Chemical Potential of He^3-He^4 Solutions Near the Tricritical Point*

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New vapor-pressure measurements of He^3-He^4 solutions in the region between 0.5 and 1.2°K have been made and are used to calculate changes in the chemical potential. Special emphasis is directed towards the region of the tricritical point. The variation of the chemical potential and its derivative along certain paths leading to the critical point yields critical indices which satisfy the scaling relation proposed by Griffiths.

In recent years, interest in the liquid He^3-He^4 phase-separation critical point[1] at a mole fraction $X^*=0.67$ of He^3 in the liquid and a temperature $T^*=0.87$°K was further heightened by the experiments of Graf, Lee, and Reppy.[2] These authors observed that at this point, the two branches of the phase-separation curve for $X<X^*$ and $X>X^*$, respectively, form an angular top in the X-T plane. The liquid mixture then has a superfluid, a normal, and a stratified region. In the X-T plane, the first two regions are separated by the λ line that ends at the critical point. Griffiths,[3] who explored the theoretical limiting behavior of certain thermodynamic quantities in the neighborhood of this point, suggested the name tricritical point.

In analogy with the usual binary fluid mixing point and the liquid-gas critical point in pure fluids, we assume that the asymptotic behavior for He^3-He^4 solutions near (T^*, X^*) can be described by power laws. For a usual binary mixture with a phase separation point (X_c, T_c), the asymptotic behavior of X, T, and Δ (the difference between the chemical potentials of the two components) can be assumed to be given by

$$|X-X_c| \propto (T_c-T)^{\beta} \quad \text{for the coexistence curve,} \tag{1a}$$

$$\partial X/\partial\Delta \propto (T_c-T)^{-\gamma'} \quad \text{along the coexistence curve,} \tag{1b}$$

$$\partial X/\partial\Delta \propto (T-T_c)^{-\gamma} \text{ for } X=X_c \text{ and } T>T_c, \tag{1c}$$

$$[\Delta(X)-\Delta(X_c)] \propto |X-X_c|^{\delta} \text{ for } T=T_c. \tag{1d}$$

For the He^3-He^4 solutions we will characterize the exponents just defined by the subscripts "+" and "−" referring to the normal and superfluid phases, respectively. It is not obvious that corresponding plus and minus exponents are necessarily equal, but from experimental evidence[2] $\beta_+=\beta_-=1$. Griffiths[3] predicts the divergence

$$(\partial X/\partial\Delta)_T = A(T-T^*)^{-\gamma_+} \tag{2}$$

at $X=X^*$. He made a "first guess" that γ_+ would be of the order of unity and suggested a scaling relation for both normal and superfluid phases, which implies that γ and γ' are identical and

$$\gamma_\pm = \delta_\pm - 1. \tag{3}$$

Similarly one might guess the relations

$$[\Delta(X)-\Delta(X^*)]_{T^*} = B_\pm|X-X^*|^{\delta_\pm}[1+O(X-X^*)+\cdots] \tag{4}$$

and

$$(\partial\Delta/\partial X) = C_\pm(T^*-T)^{-\gamma_\pm'}[1+O(T^*-T)+\cdots] \tag{5}$$

along the phase-separation line.

These considerations suggested measurements of the saturated vapor pressure $P_{sat}(X)$ of the solutions since from these the chemical potential can be obtained quite readily. This paper describes such measurements and their analysis in terms of the critical exponents. Actually, the careful specific-heat measurements by Alvesalo *et al.*[4] give $\partial\Delta/\partial X$ along the phase-separation curve and when analyzed according to Eq. (5) give $\gamma_+'=0.95$ and $\gamma_-'=1.05$ with an uncertainty of ~10%.

A careful and extensive series of measurements of $P_{sat}(X)$ was already reported by Sydoriak and Roberts,[5] who used a conventional manometer system at room temperature and made corrections for the effect of the thermomolecular pressure at sufficiently low temperatures. Their data were taken at mole-fraction intervals of 0.1 and hence their measurements did not cover the region very close to T^* and X^*. It was accordingly difficult to derive from these measurements the variations of P_{sat} in this region and to calculate the change of Δ with X and T.

