed by Lebowitz and Percus^{56,57} is to consider the deviations in density produced by an externally imposed potential $U(\mathbf{r})$ when this is chosen to be the potential $\phi(\mathbf{r})$ which would just correspond to a molecule of the fluid fixed at the origin. The induced singlet-density deviation is then related to the pair correlation function in the homogeneous fluid as follows:

$$\begin{aligned} n_1(\mathbf{r}|\phi) &= \rho + \delta n_1(\mathbf{r}) = n_2^0(\mathbf{r})/n_1^0, \\ &= \rho + \rho G(\mathbf{r}), \end{aligned} \quad (3.25)$$

where the superscripts zero denote the uniform system.⁵⁸

To obtain an equation for $n_1(\mathbf{r}|\phi)$ and hence for $G(r)$ one assumes the inhomogeneous system can be represented by a grand canonical ensemble and one asks for the relation between the external potential $U(r) = \phi(r)$ and the induced-density deviation. To this end it might be natural to try to expand $n_1(\mathbf{r}|\phi)$ as a functional Taylor series in $\phi(r)$ but Lebowitz and Percus show, on the contrary, that it is possible, and more useful, to expand $\phi(r)$ (in combination with the chemical potential) in terms of the density deviation it produces.⁵⁵⁻⁵⁷

⁵³ J. L. Lebowitz (private communication) has pointed out that by the methods of Refs. 55-57 one may show that in an appropriate grand canonical ensemble the fluctuation of the free energy is given to second order in $\delta\hat{\rho}_{\mathbf{k}}/\rho$ exactly by

$$\Delta F_{\text{total}} / N k_B T = \frac{1}{2} \sum_{\mathbf{k}} [1 - \rho \hat{C}(\mathbf{k})] |\delta\hat{\rho}_{\mathbf{k}}/\rho|^2.$$

Comparison with (3.22) shows even more directly the equivalence to the Ornstein-Zernike theory.

⁵⁴ F. H. Stillinger, Jr. and F. P. Buff, J. Chem. Phys. 37, 1 (1962).

⁵⁵ J. L. Lebowitz and J. K. Percus, Phys. Rev. 122, 1675 (1961); J. Math. Phys. 4, 116 (1963).

⁵⁶ J. K. Percus, Phys. Rev. Letters 8, 462 (1962).

⁵⁷ J. L. Lebowitz and J. K. Percus, J. Math. Phys. 4, 248 (1963).

⁵⁸ We use the notation $\delta n_1(\mathbf{r})$ rather than $\delta\rho(\mathbf{r})$ as previously, since in the thermodynamic arguments one really is considering a macroscopic or coarse-grained density fluctuation whereas here one refers directly to the microscopic distribution functions. By the same token one should replace $\delta\hat{\rho}_{\mathbf{k}}$ in Footnote 53 by $\delta\hat{n}_1(\mathbf{k})$ whereas in Eq. (3.24) and the preceding steps $g(\mathbf{r})$ and $\hat{G}(\mathbf{k})$ represent coarse-grained or macroscopic correlation functions.

One anticipates that such an expansion would converge most rapidly when taken at each point, about a uniform system with the same *local* density $n_1(\mathbf{r}|\phi)$. The successive terms of the expansion, which is conveniently derived by the technique of functional differentiation, are then found to be multiple integrals over the density deviation with kernels which involve $C(\mathbf{r}_1 - \mathbf{r}_2)$ and certain higher-order correlation functions.

Now when $C(r)$ is a short-ranged function one may expand these integrals as a "local" series in the spatial derivatives of the density deviation. The justification for this step must rest, of course, on showing that $C(r)$ decays rapidly to zero for large r [and that $n_1(\mathbf{r}|\phi)$ is not too rapidly varying]. If this is the case one finds

$$\phi(\mathbf{r}) = \mu - \mu^0[n_1(\mathbf{r})] + (R^2 k_B T \rho^2 / n_1^2) \nabla^2 G(\mathbf{r}) + \frac{1}{6} (l^2 \rho^2 / k_B T n_1^4 K_T^2) [\nabla G(\mathbf{r})]^2 + \dots, \quad (3.26)$$

where μ is the chemical potential and R^2 , defined already in Eq. (3.12), is the second moment of the direct correlation function. The length l is defined similarly in terms of $C(r)$ and the three-particle distribution function. Further terms of (3.26) can be written down explicitly and involve higher derivatives of $G(r)$ with coefficients depending on higher moments of $C(r)$ and the further many-particle distribution functions.⁵⁵⁻⁵⁷

If we now drop the terms in $(\nabla G)^2$ and higher-order derivatives and expand $n_1(r) = \rho[1 + G(r)]$ to first order in $G(r)$ we obtain

$$R^2 k_B T \nabla^2 G(\mathbf{r}) - \rho(\partial \mu^0 / \partial \rho) G(\mathbf{r}) = \phi(\mathbf{r}), \quad (3.27)$$

which should be valid in the asymptotic region where $G(r)$ is small. The derivative of μ^0 arises from expanding $\mu^0[n_1(\mathbf{r})]$ and may be eliminated through the thermodynamic relation $\rho(\partial \mu^0 / \partial \rho)_T = (\partial p / \partial \rho)_T = 1/\rho K_T$. On introducing the length Λ by

$$\Lambda^2 = R^2 k_B T \rho K_T \\ = \frac{1}{2} \langle \cos^2 \theta \rangle_\rho \int r^2 G(r) d\mathbf{r} / [1 + \hat{G}(0)] \quad (3.28)$$

