SOME CURRENT STUDIES IN LIQUID STATE PHYSICS*

1969 Award Lecture

Part 2. Dielectric and Critical State Phenomena

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DIELECTRIC BEHAVIOR IN NONPOLAR FLUIDS

THE DIELECTRIC constant of a material medium is a function of state. Upon first analysis this would suggest dependence of the dielectric constant ϵ or equivalently the refractive index n (and in these systems for all practical purposes $\epsilon = n^2$) upon two variables, for example, temperature and pressure. However, there exist the simple Clausius-Mossotti or Lorentz-Lorenz theories stemming from derivations now almost one century old, which describe the dielectric behavior of nonpolar substances solely in terms of the density:

$$CM = [(\epsilon-1)/(\epsilon+2)]\rho^{-1} = \frac{4}{3}\pi\alpha, \qquad (1)$$

$$LL = [(n^2-1)/(n^2+2)]\rho^{-1} = \frac{4}{3}\pi\alpha, \qquad (2)$$

where α is the polarizability.

The interested reader is referred to the review article by Brown[1] for discussions of derivation of above expressions. Briefly, one plausible derivation follows from an assumption that in the vicinity of a given molecule the local field from neighboring molecules vanishes. This is an assumption that can be shown to be rigorously true in the case of certain idealized solids because of the high symmetry of the crystal lattice. An equivalent justification for other states of matter is lacking, although it has been known for many years that Eqs. 1 and 2 seem to have general approximate validity even for dense fluids. Expanded theories of the dielectric behavior have produced corrections to the equations, but for fluid systems those corrections often called for a knowledge of the structure or correlation functions in liquids, information often lacking. Since those corrections are both temperature and density dependent, a test of the primitive theory is to inspect whether the computed values of the Lorentz-Lorenz function exhibit any density dependence at constant temperature, and whether there is any systematic shift from isotherm to isotherm.

There are a number of published measurements of either the dielectric constant or refractive index for argon, mostly at room temperature or near atmospheric pressure. Michels and Botzen[2] measured n at 25°C for pressures up to 2300 atm. Orcutt and Cole[3] presented very precise results for the dielectric constant at 50°, 100°, and 150°C for pressures 2-100 atm. A few measurements have been made on argon at low temperatures. Amey and Cole[4] measured the dielectric constant at the melting and normal boiling points, 84° and 85°K. Jones and Smith[5, 6] reported the refractive index of liquid argon near the triple point, 84°K. Smith and Pings[7] reported refractive index measurements for the solid at pressures up to 100 atm over a narrow range of temperatures near 90°K. These latter data were subsequently used[8] in conjunction with recent accurate density data[9] in order to compute the Lorentz-Lorenz function for the solid. Our laboratory[10] previously reported a set of measurements of the refractive index and computations of the Lorentz-Lorenz function for saturated gaseous and liquid argon.

Until 1968 there was apparently no comprehensive investigation of the refractive index or dielectric constant of the dense fluid region for a simple liquid. The author's laboratory, therefore, undertook a study of the refractive index of argon from near the normal boiling point to above the critical temperature. This filled in the unstudied region and made available a complete picture of the dielectric properties of argon from the solid region to the high temperature gas region.

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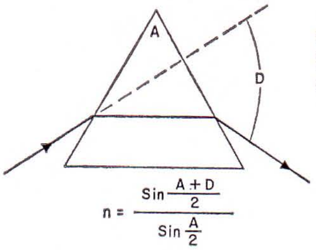

Fig. 1. Optical geometry involved in measurement of refractive index of a prism-shaped specimen.

Optical measurements were made on specimens of fluid argon under controlled conditions of temperature and pressure in a sample cell with supported sapphire windows. The windows were set at 45° to each other, effectively defining a prism-shaped specimen with an apex angle A of approximately 45°. Refractive indices were then obtained from the following formula:

$$n = \sin \tfrac{1}{2}\ (A+D)/\sin \tfrac{1}{2}A, \qquad (3)$$

where D is the measured angle of minimum deviation. See Fig. 1.

