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⁵A small change in the film thickness with superfluid velocity was predicted by V. M. Kontorovich, Zh. Eksperim. i Teor. Fiz. 30, 805 (1956) [Soviet Phys. JETP 3, 770 (1956)]. See J. Tilley, Proc. Phys. Soc. (London) 84, 77 (1964) for a full discussion. For information on the location of the dissipative region in film flow using potential probes, see L. J. Campbell, E. F. Hammel, D. M. Jones, and W. E. Keller, in Proceedings of the Eleventh International Conference on Low Temperature Physics, St. Andrews, Scotland, 1968, edited by J. F. Allen, D. M. Finlayson, and D. M. McCall (St. Andrews University, St. Andrews, Scotland, 1969), Vol. 1, p. 182.

⁶R. C. Clark, Phys. Fluids 12, 396 (1969).

⁷We here assume that the frequency observed at the beginning of the oscillations defines the film thickness during the initial dissipative level-equilibration process and that the frequency observed after about $\frac{1}{2}$ hour of oscillations (when the amplitude of the oscillations

has been reduced by a factor of about 300 and the damping is negligible) defines the thickness of a "static" film. Although K. A. Pickar and K. R. Atkins, Phys. Rev. 178, 389 (1969), have also measured the film thickness along a constricted portion of the flow path, they observed no decrease in film thickness for dissipative flow. Our potential probe measurements indicate, however, that the dissipative region in the film is not always where it is predicted to be. Alternatively, the infrared chopper used by Pickar and Atkins may have interfered with the flow of the film along their mirror surface. We recognize, obviously, that some unsuspected perturbation or systematic error may be responsible for the present results. We have, however, observed these effects under many different conditions in 60 different runs at temperatures from 0.95-1.7 K.

⁸J. F. Robinson, Phys. Rev. 82, 440 (1951), and Ref. 2.

⁹R. P. Henkel, G. Kukich, and J. D. Reppy, in Proceedings of the Eleventh International Conference on Low Temperature Physics, St. Andrews, Scotland, 1968, edited by J. F. Allen, D. M. Finlayson, and D. M. McCall (St. Andrews University, St. Andrews, Scotland, 1969), Vol. 1, p. 178.

THERMODYNAMICS NEAR THE TWO-FLUID CRITICAL MIXING POINT IN He³-He⁴†

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The two-fluid critical mixing point in He³-He⁴ differs from ordinary critical points in that it occurs at the intersection of three lines of critical points, in a suitable variable space. A free-energy function is proposed which removes certain discrepancies between classical (Landau) theory and experimental thermodynamic measurements. Certain solid-state transitions (e.g., the metamagnetic-antiferromagnetic transition in FeCl₂) are thermodynamic analogs of critical mixing in He³-He⁴.

In He³-He⁴ mixtures¹ under saturated vapor pressure, the λ transition temperature decreases with increasing mole fraction x of He³, and below a temperature $T^* = 0.87$ K corresponding to $x^* = 0.67$ a first-order phase separation takes place. The angular top of the two-fluid coexistence curve is the terminus of the line of λ transitions (Fig. 1) according to recent experiments,² in (approximate) agreement with a phenomenological argument given by Landau³ which we shall call the "classical theory" CT. In ordinary critical phenomena CT is a valuable first guide (though its detailed predictions are often in error), and in the present instance it predicts a peculiarity which suggests that the two-fluid critical mixing in helium has features quite unlike those found at "ordinary" critical points (ferromagnets, liquid-vapor critical points, λ transition in pure He⁴, etc.).

The peculiarity is seen most easily if one uses intensive thermodynamic variables, replacing x with its thermodynamic conjugate $\Delta = \mu_3 - \mu_4$, the

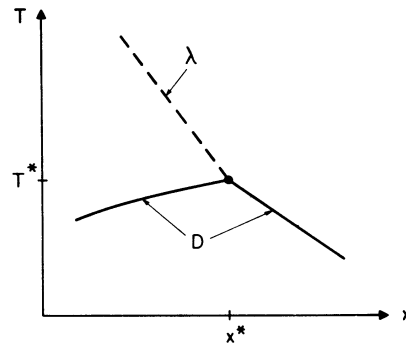


FIG. 1. Phase diagram (schematic) for He³-He⁴ mixtures near the critical mixing point. The two-fluid coexistence curve is labeled D and the dashed curve is the line of lambda transitions.

