

Proc. Roy. Soc. (London) 181, 386 (1943).

¹⁸This value follows from the work of Y. Lee and

B. H. Mahan, J. Chem. Phys. 42, 2893 (1965).

¹⁹M. Kasha, J. Opt. Soc. Am. 38, 929 (1948).

EQUATION OF STATE OF ⁴He IN THE CRITICAL REGION

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It was pointed out several years ago by one of us¹ that the thermodynamic functions are nonanalytic at the critical point and presumably exhibit branch-point singularities. Recently a great deal of progress has been achieved in providing mathematical descriptions of such singularities.² In order to integrate these results with the formalism of thermodynamics, it is necessary to choose a set of "natural variables" that are within the scheme of a single fundamental equation and are adapted to the intrinsic symmetry of the system. This point is too obvious to call for special notice, say, in the case of crystals. There is, however, evidence of a near symmetry in the critical region of fluids, the thermodynamic role of which has not been sufficiently appreciated. This symmetry is masked if the traditionally favored independent variables are used.

In order to demonstrate this thesis we shall analyze the measurement of Edwards and Woodbury³ (henceforth referred to as EW) who determined the orthobaric densities of ⁴He to within 36 mdeg of T_c for the liquid and 50 mdeg for the vapor. EW attempted at first to describe their measurements in terms of the approximate expansion of Landau and Lifshitz⁴

$$N^{-1}(\partial^2 F / \partial v^2)_{T,N} = -(\partial P / \partial v)_T = At + Bv'^2 + \dots, \quad (1)$$

where $F = F(T, V, N)$ is the Helmholtz free energy, $v = V/N$ is the molar volume, A and B are adjustable positive constants, $t = T - T_c$, and $v' = v - v_c$. Omitting higher order terms, this relation yields the coexistence curve

$$v_G' = -v_L' = (-3At/B)^{1/2}. \quad (2)$$

According to this relation the molar volumes of the coexisting phases are symmetric around the critical volume, a prediction in conflict with experiment. In order to obtain quantitative agreement with their measurements within about 110 mdeg of T_c , EW added two more terms to the above expansion. In such a way they eliminated the spurious symmetry of Eq. (2) with respect to v' . On closer examination, however, it appears that their expression leads to inconsistencies when applied at points away from the coexistence curve⁵; e.g. the critical isotherm (which is identical with that of Landau and Lifshitz) and the coexistence curve cross at a pressure close to P_c .

One might believe that these difficulties are connected with the singular character of the critical point mentioned above. This, however, does not appear to be the case; in the region under consideration, which does not extend into the immediate neighborhood of the critical point, the difficulties can be at least partially overcome by interchanging the role of the variables N and V . Instead of considering a closed system with N fixed and $v = V/N$ variable, we envisage an open system with V fixed and $\rho = N/V$ variable. We obtain a preliminary estimate of the implications of this change of viewpoint by translating the Landau-Lifshitz expansion into the present scheme.

The analog of Eq. (1) is

$$V^{-1}(\partial^2 F / \partial \rho^2)_{T,V} = (\partial \mu / \partial \rho)_T = \alpha t + \beta \rho'^2 + \dots, \quad (3)$$

where α and β are positive constants and $\rho' = \rho - \rho_c$. The slope of the isothermals is now

$$(\partial P / \partial \rho)_T = \rho(\partial \mu / \partial \rho)_T = \rho(\alpha t + \beta \rho'^2), \quad (4)$$

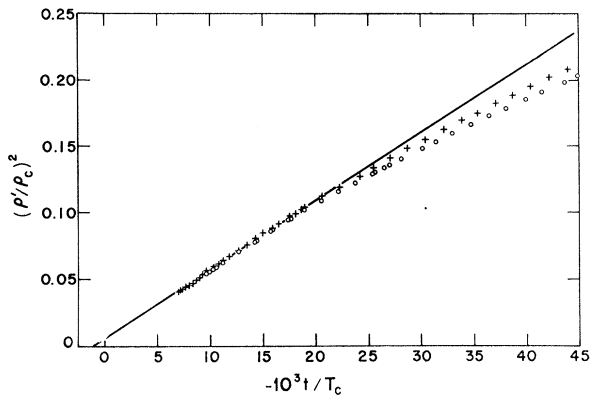


FIG. 1. Graph of $(\rho_L'/\rho_c)^2$ and $(\rho_G'/\rho_c)^2$ against $-t/T_c$ from data of reference 3. Equation (5) predicts a single straight line of slope $3\alpha/\beta$. Crosses, $(\rho_L'/\rho_c)^2$; circles, $(\rho_G'/\rho_c)^2$.