Results of measurements along eight isotherms and some data along the coexistence curve are shown in Fig. 2. Further data for the two-phase region near the critical state of argon are shown in Fig. 3. Many of those measurements were literally taken upon *coexisting* gas and liquid, i.e., with a well-defined two-phase system in the sample cell, it was possible to see both phases and to make independent determinations of the refractive indices of the gas and liquid.

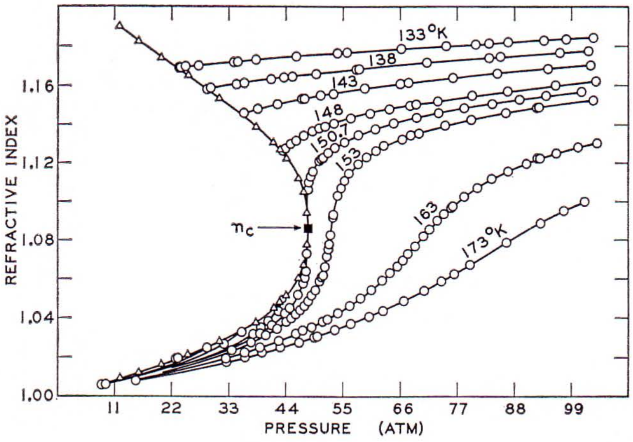

Fig. 2. Experimental values of the refractive index as a function of temperature and pressure. All of the points shown are experimental except the one indicated for the critical state, which was inferred from analysis of data in the critical region.

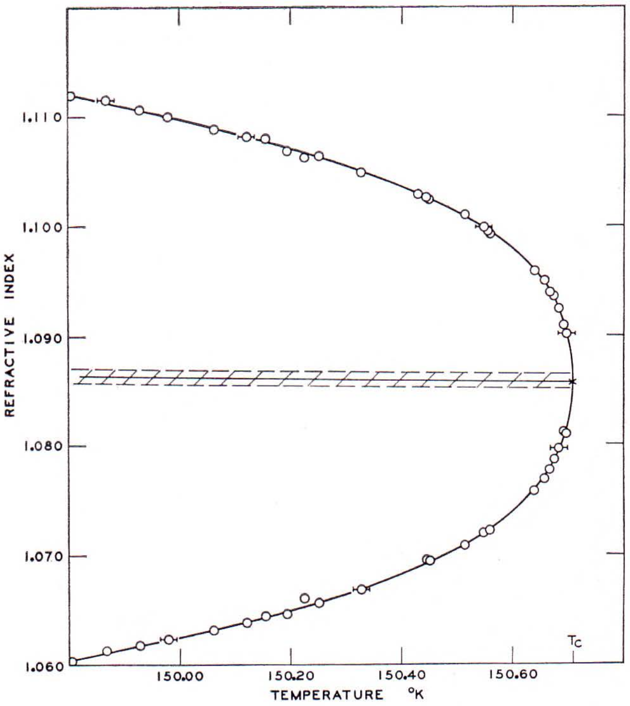

Fig. 3. Refractive index in the critical region. The almost horizontal line is the locus of the rectilinear diameter in n, including 95% confidence limits. The indicated critical temperature was ascertained by visual judgment as to the closure of the coexistence curve, yielding a provisional value of T of 150.709°K.

The temperatures of the one-phase isotherms had been selected so as to coincide with those studied in the extensive PVT measurements of Levelt.[11] Therefore, it was possible to combine our measured refractive index values with those density values as in Eq. 2 to form the Lorentz-Lorenz function as a function of pressure and temperature. The reader is referred to the article by Teague and Pings[12] for detailed analysis of the data. An indication of the test of the theory is shown in Fig. 4, which demonstrates computed values of the Lorentz-Lorenz function as a function of density for three different isotherms. Although there are faint suggestions of slight density dependence, the reader should note that those data are portrayed on a greatly expanded scale, and the general conclusion is that at the level of our experimental accuracy there can be at most minor deviation from the elementary theory even in the dense fluid region.

