Surface Tension of He^4 near T_λ *

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We have measured the surface tension of liquid He^4 for $(T_\lambda - 100\text{ mK}) < T < (T_\lambda + 100\text{ mK})$ with a resolution of 1×10^{-5} using a capacitive differential-capillary-rise technique. The results show a change in the slope of $\sigma(T)$ of 0.0226 ± 0.001 erg cm^{-2} K^{-1} centered below the bulk T_λ. A discussion of the critical behavior is given.

The behavior of surface phenomena near critical points has recently attracted interest.[1] We report in this Letter a high-resolution measurement of the surface tension of liquid He^4 in the vicinity of the λ transition. This measurement was motivated by the ease with which a clean surface can be prepared in liquid helium and by the suggestion by Sobyanin[2] that such an experiment might illuminate the interesting question of the boundary condition satisfied by the superfluid order parameter at the free (liquid-vapor) surface. Additionally, helium offers an opportunity to study surface effects at a critical point at which the phases separated by the surface do not become identical.

Sobyanin argues that the order parameter vanishes at a free surface and that the resulting curvature in the Ginzburg-Pitaevskii wave function yields a singular contribution σ^s to the surface free energy below T_λ, $\sigma^s = \sigma_0(-t)^{2-\alpha-\nu}$, where $t \equiv (T - T_\lambda)/T_\lambda$, $\sigma_0 \approx 0.28$ erg cm^{-2}, and $2 - \alpha - \nu \approx 1.35$. There is no corresponding term above T_λ.

Hohenberg[3] suggests that singular behavior in σ is expected on both sides of T_λ. The argument is dimensional in character. The singular part of the surface tension then has the temperature dependence

$$\sigma^s(t) = \tilde{\xi}(t)[g(t)/v(t)]^s \sim |t|^{2-\alpha-\nu}.$$

The surface tension of liquid helium was measured by Allen and Misener[4] and found to have a possible change in slope near T_λ. A higher-resolution experiment by Atkins and Narahara[5] suggested a slope change of about 0.02 erg cm^{-2} K^{-1}. A resolution of 7×10^5 was achieved for $T < T_\lambda$ by Gasparini, Eckardt, Edwards, and Shen[6] in an apparatus unsuited for measurement above T_λ.

We have measured the surface tension with a resolution of approximately 1 part in 10^5 in the region $-0.05 < t < 0.05$. The technique employs the differential capillary rise between a pair of coaxial capacitors with different gap widths. The capacitors, joined to permit liquid helium to flow between them, are connected in a bridge, which is balanced with the cell evacuated. Adding liquid helium unbalances the bridge, since the liquid rises higher in the narrow-gap capacitor C_n because of surface tension. A null-balance feedback system applies a sufficient dc voltage V_w to the wide-gap capacitor C_w to equalize the liquid levels in the two capacitors and rebalance the bridge. To minimize the effects of imperfections in the capacitor walls, we hold the meniscus positions fixed in the capacitors at all temperatures. A suitable dc voltage V_n applied to C_n draws liquid from a reservoir to compensate for the effects of changing liquid and gas densities.

In terms of the voltages V_w and V_n, the dielectric constants ϵ_l of the liquid[7] and ϵ_g of the gas,[8] and the capacitor gaps δ_w and $\delta_n = \delta_w/D$, the surface tension is

$$\sigma = \frac{\epsilon_0(\epsilon\ - \epsilon_g)}{4}\,\frac{V_w^{\,2} - D^2 V_n^{\,2}}{\delta_w(D-1)}$$

plus small corrections for deviations from ideal capacitor geometry. The capacitor parameters are measured *in situ* by performing external electrical measurements.

The coaxial capacitors have gap widths of about 0.067 and 0.079 mm and are arranged concentrically. A third concentric gap serves as a reservoir and also eliminates pressure differences across the capacitor walls. Capacitance measurements are made at a central active section; guard sections above and below the active section minimize end effects and ensure that nearly all of the measured capacitance has helium as its dielectric. The cell is constructed of copper and the maximum thickness of helium is held to less than 0.1 mm to achieve rapid thermal equilibration.

