Critical Fluctuation-Induced Thinning of ^{4}He Films near the Superfluid Transition

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We report dielectric constant measurements showing critical fluctuation-induced thinning of ^{4}He films near the superfluid transition. The films are adsorbed on a stack of copper electrodes suspended at different heights above bulk liquid. We calibrate the measurements by assuming that the film thickness away from the transition region at different heights is accurately given by theory. The thinning is found to be consistent with finite-size scaling, if the value of the scaling function for each thickness is normalized by its value at the minimum.

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The thermodynamic properties of a bulk system near its critical point are dominated by the diverging correlation length ξ, which measures the spatial extent of the order parameter fluctuations. For a finite system such as a liquid film adsorbed on a solid substrate, however, the fluctuations are limited to the thickness of the film. Just as the cutoff of electromagnetic zero-point fluctuations leads to a distance-dependent energy in the Casimir effect [1], this cutoff of the order parameter fluctuations translates to a thickness-dependent free energy, which is predicted to perturb the equilibrium thickness of a wetted film [2–5]. Recently, evidence has been reported for this effect in binary fluid mixture films [6]. In this Letter, we report measurements which verify the existence of fluctuation-induced thinning of the ^{4}He film adsorbed on a Cu surface close to the lambda point.

When order parameter fluctuation effects are negligible, the equilibrium film thickness d of an adsorbed film at a height h above the bulk liquid is given by

$$\left(\frac{\gamma_0}{d^3}\right)\left(1 + \frac{d}{d_{1/2}}\right)^{-1} = mgh\,. \qquad (1)$$

This equation, which is a simplified version [7] of the theory of Dzyaloshinskii, Lifshitz, and Pitaevskii (DLP) [2], describes the competition between gravitational potential energy and the van der Waals attraction of the substrate. The factor $(1 + \frac{d}{d_{1/2}})^{-1}$ corrects the van der Waals energy, γ_0/d^3, for the effect of the finite speed of light [7]. For ^{4}He film on Cu, $\gamma_0 \approx 2600$ K Å^3 and $d_{1/2} \approx 193$ Å [8]. For ^{4}He, if $h \approx 1$ cm, then $mgh = 47.21$ μK and the equilibrium film thickness can be deduced from Eq. (1) to be 282 Å. Although there have been quite a few experimental studies of the thickness of the ^{4}He film on solid surfaces, there is only one experiment, that of Sabisky and Anderson [9], showing good agreement with DLP. The discrepancy with DLP, which is particularly severe for ^{4}He films adsorbed on metal surfaces [10], has generally been blamed on surface roughness, dust particles, scratches or other imperfections, and on the effects of excitations in the film [11].

Near the lambda point, the fluctuations are predicted to introduce an additional term [2–5] to Eq. (1)

$$\left(\frac{\gamma_0}{d^3}\right)\left(1 + \frac{d}{d_{1/2}}\right)^{-1} + \frac{k_B T_\lambda V}{d^3}\,\vartheta = mgh\,. \qquad (2)$$

In this term, ϑ is a scaling function whose argument, according to the finite-size scaling hypothesis [12], is the ratio d/ξ [3]. k_B, $T_\lambda = 2.1768$ K, and $V = 45.81$ Å^3/atom are, respectively, the Boltzmann constant, the lambda temperature, and the specific volume of ^{4}He. Since $\xi = \xi_0(t)^{-\nu}$, where $t = T/T_\lambda - 1$ is the reduced temperature and $\nu = 0.6704$ is the correlation-length exponent, ϑ can be expressed in terms of the finite-size scaling variable $x = (\xi_0 \cdot d/\xi)^{1/\nu} = td^{1/\nu}$ [12]. Experimentally, if $\vartheta > 0$, this fluctuation term acts like a small enhancement to γ_0, and therefore causes the film to thicken near T_λ for a fixed h. If $\vartheta < 0$, the film thins. The sign and the functional form of ϑ are sensitive not only to the universality class of the critical fluid but also to the precise boundary conditions of the order parameter [4,5] which are somewhat uncertain [13]. A key test of Eq. (2) is whether the thinning of the film depends on the temperature and film thickness *via* the variable x [3–5].

To produce helium films of different thickness, we suspend Cu plates at different heights above the bulk liquid as shown in Fig. 1. Inside the oxygen-free high conductivity Cu cell, each of six coin-shaped Cu capacitor plates of about 1.7 cm diameter and 0.27 cm thick is epoxied into the inside of an annular Cu guard ring. The electrically grounded guard rings minimize the error due to the fringing field and provide the means to support each plate [14]. The electrode-guard ring assemblies are polished to a haze-free mirror finish using 1000-Å-diameter diamond powder. Atomic force microscopy (AFM) of similarly polished Cu plates over a 50 μm $\times$ 50 μm area indicates a rms roughness of about 100 Å. The gaps between the plates are set by three pieces of 0.2 mm thick Cu shim inserted between the guard rings. The uniformity of the gap is better than 5%. Tilt in the plates is estimated to be less than 10^{-4} rad.

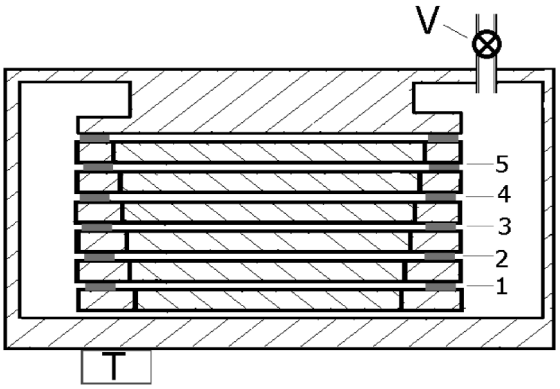

FIG. 1. Schematic of the experimental cell showing six electrodes forming five capacitors. A germanium thermometer, T, is attached to the cell bottom and the cell is sealed by needle valve, V, during the measurement.

