reversal occurs before peak field. This is possibly a consequence of the short length of the plasma but is otherwise unexplained at this point.

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SPECIFIC HEAT OF He^3-He^4 MIXTURES VERY NEAR THE λ LINE*

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We have measured the specific heat of liquid He^4 and four He^3-He^4 mixtures under their saturated vapor pressure at temperatures very close to the λ temperature of each mixture. The specific heat of mixtures with large He^3 concentration is clearly cusped at the λ line. It approaches a finite maximum with infinite slope. This supports the conjecture that the specific heat of He^3-He^4 mixtures at constant chemical potential becomes infinite at the λ line at all He^3 concentrations.

The thermodynamic properties of pure He^4 have probably been measured in greater detail and with higher precision very close to the λ point than the corresponding properties of any other system near a phase transition. This suggests that effects of an impurity on a phase transition may be recognized more clearly in this system than in others. Our specific-heat measurements on liquid-helium mixtures extend the earlier data of de Bruyn Ouboter, Taconis, le Pair, and Beenakker[1] to temperatures much closer to the λ line. They are of interest in light of recent predictions about impurity effects in general[2] and predictions about He^3-He^4 mixtures in particular.[3] The cusped specific heat we observe at large He^3 mole fraction supports the idea that an impurity will not change the nature of the phase transition if the transition is observed at constant chemical potential.

Our primary experimental problems were preparation of mixtures, isolation of the calorimeter, and the measurement of temperature with high resolution and stability.

The mixtures were prepared in gaseous form at room temperature in a specially designed Toeppler pump. The mole fraction x of He^3 was known in the gaseous state to better than ±0.1%. Mixtures were condensed into the calorimeter through a capillary while the calorimeter temperature was held slightly above the λ temperature with the aid of a mechanical heat switch. A needle valve built on the calorimeter was then closed with a detachable screwdriver. The small volume of connecting tubing was then evacuated, the calorimeter cooled, and finally the heat switch opened. The residual thermal conductivity between the calorimeter and the regulated outer helium bath was 8 erg/sec K. Usually the bath temperature and an auxiliary heater were adjusted so that the residual temperature drift of the calorimeter was less than 10^{-9} K/sec. Data were taken by observing the drift for several minutes, electrically heating for about a minute, and then observing the drift again. The apparent thermal relaxation time of the filled calorimeter was always less than a few seconds, the time constant of the recording system. After the specific-heat measurements on each mixture were completed, the quantity of helium that had been in the calorimeter was measured as the calorimeter was emptied. These values and other experimental conditions are listed in Table I.

The calorimeter was a slotted copper block similar to that used for earlier measurements[4,5] near the λ and critical points of pure He^4. The most significant change is the addition of a valve to the calorimeter itself. This permits us to obtain excellent thermal isolation and eliminates

Table I. Mole fraction x of He^3, number of moles in calorimeter N, observed lambda temperature T_λ, lambda temperature from Table III of Roberts and Sydoriak,[a] and estimated fraction of calorimeter volume filled with liquid. Filling is estimated from N, calorimeter volume, and molar-volume data from Ref. b.

x	N	T_λ This Expt.	T_λ Ref. a	Filling
0.0000	0.072 02	2.173	2.172	0.987
0.0110	0.067 92	2.158	2.157	0.933
0.0997	0.070 12	2.030	2.027	0.990
0.200	0.061 84	1.874	1.872	0.899
0.390	0.064 17	1.532	1.532	0.982

[a] See T. R. Roberts and S. G. Sydoriak, Phys. Fluids 3, 895 (1960).