difference in chemical potentials of the isotopes, and introducing the experimentally inaccessible "field" η conjugate to the superfluid order parameter ψ .⁴ (In an antiferromagnet, η would be a magnetic field pointing in opposite directions on the two sublattices.) Here and in the subsequent analysis we shall tacitly assume the pressure p to be constant; i.e., ignore changes in vapor pressure. The phase diagram is shown in Fig. 2. The surface A in the $\eta = 0$ plane, which extends to $\Delta = -\infty$ (pure He⁴), is a first-order or coexistence surface in the sense that on A , ψ is nonzero and has opposite sign depending on whether $\eta \rightarrow 0$ through positive or negative values. This surface terminates in a line of critical points, the λ line, as temperature increases, and for $T < T^*$ terminates in the two-fluid coexistence curve D (a single line in the $T\Delta$ plane, unlike the Tx plane). The interesting and peculiar feature (according to CT) is that A is connected along the line D to two first-order (coexistence) surfaces B and B' , extending symmetrically into the regions $\eta > 0$ and $\eta < 0$, respectively, which themselves terminate with increasing temperature in lines of critical points shown as dashed lines in Fig. 2. These two critical lines join the lambda line at the same point as D . This type of behavior, where three critical lines come together at a point, is rather exceptional in nature (we shall mention some other examples below) and we therefore propose a special name: tricritical point.

There is no reason to expect our present understanding of phenomena at "ordinary" critical points (and which is rather easily extended⁵ to lines of critical points, such as λ lines) to be applicable at tricritical points. Thus, for example, whereas lattice models (presumably) showing such behavior exist,⁶ the series analyses needed for accurate estimates of critical behavior do not. Analysis of such models should prove fruit-

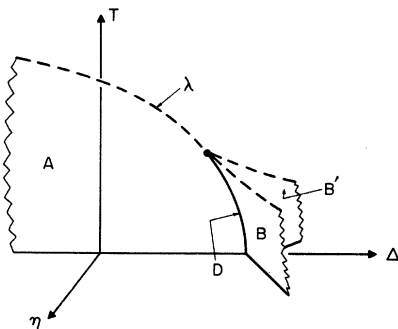


FIG. 2. Phase diagram (schematic) for He³-He⁴ mixtures in $T\Delta\eta$ space. Note that only the $T\Delta$ plane with $\eta = 0$ is experimentally accessible.

ful, because CT disagrees with experimental data near the tricritical point in several respects:

(i) CT predicts that the λ line and the right-hand curve D in Fig. 1 should have the same slope at the critical point, while measurements² indicate a definite change in slope.

(ii) As a function of T , the heat capacity $C_{\rho x}$ for $x = x^*$ should exhibit a discontinuity at the tricritical point. Experiments,⁷ though not yet definitive, suggest that any discontinuity is very small.

(iii) The quantity $(\partial x / \partial \Delta)_{pT}$, which in ordinary binary critical mixtures is the analog of compressibility in a pure fluid, should, according to CT, exhibit no anomalous behavior in the He³-rich (normal) phase upon approaching the tricritical point. Vapor-pressure measurements⁸ (from which μ_3 and μ_4 may be computed¹) definitely suggest a divergence.

(A fourth discrepancy, that CT predicts a discontinuity in $C_{\rho x}$ all along the λ line, in contrast to the finite cusp experimentally observed,^{7,9} is adequately explained in "ordinary" critical-point theory as an example of "renormalization."^{5,10})