To eliminate the problem of thermomolecular pressures and to make data taking more convenient, we have designed a pressure-measuring strain gauge in thermal equilibrium with the vapor-pressure cell capable of resolving about 3 μm pressure. The solution fills to about 85% a flat cell of 2 mm height and 2.5 cm diam filled with copper wires to reduce thermal gradients. The pressure is transmitted via a hole at the top of the cell to a cylindrical space with a 4-mil stainless-steel membrane. This membrane in turn forms the electrically grounded plate of a capacitor, the second plate being a concentric steel ring with a clearance of 1 mil. The capacitor is part of an *LC* circuit powered by a tunnel diode and oscillating at a frequency of about 15 MHz measured by an electronic counter. The circuit has a frequency stability of 0.1 Hz over periods up to about 20 min, and a systematic drift only rarely exceeding 0.3 Hz over the time of an experiment, about 4 h. A germanium resistance thermometer is attached to this unit.

The strain gauge was calibrated against P_{sat} of pure He^3 at temperatures between 0.85 and 1.2°K, using a liquid-He^3 bath connected to a conventional mercury and oil manometer system as a thermometer. The vapor pressure as measured by the strain gauge was then used to calibrate the germanium thermometer below 0.85°K. Various solutions, prepared by mixing known amounts of He^3 and He^4, were introduced into the cell and condensed at 0.5°K. The pressure P_{sat} was then measured at increasing and decreasing T, the intervals varying between about 2 and 20 mdeg K. About 3 min were needed to achieve equilibrium after heating, as indicated by the constancy of pressure and temperature. Reproducibility of P_{sat} upon successive thermal cyclings was usually better than about 8 μm. Some of this uncertainty may have been caused by drift, hysteresis of the strain gauge, or even by some irreproducibility of the conditions in the liquid; and this needs further study.

As expected from thermodynamic considerations and also from previous work,[5] $P_{\text{sat}}(X)$ below the temperature of stratification is independent of X. However, the vapor-pressure measurements were not found as sensitive in determining the coexistence curve as have been sound-velocity measurements.[6] This already was evident in the measurements of Sydoriak and Roberts.[5] Hence we select as the coordinates for the tricritical point the values $X^* = 0.673$ and $T^* = 0.871$°K, most recently determined with precision by Alvesalo *et al.*[4] from specific-heat measurements.

Once pressure measurements at mole-fraction intervals of 0.1 and a few at 0.05 intervals were taken, the pressure of a solution of known volume with $X = 0.76$ was measured. This solution was then successively diluted in steps of 0.02 in the mole fraction, by condensing a metered amount of He^4 into the cell, until a solution of $X = 0.64$ was obtained. A similar series of dilutions was conducted for $0.48 \leq X \leq 0.66$ to explore carefully the region around the critical point. A total of about one thousand vapor-pressure readings were taken. Our values for $P_{\text{sat}}(X)$ were found to be systematically lower than those of Sydoriak and Roberts by an average of about 0.7% over $0.7 \lesssim T \lesssim 1.2$°K and $0.2 \lesssim X \lesssim 0.9$.

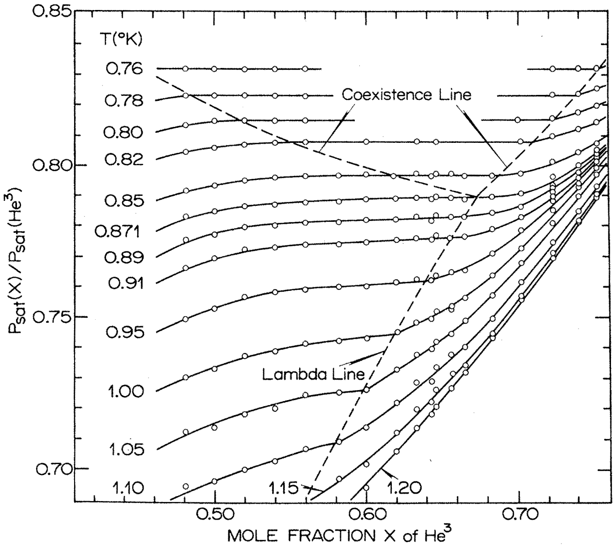

FIG. 1. The ratio $\mathcal{R} = P_{\text{sat}}(X)/P_{\text{sat}}(\text{He}^3)$ as a function of X (the mole fraction of He^3 in the liquid) for several representative isotherms, in the neighborhood of the tricritical point. The region where the isotherms are horizontal is the stratification region.

The data were analyzed by first plotting the ratio $\mathcal{R} = P_{\text{sat}}(X)/P_{\text{sat}}(\text{He}^3)$ vs T for the 28 solutions investigated, and smooth curves were drawn. This ratio was then replotted at given temperatures versus X. The portion of greatest interest in the diagram is shown in Fig. 1 for some assorted isotherms. In this representation, the phase separation curve appears "upside down" because for a given X, $\mathcal{R}$ increases with decreasing T, finally tending to unity.