[where the last formula follows from (3.12), (3.10) and (3.9)] we obtain the equation

$$\nabla^2 G(r) - \Lambda^{-2} G(r) = \phi(r) / k_B T R^2 \quad (3.29)$$

first derived by Zernike.⁴²

If the potential $\phi(r)$ is negligible for large r the asymptotic solution of (3.29) is, in three dimensions,

$$G(r) \approx D e^{-(r/\Lambda)} / r. \quad (3.30)$$

Comparison with (3.15) shows the equivalence to

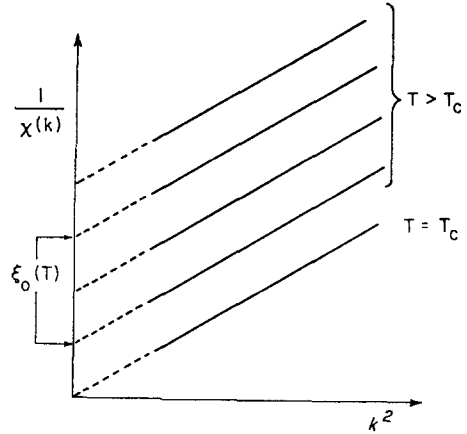


FIG. 5. Dependence of the inverse critical scattering on $k = (4\pi/\lambda) \sin \frac{1}{2} \theta$ according to the Ornstein-Zernike theory. The linear intercept $\xi_0(T)$ is proportional to $1/K_T$.

the previous theory and identifies $\Lambda = 1/\kappa$ as the range of correlation. Fourier transformation of Eq. (3.29) leads directly to the previous expression (3.13) for the scattering intensity for small κ^2 and k^2 .

The advantage of this last derivation is that the neglected terms are explicitly displayed and that the central role of the direct correlation function is apparent. It does not, however, enable us to decide if the assumption that $C(r)$ is short-ranged at the critical point is justified. On the other hand *away* from the critical point, but in a region where K_T is moderately large the analysis indicates that the Ornstein-Zernike theory should be correct. Indeed the exponential part of the asymptotic decay law for $G(r)$ appears to have a rather wide range of validity in a one-phase fluid system since it depends essentially only on the short-range nature of the interactions.⁵⁹

4. VALIDITY OF THE ORNSTEIN-ZERNIKE THEORY

The principal experimental predictions following from the classical theory of critical scattering [i.e., from Eq. (3.13)] are (a) that $1/\chi(k, T)$, the reciprocal of the relative scattering intensity, should vary *linearly* with k^2 with a temperature-independent coefficient of proportionality, and (b) that the extra-

⁵⁹ This conclusion follows from a formulation of statistical mechanics in which the system is taken to be in a cylinder of length L and cross section A . For forces with a hard core and strictly finite range b , a nonsingular integral kernel describes the addition of a layer of thickness b to the cylinder. The thermodynamics and correlation functions are related to the resolvent of this kernel: M. E. Fisher, abstract in Proc. Second Eastern Theoretical Physics Conf., University of North Carolina (October, 1963). D. Ruelle and, independently, J. Groeneveld (to be published) have also shown that in the region where the activity expansion can be proved to converge, $G(r)$ [suitably smoothed] decays to zero at least exponentially fast for strictly short-range potentials.

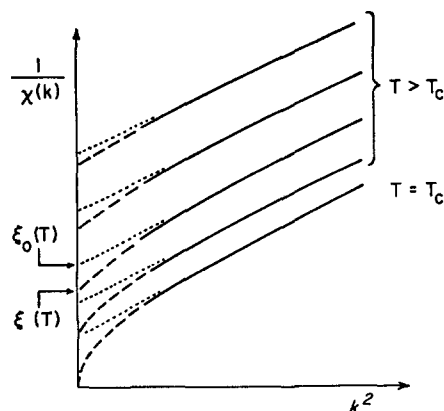


FIG. 6. Schematic variation of the inverse critical scattering expected in view of the limitations of the classical theory. (Compare with Fig. 5.) The apparent linear intercept $\xi_0(T)$ differs from the true intercept $\xi(T)$ which is proportional to $1/K_T$.

polated intercept with the $k^2=0$ axis, $\xi_0(T)$, should be proportional to $1/K_T(T)$ and hence go to zero as $T \rightarrow T_c$. The predicted behavior is shown schematically in Fig. 5.

Most modern tests of the theory have been made by light or x-ray scattering measurements on binary fluid mixtures of relatively complex organic molecules.⁶⁰⁻⁶⁶ For example, Zimm⁶⁰ studied a mixture of perfluoromethylcyclohexane in carbon tetrachloride, Brady and Frisch,⁶² perfluoroheptane in iso-octane, while Debye and co-workers⁶³ and McIntyre, Wims and Green⁶⁴ have investigated polystyrene-cyclohexane solutions.

Earlier measurements on binary fluids and other systems have been reviewed by Rice.⁶⁵ Recently Thomas and Schmidt⁶⁶ have made an extensive series of x-ray measurements on argon at various constant pressures in the critical region. They also give references to other more recent work on single-component systems such as carbon dioxide, ethylene and neon.

Accurate experiments are not easy to perform near the critical point and the interpretation can be confused by multiple scattering. Qualitatively,

⁶⁰ B. H. Zimm, *J. Phys. & Colloid Chem.* **54**, 1306 (1950).

⁶¹ Chow Quantie, *Proc. Roy. Soc. (London)* **A224**, 90 (1954); R. Fürth and C. L. Williams, *Proc. Roy. Soc. (London)* **A224**, 104 (1954).

⁶² G. W. Brady and H. L. Frisch, *J. Chem. Phys.* **35**, 2234 (1961).

⁶³ P. Debye, H. Coll, and D. Woermann, *J. Chem. Phys.* **32**, 939 (1960); *ibid* **33**, 1746 (1960); P. Debye, D. Woermann and B. Chu, *J. Chem. Phys.* **36**, 851 (1962).

