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Thermodynamic Properties near the Liquid-Vapor Critical Line in Mixtures of He^3 and He^4†

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An explicit thermodynamic equation of state is proposed for the region near the line of liquid-vapor critical points in mixtures of He^3 and He^4. The equation (of the scaling form) embodies nonclassical exponents and uses chemical potentials or activities as independent variables in place of composition and volume. The properties of the mixtures are shown to result, in the main, from an interpolation between the critical properties of the pure components, in a suitable set of variables. Failure of experiments to reveal a weak divergence in the isothermal compressibility (at fixed composition), in contrast to previous phenomenological theories, is explained through the small size of the region near the critical line where one might expect to see the "true" asymptotic behavior.

I. INTRODUCTION

The phenomenological thermodynamic description of critical points in fluid mixtures has a long history. Much of the work has been based on the van der Waals or similar "classical" equations of state,[1,2] but in recent years the apparatus of critical indices, scaling, etc., developed for pure fluids and simple ferromagnets[3] has also been applied to fluid mixtures.[4] In this paper we attempt to fit the thermodynamic properties of the mixture He^3-He^4 at all compositions along its liquid-vapor critical line using a single equation of state, of the scaling form, which embodies nonclassical exponents. So far as we know, this is the first attempt to provide an explicit thermodynamic formula (including numerical values for all parameters) for properties along such a line using a nonclassical equation of state.

Our analysis differs from many previous discussions of binary mixtures[5] in that the composition of the mixture does *not* play a fundamental role as one of the independent thermodynamic variables. Rather, our independent variables are the temperature and chemical potentials, or activities, of the two components, and the composition appears as a derived quantity, and thus a dependent variable. While it certainly should be possible to introduce nonclassical exponents in equations of state which have composition as an independent variable, it is our opinion that our choice of variable (details are found in Sec. II) has certain practical advantages and may be useful in the phenomenological analysis of critical lines in other systems.

The measurements of the equation of state in He^3-He^4 mixtures near the critical line recently published by Wallace and Meyer[6] form the basis of our analysis, together with other data on the properties of pure He^3 and pure He^4 near their respective critical points.[7-10] These measurements show that the critical temperatures, pressures, and densities are monotone and almost linear functions of composition over the entire range from pure He^3 to pure He^4. For such a simple situation, phenomenological theories[11,12] and model calculations[13] predict that the isothermal compressibility at fixed composition K_{Tx}, which exhibits a "strong" divergence in a pure fluid, should show only a "weak" divergence in mixtures, analogous to the divergence of the constant-volume heat capacity in a pure fluid. The same theories indicate that the constant-volume, constant-composition heat capacity C_{vx} in mixtures should not diverge at all but rise to a finite cusp. In fact the experiments of Wallace and Meyer[6] show no evidence that K_{Tx}, diverges at all, while a measurement of C_{vx} by Brown and Meyer[14] (with mole fraction of He^3 equal to 0.805) indicates a heat capacity diverging at about the same rate as in pure He^3. There is thus an apparent contradiction between theory and experiment which is, however, not difficult to reconcile on the basis of our equation of state. It turns out (Sec. V) that the theoretically predicted behavior should occur only very close to the critical line, and our numerical estimates indicate that this asymptotic region is so small in He^3-He^4 that it will be quite difficult to observe experimentally.

An outline of the paper is as follows: In Sec. II we discuss the choice of thermodynamic variables. An explicit form for the thermodynamic potential, with a number of adjustable constants, is set forth in Sec. III, and the procedure for determining these constants on the basis of experimental data is discussed in Sec. IV, which also contains a comparison of experimental dew-bubble curves and isotherms with those computed from our formula. The region asymptotically near the critical line is the subject of Sec. V, while Sec. VI provides a brief summary.

II. THERMODYNAMIC VARIABLES

A. Choice of Variables

The choice of independent variables in a thermodynamic analysis is not obvious *a priori* and must be based on considerations of conceptual simplicity, convenience, etc. The use of "fields" in the sense of Ref. 11 (intensive quantities which are always the same in two coexisting phases) has certain conceptual advantages in discussions of phase transitions and critical points. In addition there is the very practical advantage that the thermodynamic potential may be conveniently written (Sec. III) as the sum of a regular and a singular part, with all the discontinuities and divergences, that is, the characteristic features of the phase transition, determined by the latter. Consequently we have chosen to base our analysis on the "fields" p, T, μ_3 and μ_4 (chemical potentials of He^3 and He^4, respectively), despite the fact that the chemical potentials are not measured directly in the experiments of interest to us.

From among the fields it is necessary to single out some to serve as independent variables and one to serve as the dependent variable or thermodynamic potential. In simple pure fluids it is known[15,16] that $p(\mu, T)$ is more symmetrical between liquid and vapor phases than is $\mu(p, T)$, and there is some evidence that the coexistence curve is smooth (continuous second derivative) near the critical point in the μ, T plane but not in the p, T plane.[17] These considerations suggest that in a mixture $p(\mu_3, \mu_4, T)$ may possess some practical advantages over a choice in which p is one of the independent variables.

We shall however, for reasons to be explained below (in Sec. III), use as a potential not p but

$$Bp = \omega(\nu_3, \nu_4, B)\,, \tag{2.1}$$

which possesses all the advantages of p mentioned above; here[18]

$$B = (RT)^{-1}\,, \tag{2.2}$$

with R the gas constant, and for $j = 3, 4$

$$\nu_j = B\mu_j\,. \tag{2.3}$$

The fundamental differential relationship for ω is:

$$d\omega = \rho_3\, d\nu_3 + \rho_4\, d\nu_4 - u\, dB\,, \tag{2.4}$$

where ρ_3 and ρ_4 are the densities of He^3 and He^4 in moles per unit volume, and u is the energy per unit volume.

B. Transformed Variables

In pure He^3, ν_4 goes to $-\infty$ and in pure He^4, ν_3 goes to $-\infty$. In order to obtain variables which remain finite everywhere along the critical line it is convenient to introduce the variables

$$\Theta = C_4 e^{\nu_4} + C_3 e^{\nu_3}\,, \tag{2.5}$$

$$\zeta = C_4 e^{\nu_4}/\Theta\,, \tag{2.6}$$

which are simply expressed in terms of the absolute activities, e^{ν_j}. Here C_3 and C_4 are positive constants. Note that ζ is 0 in pure He^3 and 1 in pure He^4. To a first approximation near the line of critical points, one finds

$$\zeta \simeq 1 - x\,, \tag{2.7}$$

where x is the mole fraction of He^3. Whereas (2.7) is very valuable for conceptual purposes, it is not exact and, in fact, ζ and x are two very different sorts of variables: ζ is the same in two coexisting phases while x (in general) is not.

In constructing an expression for the potential it is convenient to introduce in place of the variables B and Θ the quantities.

$$\tau = B_c(\zeta) - B\,, \tag{2.8}$$

$$h = \ln[\Theta/\Theta_\sigma(\zeta, \tau)] = \ln\Theta - H(\zeta, \tau)\,. \tag{2.9}$$

Here B_c is the critical value of $(RT)^{-1}$ as a function of ζ, while Θ_σ is the value of Θ on the liquid-vapor coexistence surface, considered as a function of ζ and τ. Of course, the coexistence surface terminates at the critical line, but we shall assume that it can be smoothly continued through the line of critical points to define a surface which we shall, somewhat imprecisely, refer to as the "coexistence surface" even where, "above" the critical line, there is only one phase.

Let us make perfectly precise what is meant by (2.8) and (2.9). Given a point (ν_3, ν_4, B) in the thermodynamic space, we compute ζ and Θ using (2.5) and (2.6). This value of ζ determines $B_c(\zeta)$ and therefore τ by (2.8). Together, these values of ζ and τ determine a curve in the thermodynamic space which we assume intersects the coexistence surface (or its smooth extension) at a single point. The value of Θ at this point is the Θ_σ which appears in (2.9).