FINALLY, A BRIEF SUMMARY of the Lorentz-Lorenz function for argon in the three states of matter may be of interest. The present work suggests values for the effective molar polarizability, i.e., the LL function ($4\pi\alpha/3$, of 4.15 cm^3/mole for the saturated gas, 4.21 for the saturated liquid, 4.20 for the limiting value at the critical state, and values ranging from about 4.16 to 4.22 along the one-phase isotherms. For the gas at room temperature in the limit of zero pressure, Orcutt and Cole's[3] dielectric constant work cor-

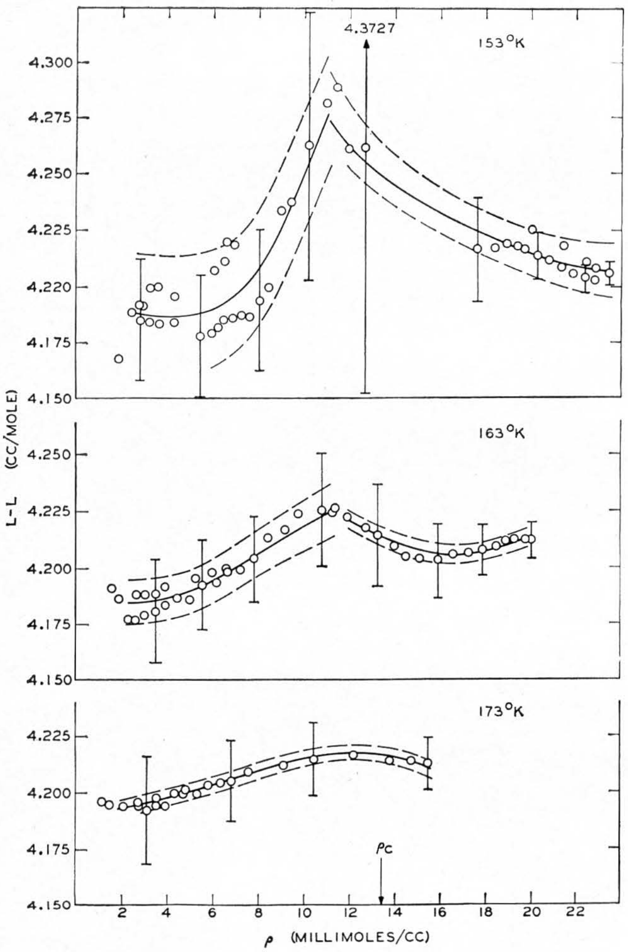

Fig. 4. The calculated Lorentz-Lorenz function for three gas-phase isotherms.

rected to 5893 Å gives a value of LL of 4.21_3. Recent analysis [8, 13, 14] of refractive index measurements by Smith and Pings[7] and Eatwell and Jones[15] (both sets at 5893 Å) for the solid indicate values of about 4.15 at 80°K decreasing to 4.12 at 20°K Considering the available evidence, it therefore seems possible to assert that there is no more than a 1.5% variation from a LL value of 4.19 cm^3/mole throughout the three states of matter, including the critical point, and with temperature variation from 20°-300°K.

There are practical ramifications to the conclusion that these elementary theories have broad range of validity. Consider Eq. 2 rewritten as follows:

$$\rho = A\frac{n^2-1}{n^2+2} \tag{4a}$$

where

$$A = \left(\frac{4\pi}{3}\alpha\right)^{-1} \tag{4b}$$

Knowledge of density, or its reciprocal the specific volume, of a fluid is usually a minimal requirement in handling any liquid system in real apparatus; also it is well-known that characterization of the specific volume as a function of pressure and temperature (or some equivalent accumulation of PVT data) in conjunction with heat capacity measurements as a function of temperature is the necessary and sufficient information for mapping of thermodynamic properties. Conventional techniques for density measurements, i.e., measuring the total volume of a measured mass of a substance are painstaking if even low accuracy is required. On the other hand, Eq. 4a is suggestive of a relatively easy intensive optical measurement with great potential for both absolute accuracy and particularly for precision. Furthermore, since the direct measurement is optical, observation of density with input to direct control systems seems plausible. This should have applications both in the research laboratory and in the monitoring and control of process streams.