⁶⁴ D. McIntyre, A. Wims and M. S. Green, *J. Chem. Phys.* **37**, 3019 (1962).

⁶⁵ O. K. Rice, "Critical Phenomena" Sec. E, in *Thermodynamics and Physics of Matter*, edited by F. D. Rossini (Princeton University Press, Princeton, New Jersey, 1955).

⁶⁶ J. E. Thomas and P. W. Schmidt, *J. Chem. Phys.* **39**, 2506 (1963).

however, the theory seems quite well confirmed by the binary fluid measurements. Plots of the reciprocal scattering intensity versus k^2 in the experimentally accessible range are well represented by sets of parallel straight lines whose intercepts $\xi_0(T)$ fall roughly linearly with $(T - T_c)$ as indicated in Fig. 5. Closer inspection, nevertheless, reveals certain "anomalies", although at present these are not much larger than the experimental uncertainties.^{64,67,68} In particular one observes (a) a tendency for the scattering curves taken near T_c to be slightly curved and to dip downwards somewhat at the lowest values of k^2 and (b) the intercepts $\xi_0(T)$ obtained by extrapolation of the best straight line fits to the data (all necessarily lying above some k_{min}^2) do not seem to approach zero as T goes to T_c ; rather plots of $\xi_0(T)$ versus T along the isochore are slightly concave upwards and tend to level off or to extrapolate to a nonzero value at T_c . These deviations are indicated in Fig. 6.

Green⁶⁸ reports that significant deviations from the Ornstein-Zernike theory were also found for the, presumably physically simpler, system of nitrogen at its critical point.⁶⁹ No deviations were observed by Thomas and Schmidt⁶⁶ in argon but they did not measure along the critical isochore and their lowest values of k^2 were relatively large.

As we show below these deviations are in the direction to be expected theoretically on the basis of an analysis of the limitations of the classical theory. Needless to say, however, it would still be desirable to have more accurate and extensive experimental data, especially for low values of k^2 and for simple systems like the noble gases, in order to elucidate fully the true nature of the critical scattering.

As we have seen the main theoretical problem in justifying the derivation of the Ornstein-Zernike result is to establish the short-range nature of the direct correlation function $C(r)$, or, what is equivalent, to show that its Fourier transform $\hat{C}(k)$ has a Taylor series expansion in powers of k^2 at the critical point. Our previous discussion of the thermodynamic variables at the critical point, has shown that the hypothesis of a Taylor expansion in temperature or density is probably not tenable. By analogy we should be prepared for a similar failure for the correlation functions.

An obvious defect of the theory can be seen by

⁶⁷ H. L. Frisch and G. W. Brady, *J. Chem. Phys.* **37**, 1514 (1962).

⁶⁸ M. S. Green, *J. Chem. Phys.* **33**, 1403 (1960).

⁶⁹ R. L. Wild, *J. Chem. Phys.* **18**, 1627 (1950).

considering its application to model systems of dimensionality d different from three. In any number of dimensions the classical expression for the (appropriate) Fourier transform is formally the same, namely

$$\chi(\mathbf{k}) = 1 + \rho \hat{G}(\mathbf{k}) \simeq A/(\kappa^2 + k^2). \quad (4.1)$$

For fixed $\kappa(T) > 0$, that is *away* from the critical point, we find⁷⁰ by inverting (4.1) that as r becomes very large

$$G(r) \simeq B_d(e^{-\kappa r}/r^{d-1})[1 + O(1/\kappa r)] \quad (r \rightarrow \infty, \kappa \text{ fixed} > 0). \quad (4.2)$$

As we argued at the end of the previous section it seems probable that this result is generally valid for *fixed* $T > T_c$ and large enough r . However, as $\kappa \rightarrow 0$ for *fixed* large r we find a different result,⁷⁰ namely, for $d \geq 3$

$$G(r) \simeq D_d(e^{-\kappa r}/r^{d-2})[1 + O(\kappa r)] \quad (\kappa \rightarrow 0, r \text{ fixed}) \quad (4.3)$$

while for $d = 2$

$$G(r) \simeq D_2(\log r)e^{-\kappa r}[1 + O(1/\log \kappa r)] \quad (\kappa \rightarrow 0, r \text{ fixed}). \quad (4.4)$$

One notices that $d = 3$ is a rather special case in which both limits (4.2) and (4.3) agree and [by comparison with Eq. (3.15)] the higher-order terms vanish identically!

Now (4.4) implies that at the critical point of a two-dimensional system the correlation function will vary as $D_2 \log r$. This is clearly nonphysical for large r and shows that the assumptions of the theory are certainly not to be trusted for two-dimensional systems.

This defect of the theory can be repaired in an *ad hoc* fashion by retaining further (nonlinear) terms in the density expansions of the free energy [in Eq. (3.20)] or in the Taylor series expansion of $n_1(\mathbf{r})$ [in Eq. (3.26)].⁷¹ It would seem difficult, however, to justify keeping nonlinear terms in $G(r)$ rather than, say nonlinear terms in ∇G or higher-order derivatives of $G(r)$: the more so as the whole question of the convergence of such an expansion is in doubt at the critical point.

The first author to question the theory in respect of the prediction $G(r) \sim 1/r$ at $T = T_c$, for three dimensions was Green⁶⁸ who based his arguments on an integral relation for the pair correlation function derived by cluster diagram summation tech-

niques.⁴⁷ This so called, hypernetted-chain integral equation may be written

$$1 + G(r) = \exp [-\beta\phi(r) + G(r) - C(r) + E(r)], \quad (4.5)$$

where

$$E(r) = \mathcal{E}\{\rho; G(r)\} \quad (4.6)$$

is a nonlinear integral functional of $G(r)$ known only as an expansion in powers of ρ representable in terms of certain, so called, "basic graphs."⁴⁷ [The leading term is of order ρ^2]. The same relations hold for a lattice system (with appropriate definition of the functional \mathcal{E}).