The variables τ and h have a simple interpretation in one of the pure fluids ($\zeta = 0$ or 1). Evidently h is $(RT)^{-1}$ times the deviation of the appropriate chemical potential (μ_3 in pure He^3, μ_4 in pure He^4) from its value on the coexistence curve [or its smooth extension in the (μ, T) plane], and τ is R^{-1} times the deviation of the inverse temperature from its critical value. Thus it is apparent that these variables are very similar to those which have been employed in scaling analyses[15] of properties of pure fluids. In terms of the Ising-model magnet analog of the liquid-vapor critical point one can (with a slight lack of precision) think of τ as the deviation of temperature from its critical value and h as the magnetic field. Note that, in any case, τ and h form a coordinate system with the τ axis ($h = 0$) parallel to the coexistence curve and h measuring (in some sense) distance away from the coexistence curve. In the fluid mixture τ and h for a fixed ζ have the same geometrical significance: τ a measure of distance from the critical line in a direction parallel to the coexistence surface, and h a measure of distance away from the coexistence surface.

In the case of pure fluids it is common practice to replace τ by a dimensionless variable t by dividing or multiplying by the critical temperature. We have purposely not done this. The reason is that there is no unique critical temperature but rather a continuum of values between those for pure He^3 and He^4. We do, indeed, introduce a ζ-dependent "normalization" for τ when it occurs as an argument in ω_s, the singular part of ω (see Sec. III below), but the ζ dependence is treated as an adjustable parameter.

C. Thermodynamic Functions in Terms of $\omega(\zeta,\tau,h)$

In Sec. III below we shall introduce a functional form for ω in terms of the variables ζ, τ, and h. The relations (2.4) through (2.9) permit one to write various thermodynamic quantities in terms of partial derivatives of ω. The derivations are straightforward but somewhat tedious, and we display here the appropriate formulae. In order to shorten the notation, partial derivatives with respect to one of the variables ζ, τ, h (the other two being held constant) are denoted by subscripts, e.g.,

$$\omega_\zeta = \left(\frac{\partial \omega}{\partial \zeta}\right)_{\tau h} ; \quad \omega_{\zeta\tau} = \left(\frac{\partial^2 \omega}{\partial \zeta \partial \tau}\right)_h , \tag{2.10}$$

$$B_\zeta = B_{c\zeta} = \frac{dB_c}{d\zeta} , \tag{2.11}$$

$$H_\tau = \left(\frac{\partial H}{\partial \tau}\right)_\zeta = \left(\frac{\partial \ln \Theta_a}{\partial \tau}\right)_\zeta . \tag{2.12}$$

The partial derivatives of ζ, τ, and h with respect to ν_3, ν_4, and B are as follows ($\partial/\partial\nu_3$ means ν_4 and B fixed, etc.):

$$\frac{\partial \zeta}{\partial \nu_3} = -\frac{\partial \zeta}{\partial \nu_4} = -\zeta(1-\zeta) , \tag{2.13}$$

$$\frac{\partial \zeta}{\partial B} = 0 , \tag{2.14}$$

$$\frac{\partial \tau}{\partial \nu_3} = -\frac{\partial \tau}{\partial \nu_4} = -\zeta(1-\zeta)B_\zeta , \tag{2.15}$$

$$\frac{\partial \tau}{\partial B} = -1 , \tag{2.16}$$

$$\frac{\partial h}{\partial \nu_3} = 1 - \frac{\partial h}{\partial \nu_4} = 1 - \zeta + \zeta(1-\zeta)(H_\zeta + B_\zeta H_\tau) , \tag{2.17}$$

$$\frac{\partial h}{\partial B} = H_\tau , \tag{2.18}$$

The following results are obtained by combining (2.4) and (2.13)–(2.18), e.g.:

$$\begin{aligned} u &= -\left(\frac{\partial \omega}{\partial B}\right)_{\nu_3 \nu_4} \\ &= -\omega_\zeta \left(\frac{\partial \zeta}{\partial B}\right)_{\nu_3 \nu_4} - \omega_\tau \left(\frac{\partial \tau}{\partial B}\right)_{\nu_3 \nu_4} - \omega_h \left(\frac{\partial h}{\partial B}\right)_{\nu_3 \nu_4} . \end{aligned} \tag{2.19}$$

Thus we have

$$u = \omega_\tau - \rho H_\tau , \tag{2.20}$$

$$\rho_3 = (1-\zeta)\rho - \zeta(1-\zeta)Q , \tag{2.21}$$

$$\rho_4 = \zeta\rho + \zeta(1-\zeta)Q , \tag{2.22}$$

$$\rho = \rho_3 + \rho_4 = \omega_h , \tag{2.23}$$

$$Q = \omega_\zeta + B_\zeta \omega_\tau - \rho(H_\zeta + B_\zeta H_\tau) . \tag{2.24}$$

Note that in the above expressions ω_h has everywhere been replaced by ρ, the total density of the mixture (in moles per unit volume). The quantity Q is a convenient abbreviation with no physical significance. The mole fraction of He^3 in the mixture is

$$x = \rho_3/\rho = 1 - \zeta - \zeta(1-\zeta)Q/\rho \tag{2.25}$$

The heat capacity at constant volume and the compressibility, C_{vx} and K_{Tx}, both at constant composition, are most conveniently expressed in terms of Jacobians. By C_{vx} we mean the heat capacity *per mole*. It is multiplied by ρ in (2.26) because u is the energy *per unit volume*. We can write

$$\rho C_{vx} = \left(\frac{\partial u}{\partial T}\right)_{\rho,x} = -RB^2 \left(\frac{\partial u}{\partial B}\right)_{\rho,x} \qquad (2.26)$$

or

$$\frac{\rho C_{vx}}{RB^2} = -\frac{\partial(u,\rho,x)}{\partial(B,\rho,x)} = \frac{E}{F}, \qquad (2.27)$$

and

$$K_{Tx} = \frac{1}{\rho}\left(\frac{\partial \rho}{\partial p}\right)_{T,x} = \frac{B}{\rho}\left(\frac{\partial \rho}{\partial \omega}\right)_{B,x} \qquad (2.28)$$

or

$$\frac{\rho K_{Tx}}{B} = \frac{\partial(\rho,B,x)}{\partial(\omega,B,x)} = \frac{F}{G}; \qquad (2.29)$$

where

$$E = \frac{\partial(u,\rho,x)}{\partial(\tau,\zeta,h)} = \left(1 + (1-2\zeta)\frac{Q}{\rho}\right)[\Omega_{\tau h} - \rho H_{\tau\tau}\omega_{hh}] + \zeta(1-\zeta)\Big[\rho^{-1}\Omega_{\zeta\tau h} - \left(H_{\zeta\zeta} - B_{\zeta\zeta}\frac{u}{\rho}\right)\Omega_{\tau h} - H_{\tau\tau}\Omega_{\zeta h} - 2H_{\zeta\tau}\Omega_1$$
$$+ [\rho(H_{\zeta\zeta}H_{\tau\tau} - H_{\zeta\tau}^2) - H_{\tau\tau}B_{\zeta\zeta}u]\omega_{hh}\Big], \qquad (2.30)$$

$$F = \frac{-\partial(B,\rho,x)}{\partial(\tau,\zeta,h)} = \left(1 + (1-2\zeta)\frac{Q}{\rho}\right)\omega_{hh} + \zeta(1-\zeta)[(\rho^{-1}B_{\zeta\zeta}u - H_{\zeta\zeta} - 2B_{\zeta}H_{\zeta\tau} - B_{\zeta}^2 H_{\tau\tau})\omega_{hh} + \rho^{-1}(B_{\zeta}^2\Omega_{\tau h} + \Omega_{\zeta h} - 2B_{\zeta}\Omega_1)], \qquad (2.31)$$

$$G = \frac{-\partial(B,\omega,x)}{\partial(\tau,\zeta,h)} = [\rho + (1-2\zeta)Q] + \zeta(1-\zeta)\{B_{\zeta\zeta}u - \rho[H_{\zeta\zeta} + 2B_{\zeta}H_{\zeta\tau} + B_{\zeta}^2 H_{\tau\tau}] + \omega_{\zeta\zeta} + 2B_{\zeta}\omega_{\zeta\tau} + B_{\zeta}^2\omega_{\tau\tau}$$
$$- 2\rho^{-1}(\omega_{\zeta} + B_{\zeta}\omega_{\tau})(\omega_{\zeta h} + B_{\zeta}\omega_{\tau h}) + \rho^{-2}(\omega_{\zeta} + B_{\zeta}\omega_{\tau})^2\omega_{hh}\} \qquad (2.32)$$