The following tentative proposal of a form for the thermodynamic potential at $\eta = 0$ suggests that the aforementioned discrepancies are probably related to each other. For simplicity, assume that in the $T\Delta$ plane the λ line and two-fluid coexistence curve D may be approximated by a single straight line

$$\Delta_1(T) = \Delta^* - A(T - T^*) \quad (1)$$

and that the free energy $f(T, \Delta)$ chosen so that $x = -\partial f / \partial \Delta$ and that the entropy per mole $s = -\partial f / \partial T$ has the form

$$f(T, \Delta) = f_0(T, \Delta) + f_o(T, \Delta), \quad (2)$$

where f_0 is a completely smooth function of its arguments, and all the singular behavior comes from f_o . Further assume that f_o is identically zero along $\Delta_1(T)$, and its first partial derivatives vanish along the λ line (but not on D). In terms of the new variables

$$\tau = T - T^*, \quad \varphi(\Delta, T) = \Delta - \Delta_1(T), \quad (3)$$

let f_o have the "scaling" form

$$f_o / \varphi^{\mu+1} = h(\tau / \varphi^\mu) \quad (4)$$

for $\varphi > 0$, where $h(x)$ is appropriately defined on $-\infty < x < \infty$. For $\varphi < 0$, let f_o have an analogous form, with φ replaced by $|\varphi|$, and (in general) a different choice for the function $h(x)$ and the in-

dex μ . The index μ should lie between 0 and 1 ($\frac{1}{2}$ might be a first guess). With a suitable choice for h , (4) yields a coexistence curve in the xT plane with the behavior shown in Fig. 1, and the right-hand branch of D need not have the same slope as the λ line. It is easily shown that for $x = x^*$, (4) predicts $(\partial x/\partial \Delta)_{T_p}$ diverging as $\tau^{-\epsilon}$ for $\tau > 0$ (i.e., in the He³-rich phase), with $\epsilon = \mu^{-1} - 1$. The analysis of C_{px} at $x = x^*$ is less trivial, but when carried through shows that C_{px} is continuous, although "anomalies" (depending on the value of μ) may occur in its first- or higher-order derivatives. Thus we see that the relatively simple form (4) at once disposes of all three discrepancies between experiment and CT (and also allows, with suitable choice of h , for the observed "cusplike" behavior of C_{px} along the λ line). Nonetheless, the above proposal should be considered very tentative; for example, curvature in the λ and D curves, not allowed for in (1), will lead to additional terms, though the qualitative behavior of C_{px} and $(\partial x/\partial \Delta)_{T_p}$ should be the same provided both the λ and D curves have identical curvature at the tricritical point.

Measurements of the divergence of $(\partial x/\partial \Delta)$ in both normal and superfluid phases near the tricritical point would be a valuable supplement to heat-capacity measurements (more measurements of C_{px} for $x > x^*$ are also needed) in elucidating the thermodynamic behavior. Measurements of superfluid properties might also reveal interesting effects.

Tricritical points also occur (if one believes molecular-field calculations) in certain magnetic compounds showing metamagnetic-antiferromagnetic transitions; e.g., DyAl garnet,¹¹ FeCl₂,¹² Ni(NO₃)₂ · 2H₂O.¹³ In these materials the internal magnetic field (the applied magnetic field corrected for sample demagnetization) corresponds to Δ and sample magnetization to x . The order parameter ψ is some form of sublattice magnetization which may be accessible to neutron-scattering or Mössbauer measurements. It seems likely that the order-disorder transition¹⁴ in NH₄Cl exhibits a tricritical point if the pressure

is increased sufficiently.¹⁵ There is no reason to expect all tricritical points to exhibit identical behavior, and experimental investigation of these different systems could help to elucidate (just as in the case of "ordinary" critical points) the crucial physical features giving rise to various critical-point indices, etc.

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¹The review article by K. W. Taconis and R. De Bruyn Ouboter, in *Progress in Low Temperature Physics*, edited by C. J. Gorter (North-Holland, Amsterdam, 1964), Vol. IV, p. 38, is still a valuable reference, though for detailed behavior near two-fluid critical mixing see E. H. Graf, D. M. Lee, and J. D. Reppy, *Phys. Rev. Letters* **19**, 417 (1967).

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³L. Landau, *Physik Z. Sowjetunion* **11**, 26 (1937); reprinted in *Collected Papers of L. D. Landau*, edited by D. ter Haar (Pergamon, London, 1965), p. 193.

⁴For our purposes the phase of ψ is irrelevant and we suppose it to be fixed (to within a plus or minus sign). This is analogous to applying a magnetic field in a particular direction to an isotropic Heisenberg ferromagnet.

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⁶M. Blume, V. Emery, and R. B. Griffiths, to be published.

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¹⁵C. W. Garland, private communication.