Green⁶⁸ considered the consequences of assuming that the term $E(r)$ involving the basic graphs, might be neglected at the critical point. Stillinger and Frisch extended his analysis to two-dimensional systems.⁷²

To follow the argument let us suppose in greater generality that at the critical point of a d -dimensional system

$$G(r) \simeq D/r^{d-2+\eta} \quad (r \rightarrow \infty), \quad (4.7)$$

where the index η ($0 \leq \eta \leq 2$) measures the departure from the Ornstein-Zernike prediction. [As in Eq. (2.7) $1/r^0$ corresponds to $\log r$.] It follows that

$$\rho \hat{G}(k) \simeq \hat{D}/k^{2-\eta}, \quad (k \rightarrow 0) \quad (4.8)$$

so that at fixed density one has, through the relation (3.9),

$$\hat{C}(k) \simeq C(0)[1 - c_0 k^{2-\eta} + \dots], \quad (k \rightarrow 0). \quad (4.9)$$

If $\eta > 0$ asymptotic inversion yields

$$C(r) \simeq F/r^{d+2-\eta} \quad (r \rightarrow \infty). \quad (4.10)$$

Thus when $\eta > 0$, the direct correlation function is *also* "long ranged" in the sense that its second moment does not exist, although it certainly decays to zero more rapidly than $G(r)$, in fact by a factor $1/r^{4-2\eta}$. Notice that if $\eta = 0$ we find instead

$$C(r) \simeq F'e^{-\kappa r}/r, \quad (\kappa^2 = 1/c_0) \quad (4.11)$$

so that only in this special case is $C(r)$ short ranged in the sense that $\hat{C}(k)$ has a Taylor series expansion at $k^2 = 0$.

To analyze the hypernetted integral relation it is convenient to define

$$S(r) = G(r) - C(r). \quad (4.12)$$

Clearly $S(r)$ must have the same asymptotic be-

⁷⁰ M. E. Fisher, *Physica* **28**, 172 (1962).

⁷¹ M. Fixman, *J. Chem. Phys.* **36**, 1965 (1962).

⁷² F. H. Stillinger, Jr. and H. L. Frisch, *Physica* **27**, 751 (1961).

havior as $G(r)$. If the potential $\phi(r)$ is short ranged we may expand the exponential in (4.5) for large r to get

$$C(r) = E(r) + \frac{1}{2}[S(r) + E(r)]^2 + \dots \quad (4.13)$$

If we now suppose $E(r)$ can be neglected or, more weakly, that $E(r)$ decays faster than $[S(r)]^2$ it follows that

$$C(r) = \frac{1}{2}[S(r)]^2 + \dots \quad (4.14)$$

On substituting (4.7) and (4.10) we obtain the consistency relation

$$\eta = 2 - \frac{1}{3}d, \quad (4.15)$$

which fixes the asymptotic form of the correlation functions.

On this basis we would predict that at the critical point in a three-dimensional system $G(r) \sim 1/r^2$ rather than $1/r$.⁶⁸ Correspondingly $\hat{G}(k) \sim 1/k = 1/(k^2)^{1/2}$ so that a plot of inverse scattering versus k^2 at, and near $T = T_c$, should be significantly curved downwards for small k^2 (see Fig. 6).

In two dimensions (4.15) leads to $G(r) \sim 1/r^{4/3}$ ($T = T_c$) which is more reasonable than the Ornstein-Zernike result $\log r$. However as pointed out by Stillinger and Frisch,⁷² this prediction can be tested against the rigorous result obtained by Onsager and Kaufman³¹ for the correlation function of the nearest-neighbor plane square lattice gas at its critical point. [Note that $G(r)$ at $\rho = \rho_c$ is proportional to the spin pair correlation function $\langle S_0^z S_r^z \rangle$ of the Ising ferromagnet in zero field.] This exact result is^{31,32,72,73}

$$G(r) \approx D/r^4 \quad (T = T_c, d = 2) \quad (4.16)$$

so that the true value of the index η is $\frac{1}{4}$ rather than $\frac{2}{3}$ or zero.

We conclude that both the Ornstein-Zernike theory and Green's argument are incorrect for a two-dimensional lattice. Consequently both must be suspect for three-dimensional lattice systems.

It is interesting to note that if, as seems to be the case, the true value of η is less than $2 - \frac{1}{3}d$ one really has, as $r \rightarrow \infty$

$$E(r) \approx \frac{1}{2}[S(r)]^2 \approx \frac{1}{2}[G(r)]^2 \approx D^2/r^{2d-4+2\eta} \quad (4.17)$$

so that the contribution of the basic graphs is also long ranged although it decays faster than $G(r)$. Since after all, $E(r)$ is a functional of $G(r)$ this is not really surprising.

Of course, the rigorous result (4.16) is known only

⁷³ See also Ref. 12, pp. 200–201 but notice that an exponent $\frac{1}{2}$ is missing on the left of Eq. (108).

for nearest-neighbor interactions and one should ask to what extent the behavior of lattices with interactions reaching to further neighbors would be similar. It seems plausible that the correct answer is that the behavior sufficiently near the critical point is qualitatively unchanged provided the range of the potential is finite [for example, if $\phi(r) = 0$ for $r > b$]. The reason for this surmise is that the range of correlation near the critical point becomes, as we have seen, very large compared to the lattice spacing and, indeed, very large compared to the potential range b . The asymptotic correlations are then determined by long chains of interactions and should thus be insensitive to the detailed variation of $\phi(r)$. [The same conclusion is really implicit in Ornstein and Zernike's and in Green's approach.]