and, by a treatment exactly parallel to that of reference 4, we find

$$\rho_L' = -\rho_G' = (-3\alpha t/\beta)^{1/2}. \quad (5)$$

The predicted coexistence curve is thus symmetric in the density. This is indeed approximately correct for fluids in general,^{6,7} and this equation fits as well with the EW results as their four-parameter expression.⁸ According to Eq. (5), a plot of $\rho_G'^2$ and $\rho_L'^2$ against $-t$ should yield a single straight line through the origin of slope $3\alpha/\beta$. Such a plot is shown in Fig. 1⁹; from the slope of the solid line we find $\alpha/\beta = (1.03 \pm 0.02) \times 10^{-4}$ mole²/cm⁶ °K. This diagram should be compared with Fig. 3 of EW, which demonstrates the discrepancy between Eq. (2) and experiment. The quantity β can be evaluated approximately, as in EW, by comparison with the measured liquid density and isothermal compressibility¹⁰ on the saturation curve at 5°K, since according to Eq. (4) we have

$$\beta = [\rho^2 \kappa_T (\alpha t/\beta + \rho'^2)]^{-1}. \quad (6)$$

The result is $\beta = (6.86 \pm 1.2) \times 10^{13}$ dyne cm¹⁰/mole⁴; most of the quoted uncertainty is due to a 15% error in the measured value of κ_T . Equations (3) and (4) can be integrated to yield the isotherms in the P, ρ and μ, ρ planes if plausible assumptions are made concerning the temperature-dependent integration constants. Families of such isotherms show none of the inconsistencies associated with the expansion of EW.¹¹

The range of usefulness of this simple approximation can be established only by further experiments. A systematic study of the critical region would be indeed most desirable. We wish to emphasize, however, that the case for the pair of conjugate variables ρ, μ depends not on the validity of approximation (3), but rather on the near symmetry of the coexistence curves.¹²

The connection between symmetry and thermodynamic singularity has previously been elaborated by one of us.¹³ In that paper critical points were discussed in terms of the diagonalized stiffness matrix. For a one-component system we have two diagonal elements that can be written as $\lambda_1 = T/c_v$, $\lambda_2 = (\partial\mu/\partial\rho)_T = \rho^{-1}(\partial P/\partial\rho)_T$. The classical critical point is characterized by $\lambda_2 = 0$, a condition that can be satisfied only at an isolated point in the P - T diagram. It is the symmetry of the system that renders $\lambda_2 = 0$ possible along a λ line in this diagram.

On the basis of the classical theory, which excludes the case $\lambda_1 = \lambda_2 = 0$ as an unlikely accidental degeneracy, c_v is predicted to be finite.^{4,13} This a priori argument against a singular c_v is removed, however, if the degeneracy is produced by symmetry rather than by accident. An intuitive interpretation of this symmetry is provided by the lattice-gas model of Lee and Yang.¹⁴ At the time this theory was advanced the injection of symmetry seemed to be a fortuitous property of the oversimplified model. It now appears that this symmetry, at least in the immediate neighborhood of T_c , may indeed be a fundamental property of the critical region.

Some aspects of this paper were clarified during the Conference on Phenomena in the Neighborhood of Critical Points, National Bureau of Standards, Washington, D. C., April 5-8, 1965.

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¹L. Tisza, in Phase Transformations in Solids, edited by R. Smoluchowski, J. E. Mayer, and W. A. Weyl (J. Wiley and Sons, Inc., New York, 1951), pp. 1-37; see particularly p. 15.