[b] E. C. Kerr, in Low Temperature Physics and Chemistry, edited by Joseph R. Dillinger (University of Wisconsin Press, Madison, Wisc., 1958), p. 158.

all problems due to the He II film flow. The maximum height difference in the sample is 0.35 cm. The volume of the calorimeter, 1.998 cm^3, was estimated by measuring how much He^4 was required to fill it and using the molar volume data of Kerr and Taylor.[6]

A four-wire ac bridge similar to the one designed by Kierstead[7] was used to measure the resistance of a germanium thermometer. Repeated measurements of the λ temperature of pure He^4 indicated that the thermometer-bridge combination drifted less than 5×10^{-6} K in 10 days. The thermometer was calibrated against the vapor pressure of He^4 and He^3 throughout the range 1-4 K in another apparatus. We believe our calibration is within ±0.002 K of T_{58}.[8] Accordingly we interpret the close agreement of our measured λ temperatures with accepted values[9] as indicating that significant fractionation of the He^3-He^4 mixtures did not occur in the filling process.

The quantity actually measured and reported here, C_m, is actually the specific heat of a two-phase system whose total volume and composition is fixed, C_{v,N_1,N_2}. Since our calorimeter was nearly filled with liquid, we believe the measured specific heat closely follows the specific heat of the liquid mixture at its saturated vapor pressure and constant mole fraction, $C_{s,x}$. This in turn is close to the specific heat of the liquid mixture at constant pressure and mole fraction, $C_{p,x}$. We have not attempted to correct our data to $C_{p,x}$ because sufficiently detailed thermodynamic data are not available near the λ line.

In Fig. 1 we have plotted our specific-heat data

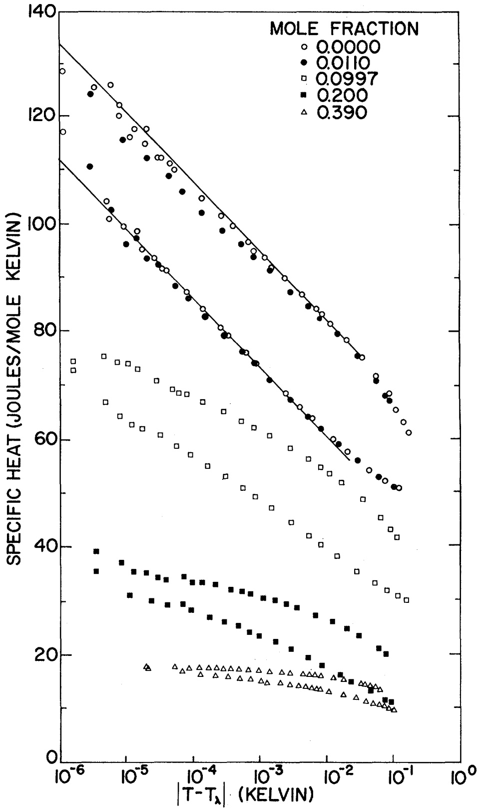

FIG. 1. Measured specific heat of He^4 and He^3-He^4 mixtures as a function of $|T-T_\lambda|$. For clarity the data for $x=0.0000$ and $x=0.0110$ have been raised 40 J/mole K and the data for $x=0.0997$ have been raised 20 J/mole K. The data for each mixture fall on two branches. In all cases the branch with higher specific heat occurs at temperatures below T_λ for that mixture. Two sets of data are plotted at $x=0.0000$ and $x=0.390$.

C_m as a function of $|T-T_\lambda|$ on a logarithmic scale. The data for pure He^4 fall close to parallel straight lines confirming the symmetrical logarithmic divergence of $C_{p,x=0}$ at T_λ reported by Buckingham and Fairbank[4] and more recently by Ahlers.[10] Close examination of the present data for $|T-T_\lambda|<1\times10^{-3}$ reveals slight (of the order of 1%) systematic deviations from a "best-fit" symmetrical logarithmic singularity. Similar deviations have been observed by Ahlers[10, 11] who has studied them in greater detail and concluded that the data actually lend themselves to several interpretations.

The specific-heat data for mixtures indicate the singularity at the λ point becomes less prominent as x increases, but remains sharp within our experimental resolution. There is no evidence of two close singularities such as those observed by Chashkin, Gorbunova, and Voronel',[12] at the critical point of a fluid mixture nor is there evidence of a rounded peak similar to those which have been observed at phase transitions in many impure solids. Our further analysis at this time has been confined primarily to the data at $x = 0.200$ and $x = 0.390$.