The independence of the indices α , β , γ and η of the lattice structure is evidence for this conclusion. Further evidence comes from numerical studies of the compressibility of lattice gases with first and second neighbor interactions which indicate unchanged values for the index γ in two and three dimensions.⁷⁴

It is more difficult to assess the relationship of the lattices gases to more realistic *continuum* models. At low temperatures and high densities the properties of a lattice gas will always deviate from continuum behavior but in the critical region the long range of the correlations again suggests an insensitivity to the details of the potential and hence, for a lattice subdivision sufficiently fine relative to the range of the potential, one would expect qualitatively very similar behavior.⁷⁵ This conclusion is supported by the apparently quite close resemblance between the critical singularities of real gases and of even the simplest nearest neighbor three-dimensional lattice gases discussed already in Sec. 2.

5. MORE GENERAL ANALYSIS OF CRITICAL SCATTERING

It is clear from the foregoing that the Ornstein-Zernike theory is probably not valid at the critical point of a three-dimensional system. On the contrary one should evidently expect that $G(r)$ behaves asymptotically as $1/r^{1+\eta}$ with $0 < \eta < 1$.^{70,72}

A natural way to extend the Ornstein-Zernike theory within the same framework is to consider further powers of k^2 in the expansion of the Fourier

⁷⁴ M. F. Sykes and N. Dalton (to be published).

⁷⁵ In one dimension one may verify explicitly that the behavior of the lattice gas approaches that of the continuum gas as the lattice spacing is made smaller relative to the scale of the potential.

transform of the direct correlation function $\hat{C}(k)$. Inclusion of such terms leads to a representation of $G(r)$ as a sum of increasingly more rapidly damped exponentials of the form (for $d = 3$)

$$G(r) \approx \frac{De^{-\kappa r}}{r} + \frac{D_1 e^{-\kappa_1 r}}{r} + \frac{D_2 e^{-\kappa_2 r}}{r} + \dots \quad (5.1)$$

with $\kappa < \kappa_1 < \kappa_2 \dots$. At a fixed temperature, however, such an expansion leads to the same asymptotic behavior for $G(r)$ and to similar scattering at small k^2 as does the original theory. (For smaller enough r and large enough k^2 one must, of course, expect derivations from any general theory since the detailed nature of the potential must eventually make itself felt.)

As one considers T approaching T_c along $\rho = \rho_c$, however, it is possible that more and more exponentials in (5.1) become "excited," so that the first exponential is no longer a good approximation except for extremely large r .⁷⁶ This certainly represents essentially what happens for the two-dimensional lattice gas. Here the higher-order range parameters $\kappa_1, \kappa_2, \dots$ obey the relation^{12,14,77}

$$\kappa_n(T) - \kappa(T) \sim n\kappa_0 |1 - (T/T_c)|, \quad (5.2)$$

so that the "spectrum" of exponentials closes up as $T \rightarrow T_c$ and in fact becomes dense at the critical point.

A similar behavior for a continuum model is suggested by the recent calculations of Hemmer, Kac, and Uhlenbeck⁷⁶ for a potential with a strongly repulsive core and a weakly attractive long-range exponential tail. A series similar to (5.1) can be derived but the amplitudes of successive terms are proportional to higher powers of the compressibility K_T and hence the expansion breaks down near the critical point.

These considerations [which really amount to a restatement of our previous conclusion that $\hat{C}(k)$ probably does not have a Taylor series expansion at the critical point although it does for $T > T_c$] indicate that (5.1) is not the best basis for analyzing the deviations from the Ornstein-Zernike theory. Indeed the asymptotic form $1/r^{1+\eta}$ at $T = T_c$ with $\eta \neq 0$ could only arise from (5.1) if the expansion broke down in some way. To investigate the possibilities more generally let us, therefore, extend (4.7)

by writing⁷⁰ for $T \geq T_c$ and $\rho = \rho_c$

$$G(r) \simeq (De^{-\kappa r}/r^{d-2+\eta})[1 + Q(\kappa r)] \quad (r \rightarrow \infty) \quad (5.3a)$$

where $D = D(T)$ is a relatively slowly varying function of temperature and where $Q(x) \rightarrow 0$ as $x \rightarrow 1$ and $Q(x)$ does not grow exponentially fast as $x \rightarrow \infty$. This expression is still in the spirit of the Ornstein-Zernike theory in as far as the main assumption implicit in (5.3a) is that in the critical region the correlation functions for large r can be described in terms of only *two* lengths: (i) the *range of correlation* $1/\kappa(T)$ which becomes infinite at the critical point, and (ii) an *effective range of direct interaction* $r_0(T)$ which remains finite at the critical point. In (5.3a) r_0 has been absorbed into the coefficient D . [Compare with R of the Ornstein-Zernike theory: Eqs. (3.12) and (3.15).] We could write in analogy with (3.15)

$$D = \bar{d}/\rho_c^{2+\eta}, \quad (5.3b)$$

where \bar{d} is a dimensionless constant.

If the classical theory is valid away from the critical point, as concluded in Sec. 3, the formula (5.3a) should reduce to (4.2) when $\kappa > 0$ and r is very large, i.e. only the first term in (5.1) should remain. [For the plane square nearest-neighbor lattice gas at $\rho = \rho_c$ one may verify that (4.2) is indeed valid above T_c .⁷⁷] This would imply that for large x

$$1 + Q(x) \approx qx^{1/(d-3)+\eta} \quad (x \rightarrow \infty). \quad (5.3c)$$

Sufficiently close to the critical point the nature of this behavior will not matter. It is clear, however, that if $Q(x)$ becomes of order unity for small x the region of significant deviation from classical theory may be rather small. [Stated alternatively, the further exponentials in (5.1) would be significantly excited only very close to the critical point.]