The quantities ρ, Q, and u which appear in these expressions are defined in (2.20) to (2.24), and, in addition the following determinants or cofactors appear:

$$\Omega_{\tau h} = \omega_{\tau\tau}\omega_{hh} - (\omega_{\tau h})^2, \qquad (2.33)$$

$$\Omega_{\zeta h} = \omega_{\zeta\zeta}\omega_{hh} - (\omega_{\zeta h})^2, \qquad (2.34)$$

$$\Omega_1 = \omega_{\tau h}\omega_{\zeta h} - \omega_{\tau\zeta}\omega_{hh}, \qquad (2.35)$$

$$\Omega_{\zeta\tau h} = \begin{vmatrix} \omega_{\zeta\zeta} & \omega_{\zeta\tau} & \omega_{\zeta h} \\ \omega_{\zeta\tau} & \omega_{\tau\tau} & \omega_{\tau h} \\ \omega_{\zeta h} & \omega_{\tau h} & \omega_{hh} \end{vmatrix}. \qquad (2.36)$$

Expressions for entropy and the chemical potentials in terms of ζ, τ, and h, in contrast to the expressions for ρ_3, ρ_4, and u, involve explicitly the constants C_3 and C_4. Thus using (2.5), (2.6), and (2.9) one finds

$$\nu_3 = B\mu_3 = h + H + \ln(1-\zeta) - \ln C_3, \qquad (2.37)$$

$$\nu_4 = B\mu_4 = h + H + \ln\zeta - \ln C_4. \qquad (2.38)$$

The entropy S per mole is easily obtained, noting that the Gibbs function for N_3 moles of He^3 and N_4 of He^4 is

$$G = N_3\mu_3 + N_4\mu_4, \qquad (2.39)$$

as

$$\rho S/R = \omega + Bu - \rho_3\nu_3 - \rho_4\nu_4 \qquad (2.40)$$

The problem of choosing appropriate zeros for the energy is discussed in Appendix B.

III. THERMODYNAMIC POTENTIAL

We shall assume that ω as a function of ζ, τ, h can be written as a sum of two terms

$$\omega = \omega_r(\zeta,\tau,h) + \omega_s(\zeta,\tau,h), \qquad (3.1)$$

where ω_r, the "regular" part of the potential, is a completely smooth (analytic) function of its arguments, and ω_s contains (in its derivatives) the singularities associated with discontinuities in density and composition at the coexistence surface as well as the various divergences at the critical line. We shall further assume that ω_s and all its first partial derivatives vanish along the critical line $\tau = 0$, $h = 0$, so that the critical values of ω, ρ_3, ρ_4, and u are determined entirely by ω_r.

Next we shall assume that ω_r can be expanded in a power series, in particular in the form

$$\omega_r(\zeta,\tau,h) = c(\zeta) + d(\zeta)\tau + f(\zeta)h, \qquad (3.2)$$

where

$$c(\zeta) = c_0 + c_1\zeta + c_2\zeta(1-\zeta) + c_3\zeta^2(1-\zeta), \qquad (3.3)$$

$$d(\zeta) = d_0 + d_1\zeta, \qquad (3.4)$$

$$f(\zeta) = f_0 + f_1\zeta + f_2\zeta(1-\zeta). \qquad (3.5)$$

Of course, additional terms are possible, and we have only listed those we actually employed in fitting experimental data. Similarly we assume that B_c and H can be expressed as smooth functions of their arguments;

$$B_c(\zeta) = a_0 + a_1\zeta, \qquad (3.6)$$

$$H = b_0 + b_1\zeta + b_2\zeta^2 + (g_0 + g_1\zeta)\tau \qquad (3.7)$$

where again additional terms are possible (but note that H is independent of h, and B_c of both h and τ).

It is not obvious *a priori* that (3.2) to (3.7) are reasonable assumptions, especially for ζ near 0 or 1, that is, in the limit of one or the other of the pure fluids. We note, however, that these equations yield a form for ω_r which is itself not unreasonable as the thermodynamic potential of a fluid mixture far from a critical point. In particular, it is in accord with Henry's law,[19] according to which the chemical potential for component j should have a leading singularity

$$\mu_j \simeq RT \ln x_j + \cdots \tag{3.8}$$

when the mole fraction x_j of this component goes to zero.

The principal considerations which influence our choice of a functional form for ω_s, the singular part of ω, are that it should reproduce the known critical properties of pure He^3 and He^4 and that it should depend smoothly on ζ.

We have chosen the form

$$\omega_s = q(\zeta)\pi(\bar{\tau}, h), \tag{3.9}$$

with

$$\bar{\tau} = l(\zeta)\tau, \tag{3.10}$$

where q and l are smooth functions of ζ;

$$q(\zeta) = 1 + q_1\zeta + q_2\zeta(1-\zeta), \tag{3.11}$$

$$l(\zeta) = 1 + l_1\zeta, \tag{3.12}$$

and π is similar to the singular part of the free energy of a ferromagnet near its critical point, with h the free energy and $l\tau$ the deviation of the temperature from its critical value.

For π we have used the Schofield[20,21] "linear model," a convenient, explicit parametric form believed to work moderately well[8,21,22] for pure He^3 and He^4. The equation is of the "scaling" or "homogeneous" form and possesses two adjustable constants once the critical indices have been fixed. Details are given in Appendix A.

There have recently been some suggestions[23] as to the form of "corrections" which may be expected to a scaling equation of state. We could, of course, include correction terms in π (in which case one would probably wish to replace the second argument by h times a function of ζ), but these hardly seemed worthwhile in a first attempt to fit properties on the critical lines of mixtures.

It is, however, worth emphasizing that there is nothing in our basic assumption, (3.1), which precludes the use of an ω_s which includes nonscaling (singular) terms, asymmetries, and the like. One would merely need to devise a functional form providing a smooth interpolation, as a function of ζ, between properties of the pure fluids.

One practical advantage of using the "fields" as independent variables is that the thermodynamic potential can be conveniently written as a sum of two terms, with the critial entropy and density determined by one and the divergences (and discontinuities) near the critical point determined by the other. This is not in general possible if the independent variables are "densities" or a mixture of "densities" and "fields" (in the notation of Ref. 11).

IV. VALUES OF CONSTANTS AND COMPARISON WITH EXPERIMENTAL DATA

A. Constants from Properties of the Pure Fluids

The expressions for ω_r, ω_s, B_c, and H in (3.2)–(3.7) contain a large number of adjustable constants. Fortunately, many of them can be determined from the known properties of He^3 and He^4 which are summarized in Table I. The constants $a_0, a_1, c_0, c_1, d_0, d_1, f_0$, and f_1, given in Table II, were determined directly from the

TABLE I. Properties of pure He^3 and He^4 at their respective critical points.

Property	Symbol[a]	Value and reference He^3	Value and reference He^4	Units
Critical pressure	p_c	860.5[b]	1705[c]	Torr
Critical temperature	T_c	3.3105[b]	5.1884[c,d]	K
Critical densities	ρ_c	0.013 82[b]	0.0173[c,d]	mole/cm^3
Critical entropy	S_c	22.5 ± 0.3[e]	22.56[f]	J/mole K
Slope of vapor-pressure curve	$\frac{dp_\sigma}{dT}$	882[b]	1289.2[f]	Torr/K

[a] Use a subscript 3 or 4 depending on the isotope: p_{c3}.