Using the relations between the vapor pressure and the chemical potential, the Gibbs-Duhem relations, and making appropriate approximations,[1] one can show that

$$\left(\frac{\partial\Delta}{\partial X}\right)_T \approx \frac{RT}{1-X}\left(\frac{\partial \ln\mathcal{R}}{\partial X}\right)_T . \tag{5}$$

Using the plot given in Fig. 1, we obtained the quantity $(\partial\Delta/\partial X)_T$ as a function of X for a large number of isotherms. At the coexistence curve,

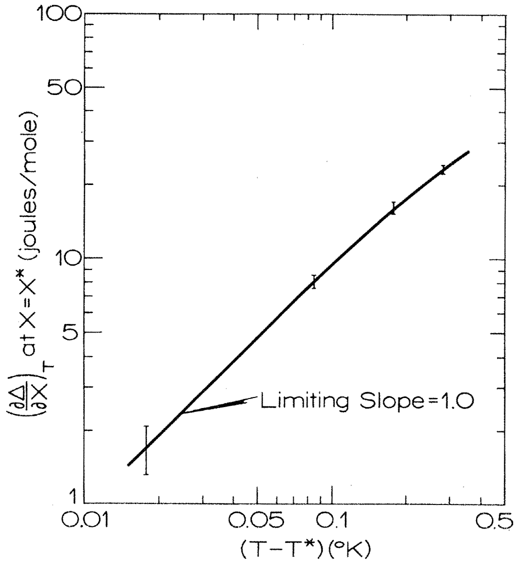

FIG. 2. Plot of the chemical potential gradient $(\partial\Delta/\partial X)_T$ at $X=X^*$ as a function of $T-T^*$. The error bars have been estimated as explained in the text.

the values of $(\partial\Delta/\partial X)_T$ so obtained extrapolated smoothly into those calculated by Alvesalo *et al.*[4] from their specific-heat measurements for $0.51 < X < 0.72$. Evaluating $(\partial\Delta/\partial X)_T$ at $X=X^*$ and plotting this quantity versus $T-T^*$ (Fig. 2) gives a limiting slope of $\gamma_+ = 1.0 \pm 0.1$ as $T \to T^*$. In Fig. 2, no points have been plotted since $\partial\Delta/\partial X$ is the product of two smoothing processes—the first one in generating the isotherms in Fig. 2, the second one in differentiating the $\mathcal{R}$ vs X curve and in plotting the isotherms $(\partial\Delta/\partial X)_T$. The uncertainty bars at arbitrarily chosen $T-T^*$ values have been estimated from the possible systematic uncertainties traced back to the original measurements.

Similarly, with the use of these isotherms, the difference $\Delta(X)-\Delta(X^*)$ was formed by numerical integration along the critical isotherm. At $X=X^*$, there is a point of inflection and the initial slope $(\partial\Delta/\partial X)_T$ near X^* is considerably smaller for $X<X^*$ than for $X>X^*$, as can be seen from Fig. 3. This is already apparent from the calorimetric measurements of Alvesalo *et al.*[4] In fact for $X^*-X<0.08$, where the change of $\mathcal{R}$ with X is smaller than its uncertainty due to the small irreproducibilities, the calorimetric results give the more reliable values of $(\partial\Delta/\partial X)_T$. Using an estimate of $\partial^2\Delta/\partial X\partial T$ near $T=T^*$ from the saturated-vapor-pressure measurements, we obtained $(\partial\Delta/\partial X)_T$ at $T=T^*$ in this mole-fraction range by an extrapolation of the calorimetric results. Within experimental uncertainty, the exponents δ_+ and δ_- were found to be equal to 2.0 ± 0.25. The error in our analysis leading to γ_+, $\gamma_\pm'$, and $\delta_\pm$ takes into account possible uncertainties in X^* and T^* of ± 0.005 and ± 0.003°K, respectively.