We have investigated the possibility of a discontinuity in C_m at the λ line by examining a log-log plot of $\Delta C_m(T-T_\lambda) = C_m(T_\lambda - T) - C_m(T-T_\lambda)$ as a function of $T-T_\lambda$. Such a plot indicates $\Delta C_m(T-T_\lambda)$ tends towards zero increasingly rapidly as $T-T_\lambda$ approaches zero. In the range $10^{-4} < T-T_\lambda < 10^{-2}$, $\Delta C_m(T-T_\lambda)$ behaves roughly as $(T-T_\lambda)^{0.1}$ at $x = 0.200$ and as $(T-T_\lambda)^{0.2}$ as $x = 0.390$. We conclude that a discontinuity in C_m at the λ line is unlikely. This conclusion differs from that of de Bruyn Ouboter, Taconis, le Pair, and Beenakker[1] based on their early specific-heat measurements on He^3-He^4 mixtures. The present data have a temperature resolution three to four orders of magnitude higher than their data. Recently measurements of intermediate resolution have been made by Alvesalo, Berglund, Islander, Pickett, and Zimmermann on several mixtures with x near 0.65. These authors also conclude that C_m is continuous.[13]

In Fig. 2 we have plotted the temperature derivative of C_m for the mixture $x = 0.390$ along with the derivative for He^4 for comparison. Although differentiation of the data emphasizes the noise present, it is clear that $|dC_m/dT|$ reaches very large values as T approaches T_λ from both above and below. In summary, our data may be described as being consistent with the following statement: C_m is continuous and approaches a finite maximum value with infinite slope as T approaches T_λ.

It is of interest to examine the present data in the context of the hypothesis that $C_{p,\varphi}$ is infinite all along the λ line. Here we follow Alvesalo et al.[13] in defining φ as $\mu_3 - \mu_4$, where μ_3 and μ_4 are the chemical potentials per mole of the He^3 and He^4 components of the mixture. Essentially this hypothesis was advanced by Rice.[3] This is also an example of more general situations considered by Fisher.[2] We further speculate that the thermodynamic analysis Buckingham and Fairbank[4] applied to the λ line in the variables P and T may be applied to the λ line in the variables φ and T. If $C_{p,\varphi}$ becomes infinite, it must follow that

$$C_{p,x}(T = T_\lambda) = T_\lambda \left(\frac{\partial S}{\partial T}\right)_{p,\lambda} + T_\lambda \left(\frac{\partial x}{\partial T}\right)_{p,\lambda} \left(\frac{\partial \varphi}{\partial T}\right)_{p,\lambda}. \qquad (1)$$

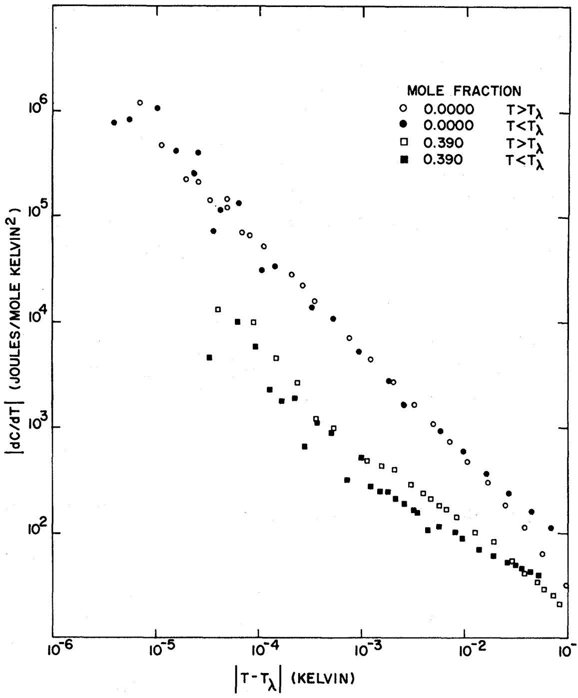

FIG. 2. The absolute value of the derivative of the measured specific heat with respect to temperature as a function of $|T-T_\lambda|$. Both branches at $x = 0.0000$ and $x = 0.390$ are shown. Two sets of data are plotted for each concentration.