[b] Reference 7.

[c] Reference 9.

[d] Reference 15.

[e] See Sec. IV A of text.

[f] Reference 17.

quantities in Table I.

Adding a constant to H is equivalent to multiplying C_3 and C_4 by a common factor [see (2.5) and (2.9)], and thus the constant b_0 is arbitrary. We have set it equal to zero. Similarly, changing g_0 in (3.7) corresponds to changing the zero of energy [see (2.20)]. The choice of energy zeros is a somewhat subtle problem in our formulation, and is discussed in Appendix B. In any case, given the choices $b_0 = g_0 = 0$, C_3 and C_4 may be determined from the absolute critical entropies of pure He^3 and He^4, respectively, using (2.37), (2.38), and (2.40), and values are given in Table II. The critical entropy of He^3 in Table I is not too reliable, since it was computed by interpolating heat capacities between the highest temperatures reported by Abraham, Osborne, and Weinstock[24] and the lowest temperatures of Brown and Meyer.[8] There seem to be no experimental data in the range 2-3 K. The corresponding inaccuracy in C_3 does not at all affect the values of ρ_3 and ρ_4 as functions of p and T.

The Schofield function π (see Appendix A) contains two adjustable coefficients and depends on two critical indices. These four constants were determined from the known properties of pure He^3 near its critical point, and are also displayed in Table II. Acutally four critical indices ($\alpha, \beta, \gamma, \Delta = \beta\delta$) are given in Table II, but the scaling relationship implies that only two of these are independent. Our particular choice for ω_s in (3.9), which satisfies the properties of "smoothness"[25] or "universality",[26] implies that pure He^3 and He^4 have identical critical indices. The experiments have been interpreted in terms of different indices, in particular for α. We do not claim that our analysis removes the discrepancy, but only that within the rather limited precision which is our aim in this paper, the difference in indices for the two fluids (assuming that it is real) does not make much practical difference. Adopting this point of view, we are able to determine the constants q_1 and l_1 by comparing the properties of He^3 and He^4 near their respective critical points (see Appendix A).

B. Constants from the Properties of the Mixture

The remaining constants not determined by properties of the pure fluids, that is to say $c_2, c_3, f_2, b_1, b_2, g_1$, and q_2, were obtained by fitting the experimental p, ρ, T, x data of Wallace and Meyer,[6] in particular their dew-bubble curves and isotherms in the one-phase region for different values of x, to theoretical values calculated from the formulas of Secs. II and III.

We first assumed that the critical inverse temperature B_c is strictly linear in ζ [see (3.6)]. This assumption is not quite as restrictive as it may appear at first sight, for reasons given in Appendix B. Next we assumed that [see (2.24)]

$$H_\zeta + B_\zeta H_\tau = b_1 + g_1 \tau, \qquad (4.1)$$

that is to say, that this quantity is independent of ζ, a condition which in turn implies that

$$b_2 = -\tfrac{1}{2} g_1 B_\zeta . \qquad (4.2)$$

Dew-bubble curves and isotherms were computed for various choices of constants and plotted

TABLE II. Constants in the equation of state for He^3-He^4 mixtures.

Constant	Value	Constant	Value
a_0	4.844×10^{-6} mole/Torr cm^3 [a] $=0.036\,33$ mole/J	g_0	0
a_1	-1.753×10^{-6} mole/Torr cm^3 [a] $=-0.013\,15$ mole/J	g_1	2.93×10^5 Torr cm^3/mole $=39.1$ J/mole
b_0	0	$\ln C_3$	1.683
b_1	0.25	$\ln C_4$	2.931
b_2	0.2568	α	0.098
c_0	0.004 168 mole/cm^3 [b]	β	0.361
c_1	0.001 101 mole/cm^3 [b]	γ	1.18
c_2	0.0001 mole/cm^3	Δ	1.541
c_3	0.0003 mole/cm^3		
d_0	2059 Torr [c] $=0.2746$ J/cm^3	$\bar{a}$	1.325
d_1	2924 Torr [c] $=0.3899$ J/cm^3	$\bar{g}$	0.012 96 mole/cm^3
f_0	0.013 82 mole/cm^3 [d]	l_1	0.844
f_1	0.003 48 mole/cm^3 [d]	q_1	0.32
f_2	0.0005 mole/cm^3	q_2	-0.25

[a] $a_0 = 1/RT_{c3}$, $a_1 = 1/RT_{c4} - a_0$.

[b] $c_0 = p_{c3}/RT_{c3}$, $c_1 = p_{c4}/RT_{c4} - c_0$.

[c] $d_0 = T_{c3}(dp_{\sigma 3}/dT) - p_{c3}$, $d_1 = T_{c4}(dp_{\sigma 4}/dT) - p_{c4} - d_0$.

[d] $f_0 = \rho_{c3}$, $f_1 = \rho_{c4} - \rho_{c3}$.

on graphs. The constants were adjusted to improve as much as possible the agreement, determined visually, with the experimental values. Dew-bubble curves in the p, T plane and isotherms in the ρ, p plane for $T > T_c$ were employed to determine b_1, g_1, c_2, and c_3, while dew-bubble curves in the ρ, p plane helped fix f_2 and q_2. The search for optimum constants was not carried out in any systematic fashion. It seemed to us of greater interest to obtain a reasonable fit to the data, and then work out various implications of our approximate equation of state. One should note that c_2, c_3, f_2, and q_2 are in any case fairly small corrections to properties of the mixture obtained by a straightforward linear interpolation (in a suitable sense) between properties of the pure fluids.

C. Comparison with Experimental Data

The accuracy with which we are able to fit the experimental data of Wallace and Meyer on mixtures is indicated in Figs. 1(a), 1(b), and 2(a)-2(e). Dew-bubble curves at fixed x in the p, T plane are shown in Fig. 1 together with experimental points for $x = 0.2$, 0.4, 0.6, 0.8, 0.886, and 0.96. For each of the compositions previously mentioned, except $x = 0.96$, dew-bubble curves and some isotherms in the ρ, p plane are shown in Fig. 2 together with the experimental results.

Examination of Figs. 1 and 2 shows that the agreement between calculations and experiment is on the whole quite good, though there is certainly room for improvement. In Table III are listed the computed and experimental critical values of pressure, temperature, and density (p_c, T_c, and ρ_c, respectively) as a function of x. The agreement of the p_c and T_c values is quite good, though the computed values are systematically a bit high. On the other hand, our values of ρ_c are systematically lower than the experimental ones. Indeed, our values in each case lie closer to the Wallace and Meyer value for ρ_s (the "symmetry density" about which the dew-bubble curves are approximately symmetrical in the ρ, p plane) than to their value of ρ_c. This may well reflect simply the imprecision of our equation of state. On the other hand, Wallace and Meyer had to compute ρ_c from their data by a somewhat indirect technique due to difficulties in experimental measurements near