Temperature is measured by a carbon resistance thermometer in contact with the cell body. The λ point is located by inflection points in graphs of cell temperature versus time with fixed power input and of liquid dielectric constant versus temperature. The two methods agree within their resolution of about 5 μK.

We have performed measurements of σ versus temperature for four different liquid levels in the capacitor. Data at the last filling level exhibit the lowest noise, corresponding to a short-term variation of about 1 part in 10^5 of the surface tension. Systematic errors in $\sigma(T)-\sigma(T_\lambda)$ are estimated at less than 3 parts in 10^4 of the total surface tension over the temperature range investigated. The largest systematic errors are believed to be uncorrelated between data taken at different fillings and to be either analytic or proportional to the liquid density.

The data confirm the suggestion of Refs. 4 and 5 of a slope change in $\sigma(T)$ near T_λ. To display the data with sufficient resolution to permit study, we show in Fig. 1 the difference between our measured surface tension and a straight line. Figure 1 shows our best data set along with points from Ref. 6. If we describe the results in terms of the second derivative σ'', we see that far from the transition σ'' is small and negative. Near T_λ it becomes large and positive, implying a large *negative* surface specific heat. The peak in σ'' appears to have a "short tail," so that one can speak of a slope change through the region of the singularity. We find a slope change of 0.0226 ± 0.001 erg cm^{-2} K^{-1} between $t \approx -0.01$ and $t \approx +0.01$; the surface entropy *decreases* by this amount as T is raised through T_λ.

A closer view of the data near T_λ is shown in Fig. 2. The region of maximum curvature is centered not at the bulk T_λ, but a few milliKelvin below it. This shift is much larger than anticipated thermometry errors or temperature inhomogeneities. Such a shift from the bulk transition temperature is typically associated with a finite-size effect.

The straightness of the plot of $\sigma(t)$ (see Fig. 1) over a range of temperatures on both sides of T_λ is very difficult to reconcile with the predicted behavior. Since $2-\alpha-\nu \cong 1.35$ the function $|t|^{2-\alpha-\nu}$ has rather strong positive cuvrature.

We show in Fig. 2, curve a, the best fit to a function of the type

$$\sigma = \sigma^r(t) + \sigma^s(t) = a_0 + a_1 t + a_2 |t-\Delta|^{1.35}. \tag{1}$$

It has $\chi^2 = 4.5$ for $|t| < 0.01$ and χ^2 is > 20 for $|t| < 0.02$, assuming a random error of $10^{-5}\sigma_\lambda$ estimated from our short-term noise. This situation is not changed if a_2 is permitted to take different values above and below $t-\Delta = 0$. For example, if $a_2 = 0$ for $t - \Delta > 0$, corresponding to Sobyanin's suggestion, $\chi^2 = 6.7$ for $|t| < 0.01$. If the power of $|t-\Delta|$ is considered a free parameter, the best value is not significantly different from 1.0. The best fit to the form

$$\sigma = \sigma_0 + a_1 t + a_2 |t - \Delta|$$

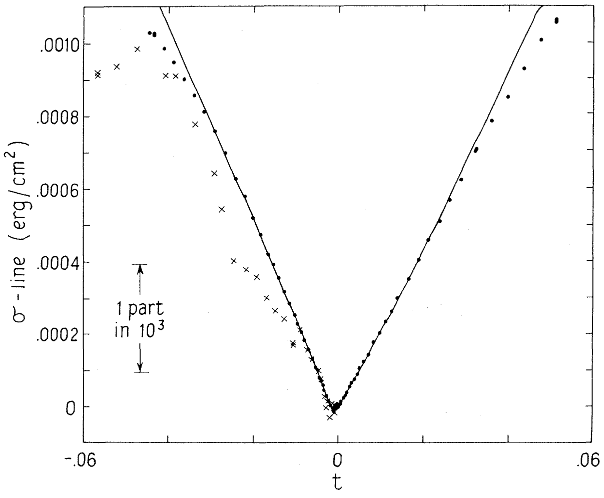

FIG. 1. Surface tension minus the linear function $(0.307-0.19t)$ erg/cm² versus $t \equiv (T-T_\lambda)/T_\lambda$. The points are from the present experiment, the crosses from Ref. 6. The curve is Eq. (3) using the average parameters given in the text, determined in the range $|t| < 0.02$.