The derivatives in Eq. (1) are not singular (except at the end of the λ line) and may be estimated from existing data.[14] Our estimates for $C_{p,x}(T = T_\lambda)$ are 22 ± 5, 66 ± 7, and 164 ± 14 J/mole K at $x = 0.390$, 0.200, and 0.0997, respectively. Our largest value of C_m at $x = 0.390$ falls within this range, supporting the hypothesis that $C_{p,\varphi}$ is infinite along the λ line. At other mole fractions the peak values of measured heat capacity are well below this estimated maximum. This indicates that measurements many orders of magnitude closer to the λ line would be needed to show in a direct way that $C_{p,\varphi}$ is infinite. Attempts at fitting the present data to various functions to extract peak values have yielded inconclusive results.

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†National Science Foundation trainee.

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LIGHT SCATTERING FROM SURFACE WAVES ON CARBON DIOXIDE NEAR THE CRITICAL POINT

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The spectrum of light scattered from surface waves thermally excited on the liquid-vapor interface of carbon dioxide has been measured at several scattering angles in the temperature range $30° \geq T_c - T \geq 3.5 \times 10^{-2}$ °K. Within experimental error no deviation of the spectrum shape from the predictions of thermodynamic fluctuation theory is observed. The temperature dependence of the surface tension is deduced from the data and fitted by the empirical law $\alpha = \alpha_0(1-T/T_c)^{\mu}$, with $\mu = 1.253 \pm 0.010$ and $\alpha_0 = 17.9 \pm 1.2$ dyn/cm. No anomaly is noticed in the temperature variation of the shear viscosity.

On a liquid interface thermal motion produces fluctuations which can propagate as capillary or gravity waves, damped by viscosity. Using a 50-mW He-Ne laser and light-beating spectroscopy, short-wavelength surface waves of this type have been observed on the free surface of various liquids.[1] The main features of the wave dispersion and absorption laws have been measured under widely varying damping conditions.[2] This kind of investigation has yielded a valid way of measuring the surface tension (and also the shear viscosity in a few cases) without disturbing thermal equilibrium. This method, then, is very well suited for measuring interfacial tension close to the critical temperature at which the interface disappears. We present here the results obtained for the liquid-vapor interface of CO_2 when the critical point is approached. There exists a surface opalescence[3] such that in the vicinity of T_c the surface still scatters more light than the volume of the fluid (at certain scattering angles). Far from T_c we have observed weakly damped capillary waves; the surface tension α can be deduced from their velocity. The decrease of α as T_c is approached produces a decrease of the wave frequency (at a fixed wave vector q). In addition, gravity forces begin to play a role in the dispersion law; the gravity and capillary restoring forces may become of the same order of magnitude because the difference between the specific masses of the liquid and gas phases, $\Delta\rho$, decreases less rapidly than α. In the range $0.025 \leq T_c - T \leq 0.2$°K, α and $\Delta\rho$ can both be obtained from analysis of the spectrum at different q. At the same time the waves become strongly damped, even though the viscosities of the two phases do not change markedly, but just because the restoring forces decrease rapidly.

The experimental procedure has already been described.[1] In this experiment the temperature of the cell filled with CO_2 (purity 99.998%) is controlled to a few times 10^{-4} deg. The spectrum of the light scattered at a given angle reflects, in the vicinity of the incident-light frequency, the power spectrum $P_q(\omega)$ of the surface fluctuations having a given wave vector q. To get a larger scattering efficiency, the incident light beam is made almost normal and the scattering angles are chosen small ($1.6 \leq \theta \leq 16$ mrad, leading to