EXPERIMENTAL STUDIES OF CRITICAL STATE SINGULARITIES

IN A BRIEF portion of one lecture it is impossible to provide a background of critical state phenomena or the scope of present theoretical experimental study of critical region singularities. Fortunately, there are several recent review articles available. [16–21]

The critical state was first described[22] one century ago, and since that time has sporadically been the subject of attention in scientific articles and text books. However, until recently this was largely confined to the curiosity of critical opalescence or to the recognition of vaguely defined, but nevertheless quite real practical diffiulties if separation units were operated too close to the critical state of any given component. About ten years ago there developed a renewed interest in the subject particularly when suggestions begin to emerge that perhaps there might be universal laws of critical region phenomena embracing not only the gas-liquid transition, but also liquid-liquid, magnetic, superfluid, and superconductor transitions. Furthermore, it appeared that rather good theoretical estimations of the singularities in equilibrium properties were predicted from one of the most primitive of the many-body theories, namely the three-dimensional Ising or lattice model.

We will attempt to discuss here only three types of singularities for the gas-liquid critical state of a single component system, namely i) the rate of the difference betwen the coexisting liquid of gas densities as the critical state is approached from below the critical temperature in the two-phase region, ii) the rate of divergence of the isothermal compressibility as the critical state is approached from above along the critical isochore, and iii) the rate of divergence of the isochoric heat capacity along the same path. These phenomena can be represented in quantitative form by the following equations:

$$\rho_L - \rho_G = D(T_C - T)^{\beta};\ T<T_C \qquad (5)$$

$$K_T = \frac{1}{\rho}\left(\frac{\partial \rho}{\partial P}\right)_T = A(T-T_C)^{-\gamma};\ \rho = \rho_C,\ T>T_C \qquad (6)$$

$$C_V = B(T-T_C)^{-\alpha};\ \rho = \rho_C,\ T>T_C \qquad (7)$$

Cast in this form, the thermodynamic behavior of a fluid near its critical state then is characterized by such exponents as α, β, γ. Inspection of the values of these exponents provides a *sharp tool* for intercomparison of various theories or models, macroscopic equations of state, and real data.

In a sense, the critical region is a domain of singularity separating gas-like from liquid-like behavior . . . it would seem that any attempts to carry gaseous theories into the liquid state . . . depend upon our ability to cope with problems in the critical region.

It is well-known that even a simple equation of state like the van der Waals equation predicts gas-liquid phase transitions (of course using some technique such as balancing of equal areas under the loops in the analytically continuous two-phase isotherms) and provides a closure of the two-phase dome. This suggests at least qualitatively the existence of a critical state. It is possible to show that not only the van der Waals equation, but *all* analytical equations of state predict the following values for the critical exponents: $\alpha = 0$ (actually a discontinuity in C_V), $\beta = 1/2$, $\gamma = 1$.

It has been known for many years that available experimental data were in disagreement with at least the above values for β and γ. The rate of divergence of the compressibility was suspected experimentally to be of the order of $\gamma = 1.25$, and it appears that β was much closer to one-third than to the classical value of one-half. In other words, the experimental data suggested that the shape of the coexistence curve involved a cubic dependence of temperature difference upon density difference compared to quadratic behavior suggested by van der Waals equation (there are alternate interpretations of the van der Waals equation which would suggest quartic or sixth power behavior but would not permit variation as any odd power such as cubic). Behavior of the heat capacity was less well understood until the appearance in 1963 of work by Voronel[23] on argon which was suggestive of a logarithmic divergence of C_V, or alternatively a value of α close to zero, but slightly positive. It was also known that the shape of magnetization versus temperature curves near magnetic critical points also was approximately cubic.