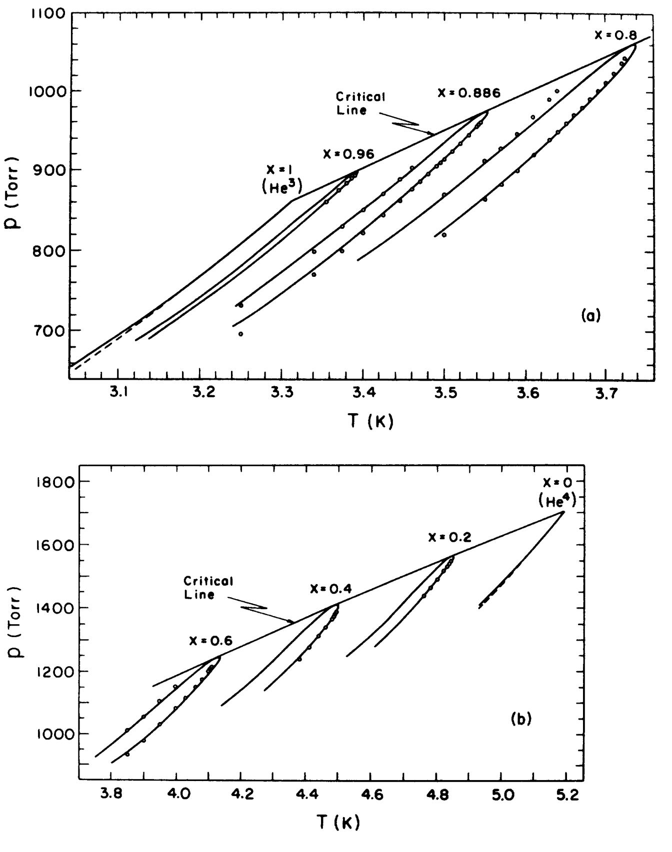

FIG. 1. Critical line and dew-bubble curves in the p, T plane for various values of x. The solid lines are computed values while the open circles are experimental results of Wallace and Meyer (Ref. 6). The computed vapor-pressure curves for pure He^3 and He^4 are also shown as solid lines, and the experimental results of Wallace and Meyer (Ref. 7) and Roach and Douglass (Ref. 9) as dashed lines.

the critical point, and it is possible these computations contain some systematic inaccuracy.

Computed values of heat capacity C_{vx} for $x=0.805$ and $\rho=\rho_c(x)$ are shown in Fig. 3 as a function of $T-T_c(x)$, together with experimental results of Brown and Meyer.[14,27] Also shown are the corresponding computations and experimental results[8] for $x=1$. The agreement is not too bad considering the fact that errors in the equation of state are likely to be more apparent in derivative functions (such as C_{vx} or K_{Tx}) than in $\rho(p,T,x)$.

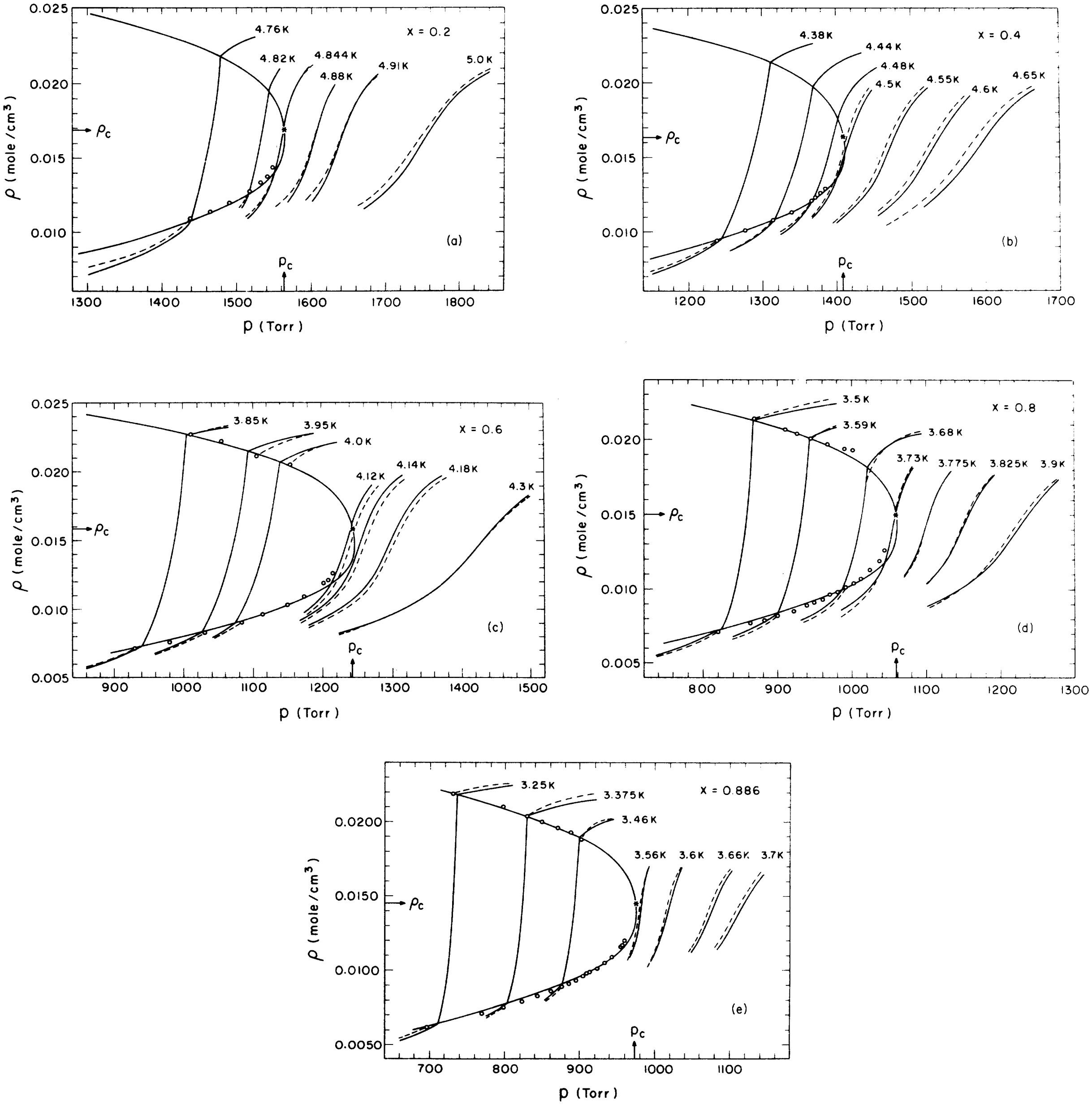

FIG. 2. Dew-bubble curves and isotherms in the ρ, p plane for various x. Computed values are indicated by solid lines, and ρ_c and p_c denote computed critical values. The circles and dashed lines denote respectively the experimental dew-bubble curve and various isotherms (Wallace and Meyer, Ref. 6). The portions of the isotherms in the two-phase region (to the left of the dew-bubble curve) have been computed assuming that the average composition of the mixture in a container holding the two phases has the appropriate value. Note that these are curved lines, in contrast to a pure fluid where they are straight lines at constant pressure.

V. PROPERTIES VERY NEAR THE CRITICAL LINE

A. Divergences: Asymptotic and Observed

As mentioned above in the introduction, our thermodynamic equations predict that K_{Tx} diverges weakly while C_{vx} remains finite upon approaching the critical line in the mixture ($0<\xi<1$), but that this asymptotic behavior occurs too close to the critical line for convenient observation. The behavior of C_{vx} is closely analogous to that of C_v near the λ transition[28] in pure He^4 and other cases[29] of what Fisher[30] has called "exponent renormalization." Fisher and Scesney[31] have shown that in some cases these "renormalization effects" will, in practice, be very hard to observe. This also turns out to be the case in He^3-He^4 mixtures, which we shall now discuss with the aid of Eqs. (2.26)–(2.32).

Note that all divergences at the critical line arise from second partial derivatives of ω and these in turn come from corresponding derivatives of π [see (3.9)]. The quantities $\partial^2\pi/\partial h^2$ and $\partial^2\pi/\partial\overline{\tau}^2$ correspond to the susceptibility and heat capacity in a constant magnetic field in the analogous Ising ferromagnet and possess strong and weak divergences (e.g., as $\overline{\tau}^{-\gamma}$ and $\overline{\tau}^{-\alpha}$ for $h=0$; see Table II for values of α and γ) at the critical point, whereas $\partial^2\pi/\partial\overline{\tau}\partial h^2$ has a (strong) × (weak) divergence. It follows that of the quantities appearing in (2.30)–(2.32), $\Omega_{\xi Th}$, Ω_{Th}, and $(\omega_{Th})^2$ have a (strong) × (weak) divergence; ω_{hh}, $\Omega_{\xi h}$, and Ω_1 have a strong divergence; ω_{TT} has a weak divergence; and all other quantities (including Q, u, and ρ) remain finite at the critical line.[32]

Thus we can summarize the principal divergences and the most important ξ dependence of E, F, and G in Eqs. (2.30)–(2.32) in the form

$$E=(\text{strong})\times(\text{weak})+\xi(1-\xi)(\text{strong})\times(\text{weak})+\cdots\,, \tag{5.1}$$

$$F=(\text{strong})+\xi(1-\xi)(\text{strong})\times(\text{weak})+\cdots\,, \tag{5.2}$$

$$G=(\text{const})+\xi(1-\xi)(\text{strong})+\cdots\,. \tag{5.3}$$

TABLE III. Experimental and computed critical constants in He^3-He^4 mixtures. The experimental values are those of Wallace and Meyer (Ref. 6). The concentration x is the mole fraction of He^3.