Accepting (5.3) we may calculate the fluctuation integral (3.3) (making the substitution $x = \kappa r$). For the divergence of the compressibility along the critical isochore this yields

$$\chi(0) = k_B T \rho K_T \simeq \hat{D}_0/\kappa^{2-\eta} \quad (T \rightarrow T_c), \quad (5.4)$$

where \hat{D}_0 is a slowly varying function of T [of magnitude dependent on $Q(x)$]. Similarly a calculation of the Fourier transform of (5.3) for small k^2 yields, near T_c , the non-Lorentzian critical scattering formula

$$\chi(k) \simeq \hat{D}/(\kappa^2 + k^2)^{1-\frac{1}{2}\eta} \quad (k^2 \rightarrow 0), \quad (5.5)$$

where \hat{D} is a slowly varying function of T and k^2 .⁷⁸

⁷⁸ If $Q(x)$ is neglected one has for small η

$$\hat{D}(k^2) = D_0\{1 - \eta k^2/(\kappa^2 + k^2) + \dots\}.$$

⁷⁶ P. C. Hemmer, M. Kac and G. E. Uhlenbeck, J. Math. Phys. 5, 60 (1964); P. C. Hemmer, J. Math. Phys. 5, 75 (1964).

⁷⁷ The correlation functions may be expressed as a sum of integrals over the complete set of eigenvalues of the basic transition matrix for an Ising lattice (see Ref. 31). The exact limiting density of these eigenvalues is known from Onsager's work (Ref. 14).

As in our discussion of the Ornstein-Zernike theory the way in which the inverse range of correlation $\kappa(T)$ vanishes as $T \rightarrow T_c$ for $\rho = \rho_c$ is related to the nature of the corresponding divergence of the compressibility as $1/(T - T_c)^\gamma$. Assuming, as in (3.19) that

$$\kappa(T) \simeq \kappa^0 |1 - (T/T_c)|^\gamma \quad (T \rightarrow T_c) \quad (5.6)$$

and substituting in (5.4) shows that the critical indices are related by

$$\gamma = (2 - \eta)\nu. \quad (5.7)$$

This relation may be checked for the plane square lattice gas since, as we have seen,^{31,32,72,73} $\eta = \frac{1}{4}$ and $\gamma = 1\frac{3}{4}$ (see Table I). Consequently we should have

$$\nu = 1, \quad (d = 2) \quad (5.8)$$

in contrast to the classical result $\nu = \frac{1}{2}$. Now the result $\nu = 1$ was in fact derived rigorously by Onsager in his original paper on the Ising model.¹⁴ His derivation is based on the relation

$$e^{-\kappa a} = \lambda_1/\lambda_0, \quad (5.9)$$

where a is the lattice spacing, and where $\lambda_0(T)$ and $\lambda_1(T)$ are the largest and next largest eigenvalues of the basic matrix which adds a row to the lattice at temperature T .⁷⁷

If we assume⁷⁹ that ν is still unity for the three-dimensional lattice gas and utilize the result⁸⁰ $\gamma = 1\frac{1}{4}$ we would predict $\eta = \frac{3}{4}$. Thence the critical point decay law would be $G_o(r) \sim 1/r^{7/4}$ in closer agreement with Green's result. However the assumption $\nu = 1$ in three dimensions is not much better justified *a priori* than the classical assumption $\nu = \frac{1}{2}$. Furthermore, examination of the other critical indices (see Table I) indicates that the classically predicted behavior is more closely approached the larger the dimensionality of the system.⁸¹ Consequently one might anticipate that for the three-dimensional nearest-neighbor lattice gas ν lies between $\frac{1}{2}$ and 1 and η is less than $\frac{1}{4}$. [As mentioned previously the assumption $\eta = 0$ leads to $\nu = \frac{1}{2}\gamma = \frac{5}{8}$ when $d = 3$.]

To decide between these various speculations it is necessary to calculate $\kappa(T)$ or some other feature of the correlation functions. Fortunately the Ising

model is again sufficiently tractable to allow some progress. It is possible at the critical density, to derive a diagrammatic expansion for the decay factor $e^{-\kappa a}$ in powers of $1/T$ via Eq. (5.9).⁸² The required graphs consist of an infinite chain of connected bonds stretching right across the lattice together with nonoverlapping closed polygons, as occur in the expansion of the partition function.¹²

Evaluation of the series⁸³ for $\kappa(T)$ (with the aid of Padé approximants) reveals a behavior near T_c clearly intermediate between the two-dimensional and classical results in a region $T = T_c$ to $2T_c$. Direct estimation of the index ν , however, proves to be not very accurate but indicates a range $\nu = 0.6$ to 0.7 . [The coefficients of the series are difficult to calculate and not very smooth.]

An alternative approach is to study the temperature dependence of the higher moments of the correlation function, namely

$$\mu_n(T) = \rho \int r^n G(r) dr. \quad (5.10)$$

The zeroth moment is essentially the compressibility but the second moment is also a direct measure of the range of correlation. It is evident furthermore, that μ_2 is proportional to the curvature of $\rho \hat{G}(k)$ for small k and hence to the true limiting slope of the curve of $1/\chi(k)$ versus k^2 as $k^2 \rightarrow 0$.⁸⁴ From (5.3) we see that when $T \rightarrow T_c$, $\mu_2(T)$ diverges as

$$\begin{aligned} \mu_2(T) &\simeq M_2/\kappa^{4-\gamma} \quad (T \rightarrow T_c), \\ &\simeq M'_2/|1 - (T/T_c)|^\delta, \end{aligned} \quad (5.11)$$

with

$$\delta = (4 - \eta)\nu. \quad (5.12)$$

The coefficients M_2 and M'_2 are slowly varying functions of T . By comparing (5.12) with the index relation (5.7) we see that η and ν can both be determined if γ and δ are known. [In particular only if $\delta = 2\gamma$ would we have $\eta = 0$.]