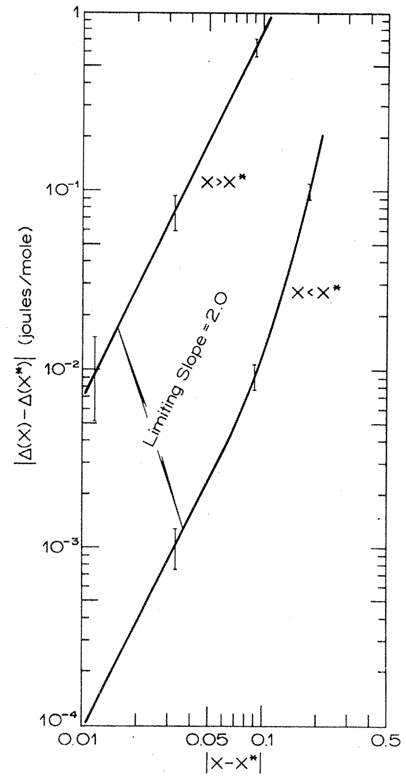

FIG. 3. Plot of $|\Delta(X)-\Delta(X^*)|$ vs $|X-X^*|$ along the critical isotherm, as explained in the text.

In summary, the limiting behavior of Δ (expressed in joules/mole) appears to be given by

$$\partial\Delta/\partial X \cong 0.7\times 10^2 (T-T^*)^{1.0} \quad (\text{at } X=X^*),$$
$$[\Delta(X)-\Delta(X^*)]_{T=T^*} \cong 75 (X-X^*)^{2.0} \quad (X>X^*),$$
$$[\Delta(X^*)-\Delta(X)]_{T=T^*} \cong 9.7\times 10^{-1} (X^*-X)^{2.0} \quad (X<X^*).$$

The scaling relation, Eqs. (1), is therefore satisfied within the admittedly large experimental uncertainty. It is rather intriguing that for this tricritical point, the critical exponents appear to be positive integers within experimental error.

The λ line is located by the inflection point of the $\mathcal{R}$ vs X isotherms. If one accepts the Griffiths and Wheeler[7] theory of weak divergences, one would expect $(\partial\mathcal{R}/\partial X)_T = 0$ along this line.[8] However, the expected (weak) divergence in $\partial X/\partial\mathcal{R}$, even if it is present, may take place over such a small interval in X that it is, for practical purposes, unobservable.

In conclusion, we have established the limiting behavior of thermodynamic potentials at the critical point and have given preliminary values for the critical exponents. These satisfy the scaling relation [Eq. (2)], and one has in addition $\gamma_+ = \gamma_+'$ within experimental error. Hence the superfluid and normal regions appear to have at least closely the same critical indices. Experiments with a still more sensitive strain gauge are being attempted with the purpose of obtaining more accurate values of these exponents. Furthermore, a study of small instabilities and the hysteresis effects of the pressure readings will be made.

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Theory of Fluctuation-Induced Diamagnetism in Superconductors

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A free-energy expression for a pure superconductor is derived microscopically which includes effects of a nonlocal order parameter. In the presence of strong field the simple transformation $\vec{q} \rightarrow \vec{q} + 2e\vec{A}/c$ is no longer valid. Using this free energy, fluctuation-induced diamagnetism of a superconductor above T_c is calculated. The resulting universal behavior for pure superconductors is in good agreement with the experiment of Gollub, Beasley, and Tinkham.

Recently Gollub, Beasley, and Tinkham[1] (GBT) reported observation of universal behavior in the fluctuation-induced diamagnetism of clean superconductors above the transition temperature. This magnetization has been calculated exactly within the framework of the Ginsburg-Landau (GL) theory by Prange.[2] However, the fluctuation spectrum of the (GL) theory overestimates the contribution from short-wavelength fluctuations when a magnetic field B is present. This results in a calculated magnetization which is considerably larger than the measured value[1] when $B > 0.05 H_{c2}(0)$. Patton, Ambegaokar, and Wilkins[3] (PAW) had dealt with this problem by introducing an energy-cutoff parameter into the fluctuation spectrum. As a result their magnetization is strongly suppressed below the Prange value if $B \gtrsim mcE/he$ (m = electron mass). Physical arguments[1,3] suggest the choice $E \approx \hbar^2/2m\xi_0^2 \approx e\hbar H_{c2}(0)/mc$. As pointed out by GBT, with this choice of E the PAW theory only begins to suppress the magnetization strongly (to $\sim\frac{1}{2}$ the Prange value) when $B \approx H_{c2}(0)$, when in fact the corresponding measured value is almost zero. Thus, it would seem that some other physical effect must play a part in depressing the magnetization of clean superconductors in a magnetic field. The present calculation treats in detail the nonlocal effects which arise because of the presence of a magnetic field. It is found that once the nonlocal effects are included, the magnetization is suppressed considerably (to $\sim\frac{1}{2}$ the Prange