IT IS POSSIBLE to make a simple model of a system exhibiting magnetic phase transitions including a Curie temperature by consideration of a idealized lattice, each site of which contains a small magnet, which can be positioned either up or down in the magnetic field. Solution of the resulting combinatorial problem suggests a phase transition and a Curie temperature, i.e., a magnetic critical state. The problem in two dimensions was solved by Onsager,[24] with explicit analytic values for the various critical state exponents. The three-dimensional case has not been solved analytically, but a sequence of investigators have obtained numerical approximations to the various critical exponents, and those results are reviewed in the paper by Fisher.[16] Results are summarized in Table I. It will be seen that the computed value of $\beta = 0.313$ while not the reciprocal of an integer is nevertheless much closer to the experimentally observed values than is the value of $\beta = 1/2$ predicted from classical equations of state. The exponent γ, is predicted from the Ising lattice model to be $1.25 \pm .01$, again significantly closer to experimental facts than the predictions of the classical equations of state.

The Ising lattice model for magnetic properties is isomorphous with a lattice gas model for fluid behavior. Instead of having the "up-down" possibility for the orientation of the magnet, we have an "occupied-unoccupied" possibility in the case of the lattice gas. Of course, the nature and characteristic of the short-range forces acting

Table I. Summary of Critical Exponents

Equations:

(1) $\rho_L - \rho_G = D(T_C - T)^{\beta}$ (3) $C_V = B(T - T_C)^{-\alpha}$

(2) $K_T = A(T - T_C)^{-\gamma}$ (4) $|P - P_C| = E|\rho - \rho_C|^{\sigma}$

Equation	(1)*	(2)**	(3)**	(4)†
Classical	½	1	0 (discontinuity)	3
Primitive Expt	1/3	1¼	—	—
2-d Ising	⅛	1¾	0 (los)	15
3-d Ising	0.313 ± .003	1.250 ± .003	⅛ ± .015	5.20 ± .015
Refined Expt	0.34 to 0.36	1.21 ± .01	0 (log?)	> 4.2

* $T < T_C$; ** $\rho = \rho_C$; † $T = T_C$

between the particles in the two cases is quite different. Furthermore, any sort of lattice model for liquids is surely overstructured, although a type of fluidity is introduced by the randomization of the occupied and unoccupied sites. Therefore, although the lattice gas model may be a good qualitative representation of the gas-liquid behavior, and in actual fact has semiquantitative agreement with observed experimental behavior, one should not be too surprised if agreement is not exact, nor if there is systematic variation of properties from one fluid system to another. Refined experimental values of the critical exponents on selected systems are highly desirable. This becomes an interesting intellectual quest on its own merits as an attempt to better understand the critical region as such. There is a further enticement steming from the fact that in a sense the critical region is a domain of singularity separating gas-like from liquid-like behavior, and therefore it would seem that any attempts to carry gaseous theories into the liquid state would be dependent upon our ability to understand and cope with problems in the critical region.

The author's laboratory has been conducting critical region experiments for several years. Specifically, we reported in 1965-66 an extensive set of sound absorption measurements near the lower consolute (critical point) of the nitrobenezene-isooctane system. [25, 26] Frequency dependent deviations from the classical predictions of sound absorption in fluids were found, reaching as much as factors of fifty times the classical value at frequencies of 1.5MHz. Those measurements were in reasonable agreement with the predictions from a semiphenomenalogical theory for transport in the critical region due to Fixman.[27] Our research group is currently studying the viscosity of xenon as its critical state is approached from above in the one-phase region. We have also been making heat capacity measurements near the upper consolute point of the CH_4-CHF_3 system, and provisional results suggest a lambda-like transition of the type by Voronel for argon. Analysis of those date are incomplete, but preliminary inspection indicates a value of α that is either logarithmic or compatible with a small positive value.

Classical theories describe dielectric behavior of non-polar substances solely in terms of density.