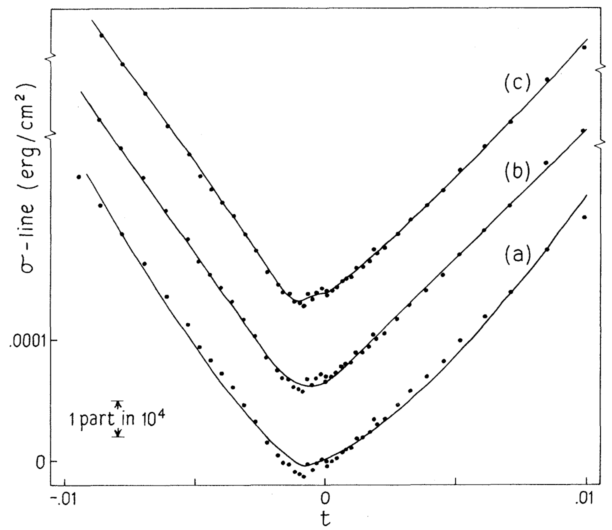

FIG. 2. Expanded view of the region $|t| < 0.01$. The same data are plotted three times, displaced vertically showing three fitted curves: a, fitted to Eq. (1), b, fitted to Eq. (2), and c, fitted to Eq. (3).

has $\chi^2 \cong 2.5$ for $|t| < 0.01$. The fit is improved if the transition is rounded as well as being shifted. Both rounding and shifting can arise from finite-size effects. We have accomplished this rounding phenomenologically by writing

$$\sigma^s(t) = a_2 \int f(\Delta)|t-\Delta|\,d\Delta . \qquad (2)$$

The weighting function

$$f_1(\Delta) = \begin{cases} w^{-1} \text{ for } \Delta_0 - \frac{1}{2}w < \Delta < \Delta_0 + \frac{1}{2}w, \\ 0 \text{ elsewhere}, \end{cases}$$

and $f_2(\Delta) = (2w)^{-1}\,\mathrm{sech}^2(\Delta - \Delta_0)/w$ produced equivalent results. We show in Fig. 2, curve b, such a fit to a rounded transition. This fit has $\chi^2 = 1.2$, but the shift and width parameters, Δ_0 and w, depend on the temperature range included in the fit, as does χ^2 which increases from 1.1 to 1.6 as the range of $|t|$ increases from 0.005 to 0.02. As expected, addition of a quadratic analytic part does not alter the situation for $|t| < 0.02$. Although these fits are quite good, these systematic variations with the temperature range suggest that something has been omitted.

Most known possible distortions of our results either are analytic or have the singularity of the liquid density $\rho_l \sim |t|^{1-\alpha}$. Accordingly we have tried adding to our fitting function a multiple of the density:

$$\sigma(t) = a_0 + a_1 t + a_2 \int f_1(\Delta)|t-\Delta|\,d\Delta + a_3[\rho_l(t) - \rho_l(0)] . \qquad (3)$$

We show such a fit in Fig. 2 as curve c. The fit is markedly improved. We obtain a χ^2 of 0.59 for this temperature range, and there is no evidence of systematic variation in the parameters or in χ^2 as we vary the limits of the range from 0.005 to 0.02. If $|t-\Delta|$ in (3) is replaced by $|t-\Delta|^{\tilde{\mu}}$, the best value of $\tilde{\mu}$ is found to be $\tilde{\mu} = 1.003 \pm 0.03$; the result is consistent either with $\tilde{\mu} = 1.0$ exactly or $\tilde{\mu} = 1 - \alpha \cong 1.026$.

The density coefficient is approximately one order of magnitude larger than can be accounted for by known systematic errors. Further, our four data sets give quite consistent values for this coefficient, whereas the systematic errors are expected to be uncorrelated between data sets.