For the two- and three-dimensional lattice gases expansions for $\mu_2(T)$ is series of powers of $1/T$ at $\rho = \rho_c$ are not too difficult to calculate.⁸³ [The labor and graphical analysis is similar to that for the compressibility.] The coefficients prove to be rather smoothly varying and for the plane lattices numerical analysis confirms quite accurately the relation (5.12)

⁷⁹ This assumption was made tentatively in Ref. 70 and tested experimentally by Frisch and Brady (Ref. 67). A good fit was obtained but although the data revealed definite nonclassical behavior, they were not sufficiently accurate to distinguish between $\nu = 1$ and some appreciably lower value.

⁸⁰ See the discussion in Sec. 2 and Refs. 23 and 28.

⁸¹ From Table I we see $\gamma = 1\frac{1}{4}$, $1\frac{1}{2}$ for $d = 2$, $d = 3$ to which we may add $\gamma = 1.094$ ($d = 4$); see M. E. Fisher and D. S. Gaunt, Phys. Rev. 133, A224 (1964). The classical result $\gamma = 1$ corresponds to $d \rightarrow \infty$.

⁸² M. E. Fisher (to be published).

⁸³ M. E. Fisher and R. J. Burford (to be published).

⁸⁴ The second moment μ_2 is closely related to the length Λ defined in (3.28) and to the "persistence length" L defined by Debye (Ref. 44) explicitly: $\Lambda^2 = \frac{1}{2} \langle \cos^2 \theta \rangle \mu_2 / (1 + \mu_0)$ and $L^2 = \mu_2 / \mu_0$. From (3.28) one sees that $1/\chi(k) = 1/\chi(0)\{1 + \Lambda^2 k^2 + O(k^4)\}$.

[which predicts $\delta = 3.75$]. This is an important result since it provides support for the original hypothesis (5.3).

Initial estimates for the simple cubic lattice gas⁸³ yield $\delta = 2.538 \pm 0.003$ and hence

$$\nu = 0.644 \pm 0.003, \quad \eta = 0.060 \pm 0.007. \quad (5.13)$$

Results for other three-dimensional lattices confirm these estimates with lower accuracy. [One might mention that (5.14) is not inconsistent with the conjecture $\eta = \frac{1}{16} = 0.0625$ which is rather natural in view of the estimate $\beta \simeq \frac{5}{16}$ discussed in Sec. 2.]

The values (5.13) are in accordance with our expectation that the three-dimensional results should be closer to the classical predictions.⁸¹ The magnitude of η for the lattice gas is indeed rather close to zero but it is not unlikely that a more realistic continuum model would lead to somewhat larger value, say $\eta \simeq 0.1$.⁸⁵ Until more rigorous theories are developed and more realistic models become soluble we must content ourselves with these rough estimates. Accordingly let us review the nature of the critical scattering to be expected on the basis of our analysis.

The peak in the critical scattering is described by (5.5) and (for $\eta > 0$) should be narrower at a fixed temperature near T_c than the Lorentzian curve of same peak height. Correspondingly a plot of the inverse scattering intensity versus k^2 should be somewhat convex although, as suggested in Fig. 6, for larger values of $k^2 > k_{\min}^2$ the curves might appear to be reasonably linear. For small values of η , of the magnitude (5.13), it might indeed be rather difficult experimentally to detect the increasing curvature of the scattering plots as $k^2 \rightarrow 0$ even though the curve for $T = T_c$ will theoretically have an infinite slope at $k^2 = 0$. In practice a nonzero value of η can probably best be detected by the observation that the apparent linear intercepts $\xi_0(T)$ [see Fig. 6] would not approach zero when $T \rightarrow T_c$ as must the true intercepts $\xi(T) = 1/\chi(0)$. In particular the scattering plot taken at $T = T_c$ would tend to extrapolate to a small positive value at $k^2 = 0$. [Of course to detect this behavior it is important to have an independent measurement of T_c and not to judge T_c by extrapolating $\xi_0(T)$ to zero with T as would otherwise be tempting!] This behavior is reminiscent of the experimental "anomalies" described in the previous Section although, as yet, these can probably not be regarded as fully established.

The likely fact that γ exceeds unity for a real

⁸⁵ For example the effectively more "continuum-like" Heisenberg model of ferromagnetism yields $\gamma \simeq 1\frac{1}{2}$ compared with the Ising value $\gamma = 1\frac{1}{2}$ ($d = 3$). (See Refs. 90, 91).

gas and the consequent curvature of $1/K_T$ versus T would indicate that a plot of the true intercepts, $\xi(T)$, versus T should flatten out as T approaches T_c (and theoretically have zero slope at $T = T_c$). This effect might well be less obvious in a plot of the apparent intercepts $\xi_0(T)$ although it does seem to have been observed.⁸⁶

6. SUMMARY AND CONCLUSIONS

We have shown that the classical theories of the gas-liquid critical point are unsatisfactory both on experimental and theoretical grounds. Thus the coexistence curve must be described experimentally by

$$\rho_L - \rho_G \sim (T_c - T)^\beta, \quad (6.1)$$

with $\beta \simeq 0.33$ to 0.36 (rather than with $\beta = \frac{1}{2}$) while for three-dimensional lattice gas models one finds $\beta \simeq 0.31 \simeq \frac{5}{16}$. The specific heat $C_V(T)$ measured along the critical isochore of a fluid becomes infinite at T_c , diverging approximately as $\log|T - T_c|$. A similar result holds for the lattice gas. Theoretically one also expects that the compressibility above and below T_c should diverge as

$$K_T \sim 1/|T - T_c|^\gamma \quad (6.2)$$

with $\gamma > 1$. This prediction while qualitatively correct awaits quantitative experimental verification. (Values of these indices are given in Table I.)