	T_c in K		p_c in Torr		ρ_c in mole/cm^3	
x	Expt	Comput	Expt	Comput	Expt	Comput
0.96	3.393	3.394	898.5	900	0.014 53	0.014 09
0.886	3.545	3.550	968	974	0.015 21	0.014 55
0.8	3.717	3.729	1049.5	1058	0.015 71	0.015 01
0.6	4.100	4.123	1229	1242	0.016 74	0.015 84
0.4	4.487	4.491	1406	1409	0.017 35	0.016 45
0.2	4.837	4.843	1558.5	1562	0.017 66	0.016 92

The use of (3.6) and (3.7) for B_c and H, without the presence of higher-order terms, means that $B_{\xi\xi}$ and H_{TT} vanish identically. While this leads to some slight simplification of (2.30)–(2.32), one should note that it does not alter the pattern of divergences indicated in (5.1)–(5.3).

It is then evident that in the pure fluids, $\xi=0$ or 1, $C_{vx}\propto E/F$ and $K_{Tx}\propto F/G$ have a weak and a strong divergence, respectively, while in the mixtures, $0<\xi<1$, C_{vx} approaches a constant while K_{Tx} possesses a weak divergence asymptotically close to the critical line, in accord with phenomenological predictions.[11]

However, the coefficient of the (strong) × (weak) term in (5.2) is numerically small compared to that of the strong term, even at $\xi=\frac{1}{2}$. Eventually, sufficiently close to the critical point, the more divergent term must win out. But since its ratio to the other term is only a weak divergence, its relative magnitude increases rather slowly, and "sufficiently close" turns out to be very close indeed. Thus within the easily accessible experimental range F appears to have only a strong divergence. Note that this single fact explains simultaneously the "anomalous" experimental behavior of both K_{Tx} (which appears to rise to a finite maximum) and C_{vx} (which appears to diverge).

A somewhat similar phenomenon occurs in the case of G, see (5.3). Usually in the mixtures G is dominated by the strongly divergent term near the critical line, including the region easily accessible to experiment. However when ξ is sufficiently small, or close to 1, which is to say the composition is very close to that of one or the other of the pure fluids, the divergence of G

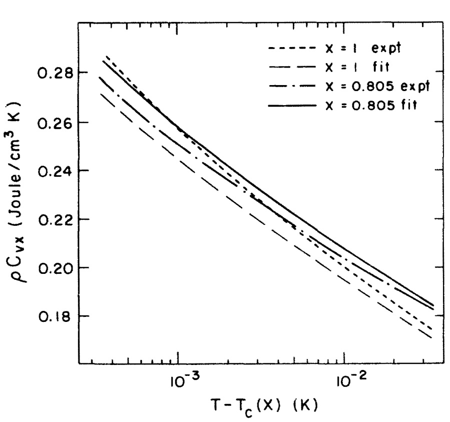

FIG. 3. Experimental and computed heat capacities C_{vx} at $x=1$ (pure He^3) and $x=0.805$.

is harder to observe and K_{Tx} appears to diverge strongly, as in a pure fluid.

B. Crossover Condition

By equating the dominant strong and (strong) ×(weak) terms in (2.31), it is possible to make a rough estimate of the point at which F "crosses over" from one sort of behavior to the other. This leads to the condition

$$\frac{\Omega_{Th}}{\omega_{hh}}=\frac{\rho[1+(1-2\zeta)Q/\rho]}{\zeta(1-\zeta)B_{\zeta}{}^{2}}. \tag{5.4}$$

In writing (5.4) we have ignored a certain number of strongly divergent terms which occur inside the square bracket in (2.31), but which (for our choice of constants) amount to only a few percent of the initial strongly divergent term.

In using (5.4) the right-hand side may be evaluated on the critical line itself and is there a smooth function of ζ except near $\zeta=0$ and 1, where it diverges because of the explicit ζ dependence in the denominator. The left-hand side is equal to

$$q(\zeta)[l(\zeta)]^{2}\left\{\frac{\partial^{2}\pi}{\partial\bar{\tau}^{2}}-\left(\frac{\partial^{2}\pi}{\partial\bar{\tau}\partial h}\right)^{2}\Big/\frac{\partial^{2}\pi}{\partial h^{2}}\right\}, \tag{5.5}$$

where the quantity in curly brackets is, apart from a slowly varying factor, the heat capacity at constant magnetization in the analogous Ising ferromagnet, and in the Schofield linear equation of state (Appendix B) depends only on r, not on θ.

In the h, τ, ζ space (5.4) defines a "tube" of roughly elliptical cross section surrounding the critical line $\tau=h=0$, with dimensions which approach zero as ζ approaches 0 or 1. At the position where the tube is largest, near $\zeta=0.5$ ($x\simeq0.65$), the maximum value of $|\tau|$ on the tube corresponds to a temperature deviation, at fixed ζ, of about 2×10^{-12} K from its critical value; the maximum value of $|h|$ is 5×10^{-20} (note that h is dimensionless), and the maximum deviation of density from its critical value is 5×10^{-7} cm^3/mole, if one adopts the constants of Table II. For other values of ζ these values will be even smaller. None of these numbers is to be taken too seriously, since each depends on extrapolating the scaling equation of state, Appendix B, into a region very close to the critical point where it has never been verified in the pure fluids, much less in the mixture, and this extrapolation makes use of the exponents in Table II and depends rather sensitively on the choice of α. Thus, for example, by assuming a value for α of 0.15 the crossover $T-T_c$ (with $h=0$) increases to 3×10^{-9} K at $\zeta=0.5$.

The above numbers refer, of course, to deviations from the critical point at constant ζ. One can also consider the crossover curve, along which (5.4) is satisfied, in the ρ, T plane at constant x. We have investigated this situation numerically for $\zeta=0.5$ ($x\simeq0.65$) and find the following result. Very near the critical point the dew-bubble curve (which separates the one-phase from the two-phase region) is practically a straight line with a finite slope $dT/d\rho$ (in contract to the coexistence curve in a pure fluid which has $dT/d\rho=0$ at the critical point). The crossover curve is practically parallel to the dew-bubble curve but lies at a slightly higher temperature, which never exceeds 4×10^{-12} K, at any given value of the density. This temperature deviation gradually goes to zero as the density moves away from the critical density, and the crossover curve meets the dew-bubble curve at density deviations of $+5\times10^{-7}$ and -5×10^{-7} cm^3/mole from the critical density. The temperatures at which the crossover and dew-bubble curves meet are (due to the finite $dT/d\rho$) at temperature deviations of -5×10^{-6} and $+5\times10^{-6}$ K from the critical value of temperature. The situation is indicated schematically in Fig. 4. The region between the crossover and dew-bubble curves where one might expect the "true" asymptotic behavior to become apparent is, thus, a long, thin, needle-shaped region lying along the dew-bubble curve. For ζ differing from 0.5 one would expect this region to grow even smaller. Again, the precise magnitudes of these numbers are not to be taken too seriously.