²G. S. Rushbrooke, *J. Chem. Phys.* **39**, 842 (1963); M. E. Fisher, *J. Math. Phys.* **5**, 944 (1964); R. B. Griffiths, *Phys. Rev. Letters* **14**, 623 (1965).

³M. H. Edwards and W. C. Woodbury, *Phys. Rev.*

129, 1911 (1963).

⁴L. T. Landau and E. M. Lifshitz, *Statistical Physics* (Pergamon Press, New York, 1958), p. 259 ff.

⁵We noticed these difficulties in connection with recent measurements of the sound velocity in ⁴He near the critical point; we needed values of the density in order to calculate the adiabatic compressibility from the relation $\kappa_S^{-1} = \rho u^2$, and in the absence of direct density measurements we used the expression of EW to extrapolate the densities away from the coexistence curve. [C. E. Chase, R. C. Williamson, and L. Tisza, *Phys. Rev. Letters* **13**, 467 (1964).]

⁶L. Cailletet and E. Mathias, *Compt. Rend.* **102**, 1202 (1886).

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

⁸It is a curious fact that in ⁴He the orthobaric densities as measured by EW are indeed proportional to $t^{1/2}$ within the region indicated, although further away the dependence is more nearly $t^{1/3}$ as seems to be the case for most fluids. (See references 2 and 7.) If the former result is real, it might be attributed to the quantum corrections to the law of corresponding states. [J. de Boer, *Physica* **14**, 139, 149 (1948); J. de Boer and R. J. Lunbeck, *Physica* **14**, 509 (1948).] Similar behavior ought to be expected then in ³He, and has in fact recently been observed [R. H. Sherman, Proceed-

ings of the Conference on Phenomena in the Neighborhood of Critical Points, National Bureau of Standards, Washington, D. C., 1965 (to be published)].

⁹The straight line in the figure actually has a finite intercept on the abscissa, corresponding to +4.6 mdeg. This may indicate flattening of the coexistence curve close to the critical point, or be the result of errors in the measured temperatures in EW or in the assignment of T_c .

¹⁰M. H. Edwards and W. C. Woodbury, *Can. J. Phys.* **39**, 1833 (1961).

¹¹For a plot of these curves, see C. E. Chase and R. C. Williamson, Proceedings of the Conference on Phenomena in the Neighborhood of Critical Points, National Bureau of Standards, Washington, D. C., 1965 (to be published).

¹²The arguments in favor of this scheme far outweigh the slight inconvenience of using the chemical potential which, like the entropy, is measurable only indirectly. The compromise scheme p, ρ turns out to be impractical; this may be connected with the fact that these variables do not form a conjugate pair.

¹³L. Tisza, *Ann. Phys. (N.Y.)* **13**, 1 (1961).

¹⁴T. D. Lee and C. N. Yang, *Phys. Rev.* **87**, 410 (1952); see also C. N. Yang and C. P. Yang, *Phys. Rev. Letters* **13**, 303 (1964).

RELATIVE PHASE MEASUREMENT BETWEEN FUNDAMENTAL AND SECOND-HARMONIC LIGHT*

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The nonlinear susceptibility describing the second-harmonic generation of light is real, when the medium is transparent at both the fundamental and the harmonic frequency. When the medium is absorbing at either or both of these frequencies, this nonlinear susceptibility is a complex quantity.¹ The nonlinear polarization has a phase shift with respect to the fundamental field. Measurement of the second-harmonic intensity only determines the absolute value of the nonlinear susceptibility. For some III-V and II-VI compounds, which are absorbing at the second-harmonic frequency, such measurements have been carried out in reflection.^{2,3} In this note an experiment is described which determines the phase of the non-

linear susceptibility.

The experimental arrangement is shown in Fig. 1. A linear polarized laser beam from a Q-switched ruby laser enters an evacuated box and generates second-harmonic radiation by reflection from a nonlinear mirror of a crystal with $\bar{4}3m$ symmetry, whose complex nonlinear susceptibility must be determined. The laser beam subsequently generates an additional second-harmonic field in a potassium-dihydrogen-phosphate (KDP) platelet which serves as a reference signal. The second-harmonic fields generated in the two samples will have a definite phase relationship with respect to each other, as each has a specific relationship to the phase of the fundamental