On theoretical grounds the classical (Ornstein-Zernike) theory of critical scattering has been shown to be unsatisfactory close to the critical point (although it probably is valid away from the critical region when the compressibility is still moderately large). More generally one should expect the scattering intensity to vary as

$$I(k) \sim 1/(\kappa^2 + k^2)^{1-\eta}, \quad (6.3)$$

where $\eta > 0$ and where the range parameter vanishes along the critical isotherm as

$$\kappa(T) \sim (T - T_c)^\nu \quad (6.4)$$

with $\nu(2 - \eta) = \gamma$. Theoretical analysis suggests that the index η might be no larger than 0.1 (see Table I). Consequently it is probably not easy experimentally to detect deviations from the classical theory (for which $\eta = 0$). Nevertheless there are experimental indications of the failure of the classical predictions for small k^2 near T_c and these are consistent with $\eta > 0$. Final confirmation of the theory must, however, rest on further, more extensive and accurate measurements on sufficiently simple fluid systems.

⁸⁶ D. McIntyre, Ref. 64 and a private communication.

In conclusion one should mention the rather close analogy between the gas-liquid critical point and the Curie point of a ferromagnetic crystal.⁸⁷ Indeed almost all our analysis and conclusions apply directly to ferromagnetic systems if appropriately translated. The density deviation $\rho - \rho_c$ should be identified with the magnetization M while the magnetic field H is isomorphic to the chemical potential of the fluid. The critical isochore, $\rho = \rho_c$, corresponds to zero magnetic field (since the mean magnetization then vanishes) and the coexistence curve corresponds to the curve of spontaneous magnetization $M_0(T)$. The specific heat $C_V(T)$ along the critical isochore of a fluid is isomorphic to the specific heat $C_H(T)$ of a ferromagnet in zero field and the compressibilities at condensation and above T_c for $\rho = \rho_c$ correspond essentially to the initial susceptibilities $\chi_0(T) = (\partial M / \partial H)_T$, ($H \rightarrow 0$).

The van der Waals and equivalent classical theories find their precise parallel in the Weiss molecular field theory and its extensions.⁸⁸ Similarly the Ornstein-Zernike theory and its developments have been adapted to describe the critical scattering of neutrons by ferromagnets.^{89,90} The net pair correlation function $G(r)$ is replaced by the spin-spin correlation functions $\Gamma_{\alpha\beta}(r) = \langle S_\alpha^z S_\beta^z \rangle$. Theoretically one is able to estimate the susceptibility index γ for the nearest neighbor Heisenberg model above T_c with the approximate result^{91,92} $\gamma = \frac{4}{3}$ (independent of spin and lattice structure in three-dimensions).

⁸⁷ As mentioned in Sec. 2, this relationship is formally exact for a lattice gas and an Ising model ferromagnet. See, for example, T. D. Lee and C. N. Yang, Phys. Rev. **87**, 410 (1952).

⁸⁸ See, for example, J. H. Van Vleck, Rev. Mod. Phys. **17**, 27 (1945); P. W. Kasteleijn and J. Van Kranendonk, Physica **22**, 317 (1956).

⁸⁹ L. Van Hove, Phys. Rev. **95**, 1374 (1954).

⁹⁰ R. J. Elliott and W. Marshall, Rev. Mod. Phys. **30**, 75 (1958).

⁹¹ C. Domb and M. F. Sykes, Phys. Rev. **128**, 168 (1962).

⁹² J. L. Gammel, W. Marshall, and L. Morgan, Proc. Roy. Soc. (London) **A275**, 257 (1963).

It is interesting that this nonclassical prediction has been quite accurately confirmed recently.⁹²⁻⁹⁵ Furthermore modern neutron scattering experiments⁹⁶ have also given a definite suggestion of deviations from the Ornstein-Zernike theory consistent with a small positive value of the index η .

The spontaneous ferromagnetic moment $M_0(T)$ is not easy to measure near T_c but nuclear magnetic resonance experiments by Benedek and Heller⁹⁶ have shown that the somewhat analogous sublattice magnetization (or long range order) of an *antiferromagnet* (actually MnF_2) varies as $(T - T_c)^\beta$ with $\beta = 0.335 \pm 0.010$. The relation holds with remarkable accuracy up to within millidegrees of the critical or Néel point [$\Delta T / T_c = 0.007\%$].⁹⁷ Experiments on antiferromagnets also reveal specific heat infinities at T_c which are approached in approximately logarithmic fashion.⁹⁸ The close similarity of these results to the corresponding behavior of fluid systems presents a striking challenge to our theoretical understanding.

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⁹³ J. E. Noakes and A. Arrott, J. Appl. Phys. Suppl. **35**, 931 (1964).

⁹⁴ J. S. Kouvel [private communication based on an analysis of the measurements by P. Weiss and R. Forrer, Ann. Phys. **5**, 153 (1926).]

⁹⁵ L. Passell, K. Blinowski, T. Brun, and P. Nielsen, J. Appl. Phys. (Suppl.) **35**, 933 (1964). Note that the linear intercepts with the $k^2 = 0$ axis of the inverse scattering appear to approach a positive value at $T = T_c$.

⁹⁶ P. Heller and G. B. Benedek, Phys. Rev. Letters **8**, 428 (1962).

⁹⁷ More recent NMR experiments by Heller and Benedek (private communication) reveal a similar behavior for the spontaneous magnetization of the ferromagnet EuS.

⁹⁸ See, for example, W. K. Robinson, and S. A. Friedberg, Phys. Rev. **117**, 402 (1960).