One should, of course, note that the apparent divergences of C_{vx} and K_{Tx} do not change abruptly at the position given by (5.4). The change is a gradual one and if experiments would be carried out sufficiently close to the critical line one might expect a gradual acceleration of the rate of in-

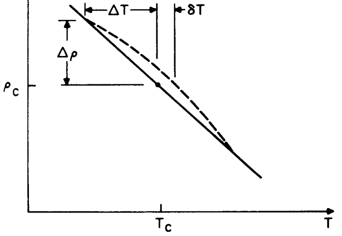

FIG. 4. Schematic drawing, not to scale, showing the dew-bubble curve (solid line) and crossover curve (dashed line) near the critical point (solid circle) in the ρ, T plane for fixed x. At $x=0.65$ the computed values (see text) are $\Delta T\simeq5\times10^{-6}$ K, $\delta T\simeq4\times10^{-12}$ K, $\Delta\rho\simeq5\times10^{-7}$ mole/cm^3.

crease of K_{Tx} and a corresponding deceleration of the rate of increase of C_{vx} while approaching the critical point and passing through the region where (5.4) is satisfied. The detailed behavior can be calculated if our equation of state is assumed valid.

C. Crossover and Heat Capacity Maximum

An alternative and in some ways preferable point of view towards (5.4) comes about upon noting that the right-hand side is, for a given ζ, closely related to the value of C_{vx} on the critical line, C_{vxc}, which can be obtained from (2.27) by retaining only the most divergent terms in E and F. The result is

$$\frac{C_{vxc}}{R}=\frac{B^2}{\rho\zeta(1-\zeta)B_\zeta^2}\left[\rho+(1-2\zeta)Q+\zeta(1-\zeta)\omega_{\zeta\zeta}\right], \tag{5.6}$$

where the right-hand side is to be evaluated on the critical line $h=\tau=0$. Apart from a factor of B^2/ρ, it differs from the right-hand side of (5.4) only in the presence of the $\omega_{\zeta\zeta}$ term which, however, is only a few percent of the other terms in the square brackets and can be neglected for our purposes.

The left-hand side of (5.4) is proportional to

$$\frac{\hat{C}_{v\zeta}}{R}=-\frac{B^2}{\rho}\left(\frac{\partial u}{\partial B}\right)_{\rho,\zeta}=B^2\left(\frac{\Omega_{\tau h}}{\rho\omega_{hh}}-H_{\tau\tau}\right), \tag{5.7}$$

since for our choice of constants $H_{\tau\tau}=0$. Now $\hat{C}_{v\zeta}$, while it is not a real heat capacity, reduces to C_v at $\zeta=0$ and 1, and has a weak divergence near the critical line for all values of ζ. One can regard it as in some sense a smooth interpolation between the pure fluids, the heat capacity of a hypothetical pure fluid with properties intermediate between those of pure He^3 and He^4.

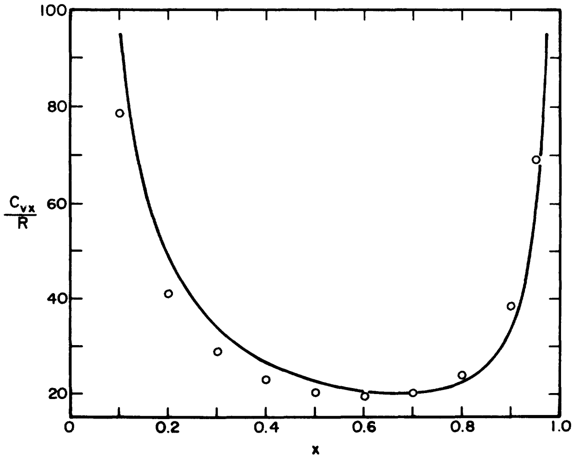

FIG. 5. Value of C_{vx}/R along the critical line as a function of x. The solid curve has been computed from Eq. (5.6) and the circles from the approximate Eq. (5.11).

Using (5.6) and (5.7), one finds that (5.4) amounts to:

$$\hat{C}_{v\zeta}/R=C_{vxc}/R. \tag{5.8}$$

The right-hand side of (5.6), and thus of (5.8), is easily calculated. It depends only on ω_r and is thus independent of all assumptions about ω_s, including the value of α. The result is plotted in Fig. 5 as a function of x. The minimum value of about 20 occurs near $x=0.65$. This leads to a simple interpretation of the crossover condition: to observe the "asymptotic" behavior in the fluid mixture even with an optimum choice of x one needs a proximity to the critical point which in either of the pure fluids would correspond to C_v/R of about 20 or more. The largest values[8,10] of C_v which have been observed in pure He^3 and He^4 are about $5R$ and $7R$, respectively. These maximum values have presumably been observed in the two-phase region, so that the maximum values in the one-phase region are somewhat smaller. In the range which has been observed, C_v increases by $1R$ or $2R$ for every tenfold decrease in $T-T_c$. Thus one should not be surprised that measurements in the mixtures have always been well outside the asymptotic region.

In place of (5.6), one can compute C_{vxc} from the formula[33]

$$C_{vxc}=T\left(\frac{dS}{dT}-\frac{dp}{dT}\frac{dv}{dT}+\sum_{j=3}^{4}\frac{dx_j}{dt}\frac{d\mu_j}{dT}\right), \tag{5.9}$$

where C_{vxc}, S, and $v=\rho^{-1}$ refer to one mole of material, $1-x_4=x_3=x$, and the derivatives on the right-hand side of (5.9) are along the critical line itself.

As a rough approximation let us assume "ideal mixture"[34] behavior along the critical line

$$\mu_j=RT\ln x_j, \qquad S=-R\sum_j x_j\ln x_j. \tag{5.10}$$

Upon inserting (5.10) in (5.9) and discarding all terms which do not diverge in one or the other of the pure fluids, one has

$$C_{vxc}=\frac{RT^2(dx/dT)^2}{x(1-x)}. \tag{5.11}$$

If, in addition, dT/dx is approximated by the difference in critical temperatures, one obtains the result shown for selected values of x by the circles in Fig. 5. Although (5.11) is only a rough approximation, it gives a curve of the same general form as (5.6) and, perhaps by accident, approximately the same minimum value for C_{vxc}.

These considerations indicate that the experimental "invisibility" of the asymptotic region in the mixtures is not simply an artifact of our choice of constants or the precise functional form of ω_s. It is perhaps fruitless to argue about the properties of the "true" asymptotic region in helium mixtures. However, it seems safe to assert that our formulation provides a thermodynamically consistent description which agrees reasonably well with experimental measurements in the region where these have been carried out and serves to reconcile them with earlier phenomenological predictions.

All of the above calculations refer to a "crossover" in the thermodynamic region where one phase is present. We have not attempted to calculate the asymptotic behavior of bulk properties in a container in which two phases are present, though it seems likely that (5.8) will again give the order of magnitude of the crossover to asymptotic behavior. In the pure fluids the heat capacity in the two-phase region is larger than the one-phase region, but not sufficiently large [see remarks following (5.8)] as to make the asymptotic behavior easily accessible. In addition the long relaxation time found by Brown and Meyer[14] makes experiments in the two-phase region rather difficult.

VI. SUMMARY

We have shown that a relatively simple equation of state is able to account qualitatively and, with limited precision, quantitatively for the experimental data on He^3-He^4 mixtures near the liquid-vapor critical line. The critical properties of the mixture are largely determined by an interpolation, in a suitable set of variables, between the critical properties of the respective pure fluids.

Our equation of state differs from other formulations of the problem of mixtures (at least those of which we are aware) in two important respects: the behavior near the critical point involves nonclassical critical exponents, and the independent variables are "fields" (temperature and chemical potentials), while the composition is a dependent variable. One disadvantage of our formulation is that the independent variables are not so simply related to experimentally observable quantities as in other formulations. Hence numerical computations are required to generate properties of the system at constant composition. In discussion of phase equilibria and critical points, on the other hand, the van der Waals equation must also be supplemented by numerical computation.[1]

By examining asymptotic properties of our equation of state near the mixture critical line we have been able to reconcile phenomenological predictions on the behavior of K_{Tx} and C_{vx} with experimental observation. The problem is essentially the "invisibility" of the asymptotic region to experimental observation.