We have also made extensive measurements of the equation of state surface in the vicinity of the critical state of liquid argon. The optical cryostat described in the previous section is used as a means of deducing density from direct observation of refractive index, assuming that the Lorentz-Lorenz theory of Eq. 2 holds. Data of the type show in Fig. 3 were used directly to ascertain a value of β. Those measurements were carried to within 7×10^{-3}°C of the critical temperature requiring temperature control under these conditions to be better than $\pm 10^{-4}$°C. The reader is referred to a paper by Teague and

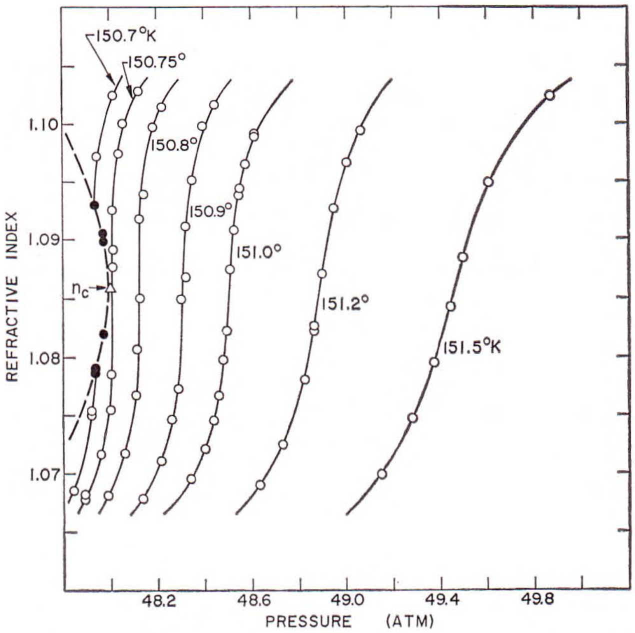

Fig. 5. Detailed refractive index measurements near the critical state of argon. Tc is approximately 150.72°K.

Pings[12] for details of the refined analysis of the data, which leads to a value of $\beta = 0.364 \pm .007$.

We are currently making extensive measurements on one-phase isotherms above the critical temperature of argon using the same technique. Preliminary data, in terms of refractive index versus pressure, are shown in Fig. 5, and the resulting values of computed compressibilities in Fig. 6. It is apparent from Fig. 6 that the compressibility is indeed rising very rapidly and sharply as the critical state is approached from above. Provisional analysis of those data indicates a value of $\gamma = 1.21 \pm 0.1$. That number will doubtlessly be revised somewhat as more experimental information are obtained and as a refined data analysis is carried out.

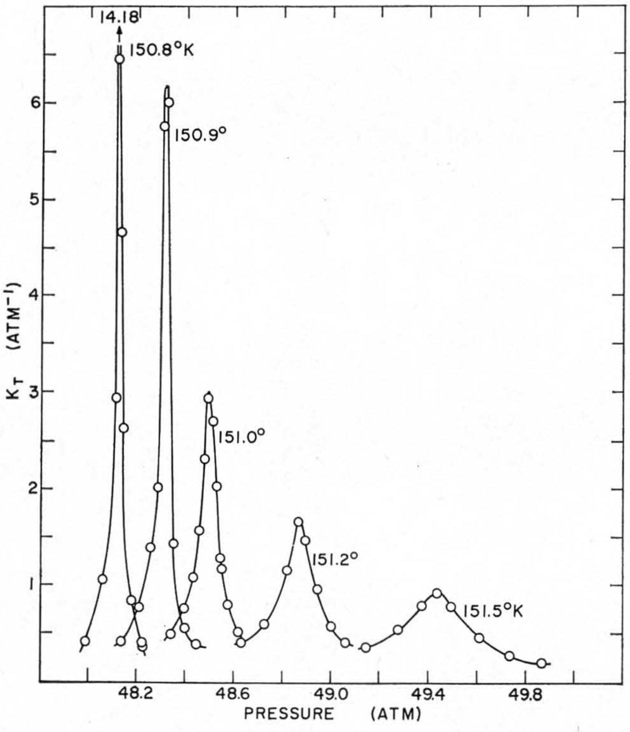

Fig. 6. Compressibility of argon near the critical state. Values obtained by differentiation of the data shown in Figure 5.