A weighted average set of parameters, consistent with all data sets and temperature limits between 0.005 and 0.02, is

$$\bar{a}_1 = -0.190 \pm 0.002 \text{ erg/cm}^2,$$
$$\bar{a}_2 = 0.0207 \pm 0.0007 \text{ erg/cm}^2,$$
$$\bar{a}_3 = -0.80 \pm 0.10 \text{ erg/g},$$
$$\bar{\Delta}_0 = (-1.25 \pm 0.07) \times 10^{-3},$$
$$\bar{w} = (0.9 \pm 0.3) \times 10^{-3}.$$

For larger temperature ranges, higher terms are required to fit the data. The data imply a transition very nearly first order ($\mu = 1.0$), rounded and shifted by approximately 2 mK, and a probable $|t|^{1-\alpha}$ singularity at the bulk T_λ.

We would like to suggest two mechanisms which might give rise to the rounding and shifting of the transition. The first possibility is that it is an artifact of the capillary-rise technique, for the system under study includes both bulk helium and the film on the walls above the bulk liquid. The λ transition is depressed in thin films, and the depression in the film at the top of our apparatus (thickness $d \sim 200$ Å) is of the same order as our observed Δ_0 and w. Far from T_λ, where the coherence length $\xi \ll d$, we can speak of the surface tension of the film, which is presumably the same as the bulk value. In this regime the capillary rise can be calculated in the presence of the van der Waals interaction with the wall; the gap width is effectively reduced and the capillary rise is increased. Near T_λ where $\xi \sim d$, the film properties cannot be separated into bulk and surface contributions, and the system free energy must be minimized without making this separation. We have not carried out such a calculation. We do not detect any anomaly in film thickness near T_λ experimentally for a meniscus position below the active section of a capacitor.

It would be much more interesting if these results were properties of bulk helium. We would suggest the following possibility: Thermodynamic stability requires that a macroscopic system must have $C_p > 0$. The surface contributes an entropy which *decreases* as T is raised through T_λ, so the total specific heat will be negative if the surface has an unrounded first-order transition. If the surface entropy change occurs over a region of width w then the total specific heat will be non-negative for a section of fluid (including the surface) of thickness $D > D_c$, with D_c given approximately by $D_c \approx \Delta S_s / C_p(w) w$. Since $D_c \approx \xi(w)$, it is tempting to suppose that w is determined by an equation of the type

$$w C_p(w) \xi(w) \approx \Delta S_s ,$$

which has the solution

$$w \approx 0.6 \times 10^{-3}.$$

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Phase Separation in Fluid Systems by Spinodal Decomposition: A Molecular-Dynamics Simulation

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Using the molecular-dynamics technique, we describe the dynamical evolution of phase separation by spinodal decomposition for a Lennard-Jones fluid quenched to the unstable region. This is the first direct observation of the initial stages of spinodal decomposition.

We describe a numerical molecular-dynamics simulation of phase separation of a single-component Lennard-Jones fluid within the unstable (spinodal) region of the phase diagram. This computer "experiment" yields the first direct observation on an atomic scale of the spatial density variations during the early stages of spinodal decomposition. Until now, spinodal decomposition has been experimentally studied in real physical systems, such as glasses and metallic alloys,[1-3] and binary fluids near the critical point,[4] but experimental limitations have prevented microscopic observations of the early-time morphologies. As a result, x-ray and light-scattering experiments and micrographs of the later stages of phase separation have been used to surmise the features of the initial decomposition process. Our experiment eliminates this bottleneck. The practicality of this experiment was indicated by recent advances in spinodal-decomposition theory which elevated it from a phenomenological theory[5,6] to a first-principles (microscopic) theory.[7-9] However, the computer experiment itself is, of course, quite independent of any theory. We observe a highly connected morphology in the spatial density variations during the early stages of spinodal decomposition, corroborating the prediction of Cahn's linear theory.[6]

Our computer experiment consists in solving the equations of motion for a classical fluid of 1372 Lennard-Jones (LJ) atoms by numerical integration using an IBM 360/195 digital computer. We adopt the numerical procedures first developed by Verlet[10] for his molecular-dynamics experiments on the equilibrium properties of classical LJ fluids. The thermodynamic quantities are measured in the usual "reduced" units.[11] Our system of atoms is enclosed in a cube of length $L = 15.8\sigma$ and reduced density $\rho^* = 0.35$, with the standard periodic boundary conditions being imposed in order to simulate an infinite fluid system.[10] We make special note of the fact that the periodic boundary prevents the occurrence of in-