It is probable that from a thermodynamic point of view the He^3-He^4 system is comparatively simple. But there is no reason to suppose our formulation cannot be extended to other mixtures which have a continuous line of critical points extending between the liquid-vapor critical points of the pure components. Still other cases[35] can in principle be discussed in a similar fashion, but the (relatively) complicated geometry of the coexistence surface may make our formulation impractical.

ACKNOWLEDGMENTS

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APPENDIX A: SCHOFIELD LINEAR MODEL

We have assumed that $\pi(\bar{\tau}, h)$ has the form given by Schofield's linear model,[20,21] with $\bar{\tau}$ and h corresponding to T and H in Schofield's notation. Thus we write

$$\pi = r^{2-\alpha}\bar{p}(\theta)\,, \tag{A1}$$

$$h = \bar{a} r^{\Delta}\theta(1-\theta^2)\,, \tag{A2}$$

$$\bar{\tau} = r(1-\bar{b}^2\theta^2)/RT_{c3}\,, \tag{A3}$$

$$\frac{\partial \pi}{\partial h} = \bar{g} r^{\beta}\theta\,, \tag{A4}$$

and, following Ref. 21, choose $\bar{b}^2$ equal to

$$\bar{b}^2 = (\delta-3)/(\delta-1)(1-2\beta)\,. \tag{A5}$$

Various symbols appear in the above equations with a bar (e.g., $\bar{b}$) to avoid confusion with other constants in this paper. Note that in (A3) an extra factor of $(RT_{c3})^{-1}$ appears, with T_{c3}, the critical temperature of pure He^3. It is included here because $\overline{\tau}$ has (in our formulation) the dimensions of $(RK)^{-1}$, and it is convenient in the Schofield formulation to have r dimensionless.

The critical indices are assumed to satisfy the usual scaling relationships[3];

$$\Delta = \beta\delta = \gamma + \beta = 2 - \alpha - \beta \tag{A6}$$

The various partial derivatives of π are given by[36]

$$\frac{\partial \pi}{\partial \overline{\tau}} = r^{1-\alpha}\overline{s}(\theta) R T_{c3}, \tag{A7}$$

$$\frac{\partial^2 \pi}{\partial h^2} = \left(\frac{\overline{g}}{\overline{a}}\right)\frac{r^{-\gamma}}{\overline{d}(\theta)}, \tag{A8}$$

$$\frac{\partial^2 \pi}{\partial \overline{\tau}^2} = \overline{a}\,\overline{g}(RT_{c3})^2 r^{-\alpha}\frac{\overline{n}(\theta)}{\overline{d}(\theta)}, \tag{A9}$$

$$\frac{\partial^2 \pi}{\partial h \partial \overline{\tau}} = -\overline{g}(RT_{c3}) r^{\beta-1}\frac{(\Delta-\beta)\theta}{\overline{d}(\theta)}, \tag{A10}$$

where

$$\overline{p}(\theta) = \frac{\overline{a}\,\overline{g}}{\alpha}\left(\frac{(\Delta-\beta)^2(1-2\beta)(\Delta-1-\beta)}{2(1-\alpha)(2-\alpha)(\Delta-3\beta)} + \frac{(2\Delta+\beta-\Delta^2-\beta^2-1)}{1-\alpha}\theta^2 + (\Delta-\tfrac{3}{2})\theta^4\right), \tag{A11}$$

$$\overline{s}(\theta) = \frac{\overline{a}\,\overline{g}}{2\alpha}(\Delta-\beta)(1-2\beta)\left(\frac{(\Delta-1-\beta)(\Delta-\beta)}{(1-\alpha)(\Delta-3\beta)} - \theta^2\right), \tag{A12}$$

$$\overline{d}(\theta) = 1 + \left(\frac{2\Delta-3}{1-2\beta}\right)\theta^2, \tag{A13}$$

$$\overline{n}(\theta) = \frac{(\Delta-\beta)^2(1-2\beta)}{2\alpha(\Delta-3\beta)}[\Delta-1-\beta+(3-3\beta-\Delta)\theta^2]. \tag{A14}$$

The critical indices β and γ [from which the others follow by (A6)] and the constants $\overline{a}$ and $\overline{g}$ were determined using the results of Wallace and Meyer[7] for the discontinuity in density along the coexistence curve and the divergence of the isothermal compressibility along the critical isochore in pure He^3. Note that in this case $\zeta = 0$ and the functions q and l which appear in (3.11) and (3.12) are equal to 1. When $\zeta = 1$ (pure He^4) these functions are $1 + q_1$ and $1 + l_1$, respectively, and their values were determined by comparing the density discontinuity and C_v in He^4 with the corresponding quantities in He^3 at comparable deviations of temperature from its critical value. Results are given in Table II. The results are in reasonable agreement with those of Huang and Ho[22] when one takes account of the difference between their choice and our choice of critical indices.

APPENDIX B: CHOICE OF ZEROS OF ENERGY

If one adds a constant ϵ to the total energy per mole of the mixture, this is equivalent to adding ϵ to μ_3 and μ_4, or $B\epsilon$ to ν_3 and ν_4, and hence to adding a term $B\epsilon$ to H [see (2.37) and (2.38)] or a term $-\epsilon$ to H_T and thus $\rho\epsilon$ to u [see (2.20), and note that u is an energy *per unit volume*]. Obviously there is no change in measurable physical properties induced by this transformation, and only a minor change in the formal relationships of Secs. II and III. In particular, ζ remains unaffected by the transformation, and the functions $\omega(\zeta, \tau, h)$ and $B_c(\zeta)$ remain unaltered. Only $H(\zeta, \tau)$ is changed, and this by the addition of a term which depends very simply on τ and is independent of ζ.

The situation is quite different if one alters the energy zeros of He^3 and He^4 by different amounts by adding ϵ_3 to μ_3 and ϵ_4 to μ_4, with $\epsilon_3 \neq \epsilon_4$. Again there is no effect on measured physical properties and the fundamental differential relationship (2.4) remains correct with ω unchanged and the addition of $B\epsilon_3$ to ν_3, $B\epsilon_4$ to ν_4, and $\rho_3\epsilon_3 + \rho_4\epsilon_4$ to u. However, when these changes are carried through in (2.5) and (2.6) we find that ζ is altered to a quantity $\overline{\zeta}$ which is a nonlinear function of ζ. This in turn induces fairly complex changes in the functions $B_c(\zeta)$ and $H(\zeta, \tau)$ if they are now expressed in terms of $\overline{\zeta}$ and $\overline{\tau}$, the latter defined by (2.8) using the new function $\overline{B}_c(\overline{\zeta})$. In particular since $\overline{\zeta} = 0$ and 1 in pure He^3 and He^4, the same as ζ, and B_c is unaltered in the pure fluids, $\overline{B}_c(\overline{\zeta})$ is no longer a linear function if $B_c(\zeta)$ is a linear function (and *vice versa*).

There seems to be no *a priori* reason to choose one zero of energy for He^3 relative to He^4 rather than another, although one or another energy zero might be preferred on grounds of elegance or convenience, etc. The appearance of, if not the ultimate physics contained in, the functions ω, B_c, and H depends strongly on the difference of energy zeros of the two pure fluids (the absolute energy, with difference held constant, enters the formalism in a rather trivial way, as previously indicated). What we have in fact done is to leave this energy difference as a free parameter. However, we have chosen $B_c(\zeta)$ as a linear function [see (3.6)]. There is no reason to expect that any choice of energy difference will yield the real B_c a strictly linear function of ζ. However, our approximation consists in retaining only the first few powers of ζ in our expansion and it is not unreasonable to suppose that an appropriate choice of energy difference might make the

$\xi(1-\xi)$ contribution to B_c vanish, leaving only the linear and higher-order terms. Assuming this to be the case, one can justify the omission of the quadratic term in (3.6) on the grounds that we are merely making a useful choice for the energy difference.

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