To the extent that the above numbers are credible, they are clearly in disagreement with a) classical values, b) Ising lattice values, and c) numeralogical guesses that β should be the ratio of integers, i.e., 1/3, 5/16, etc. Experimental values from other sources are discussed in the review article by Heller[17] and in a recent paper by Vicentini-Missoni, Sengers, and Green.[28] Information now available on a number of different substances seems to indicate the emergence of vlaues of β in the range of 0.34 to 0.36. See Table I. Incidentally, the latter paper contains an interesting discussion of a scaling analysis in the critical region which suggests the possibility of a universal law of critical behavior in terms of reduced variables.

. . . there can be at most minor deviation from elementary theory of the Lorentz-Lorenz function even in the dense fluid region.

REFERENCES

1. W. F. Brown, Jr., in Handbuch der Physik, S. Fluggle, Ed. (Springer-Verlag, Berlin, 1956), Vol. **17.**
2. A. Michels and A. Botzen, *Physica* **15,** 769 (1949).
3. R. H. Orcutt and R. H. Cole, *Physica* **31,** 1779 (1965).
4. R. L. Amey and R. H. Cole, *J. Chem. Phys.* **40,** 146 (1964).
5. G. O. Jones and B. L. Smith, *Phil. Mag.* 5, 355 (1960).
6. B. L. Smith, *Phil. Mag.* **6,** 939 (1961).
7. B. L. Smith and C. J. Pings, *Physica* **29,** 555 (1963).
8. C. J. Pings, *Physica* **33,** 473, (1967).
9. O. G. Peterson, D. N. Batchelder, and R. O. Simmons, *Phys. Rev.* **150,** 703 (1966).
10. C. P. Abbiss, C. M. Knobler, R. K. Teague, and C. J. Pings, *J. Chem. Phys.* **42,** 4145 (1965).
11. J. M. H. Levelt, doctoral thesis, Amsterdam, 1958; this work also reported in A. Michels, J. M. Levelt, and G. J. Wolkers, *Physica,* 24, 769 (1958).
12. R. K. Teague and C. J. Pings, *J. Chem. Phys.* 48, 4973 (1968).
13. B. L. Smith and C. J. Pings, *J. Chem. Phys.* 48, 2387 (1968).
14. B. L. Smith, *Physica* **35,** 475 (1967).
15. A. J. Eatwell and G. O. Jones, *Phil. Mag.* **10,** 1959 (1964).
16. M. E. Fisher, *Rep. Prog. Phys.* **30,** 615 (1967).
17. P. Heller, *ibid,* 731.
18. L. P. Kadanoff, etal, *Rev. Mod. Phys.* **39,** 395 (1967).
19. C. Domb, *Bull. Inst. Phys., London,* **19,** 36 (1968).
20. B. L. Smith, *Contemp. Phys.* **10,** 305 (1969).
21. M. S. Green and J. V. Sengers, Critical Phenomena, Misc. Pub. No. 273, Natl. Bur. Stds. (1966).
22. T. Andrews, *Phil. Trans. Roy. Soc.* London **159A,** 575 (1869).
23. A. V. Voronel, Yu R. Chashkin, V. A. Popov, and V. G. Simkin, Z. h. Eksper. *Teor. Fiz.* 48, 828 (1963). (Soviet Physics—*JETP* 18, 568 (1964).
24. L. Onsager, *Phys. Rev.* **65,** 117 (1944).
25. C. J. Pings and A. V. Anantaraman, *Phys. Rev. Letters* 14, 781 (1965).
26. A. V. Anantaraman, A. B. Walters, P. D. Edmonds, and C. J. Pings, *J. Chem. Phys.* **44,** 2651 (1966).
27. M. Fixman, *J. Chem. Phys.* **36,** 1957 (1962); *ibid.* 36, 1961 (1962).
28. M. Vicentini-Missoni, J. M. H. Levelt Sengers, and M. S. Green, *J. Res. N.B.S.* **73A,** 563 (1969).