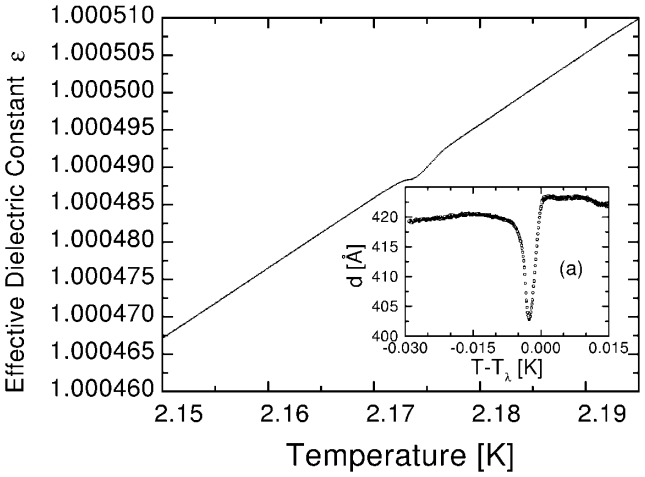

FIG. 2. Effective dielectric constant for capacitor 1 as a function of temperature. Inset (a) shows the film thickness calculated using Eq. (3), where a dip is found 2.6 mK below T_λ.

The experiment is conducted with 0.75 cm^3 of bulk liquid at the bottom of the cell. The height of each capacitor above the bulk liquid is determined from the cell geometry to be $h = 0.228$, 0.516, 0.806, 1.091, and 1.382 ± 0.005 cm. For these h, the film thicknesses d_0 expected from Eq. (1) are 423, 339, 299, 275, and 257 Å. The film thicknesses on the two electrodes comprising each capacitor are within 0.5% of each other. The vertical dimension of the cell limits the maximum h and thus the minimum film thickness. The maximum film thickness that we can measure is limited by the onset of capillary condensation between the plates. The 0.2 mm capacitor gap, which is large in comparison to the thickness of the adsorbed films, has been found necessary to forestall capillary condensation.

To eliminate film flow after the cell is filled, a mechanical needle valve V positioned on top of the cell is shut and the fill line is evacuated. The fill line, electrical leads, and mechanical valve are progressively heat sunk to an isothermal shield S1, to a stage S2, and finally to the cell. During measurements, S1 is controlled at 2.05 K $\pm$ 50 μK. The cell temperature, which is monitored by a thermometer attached to the cell, is controlled to ± 2 μK by applying heat to S2. It is estimated that the temperature difference between V and the cell is less than 2 μK and the temperature homogeniety in the cell for $T > T_\lambda$ is of the same order. T_λ is determined to ± 5 μK by means of the thermal conductivity anomaly of bulk ^{4}He.

The capacitance between adjacent plates is measured using a standard bridge technique [14] with a reference capacitor of similar construction anchored to the outside bottom of the cell. The empty capacitance C_0 of each of the five capacitors is found to be constant over the temperature range studied. In Fig. 2, we show for capacitor 1 a plot of the effective dielectric constant $\varepsilon(T) = C/C_0$, where T is the temperature and C is the capacitance when bulk liquid is present at the bottom of the cell. Because of the large gaps used in the experiment, $\varepsilon \simeq 1.000\,49$, where the vapor contributes about 4.4×10^{-4} to ε and the film contributes only about 5×10^{-5}. The temperature dependence of ε reflects the density of the saturated vapor.

In Fig. 2, a dip can be seen just below T_λ. A similar dip is found in $\varepsilon(T)$ for every capacitor. This dip cannot be accounted for by any known anomaly in the vapor phase [15]. The dip is reproducible upon warming and cooling and independent of frequency and voltage used in the bridge. The observed dip is more than 40 times sharper and 30 times larger than can be accounted for by critical anomalies in the surface tension [16] and the liquid density [17]. The addition of 10% ^{3}He reduces the thermal conductivity of the superfluid film 1000-fold [17], but it has no significant effect on the shape, magnitude, or position of the dip relative to (the now lowered) T_λ. A similar dip, twice the size of the background scatter, has been seen in an earlier measurement of the ^{4}He film thickness on Ag [18].

Ideally, because the capacitances due to the liquid film and the vapor in the capacitor gap add in series, we can calculate the film thickness d from $\varepsilon(T)$, according to

$$d = \frac{G}{2}\left(\frac{1}{\varepsilon_{\text{vapor}}} - \frac{1}{\varepsilon(T)}\right) \Big/ \left(\frac{1}{\varepsilon_{\text{vapor}}} - \frac{1}{\varepsilon_{\text{film}}}\right), \quad (3)$$

where G is the capacitor gap. For films of 100 Å or thicker, the average density of the film changes by less than 1% due to compression by van der Waals forces of the substrate. Thus, the dielectric constant of the film can be assumed to be the same as in bulk $\varepsilon_{\text{film}} \approx 1.0576 \pm 0.000\,05$. The uncertainty quoted corresponds to the variation between 2.14 and 2.2 K. To calculate the dielectric constant of the vapor $\varepsilon_{\text{vapor}}(T)$, we use the Clausius-Mossotti equation, where the molar polarizability is $0.123\,296 \pm 0.000\,030$ cm^3/mole [19] and the gas

density is estimated using an effective second virial coefficient $B'(T) = 1.08 \times B(T)$ from Ref. [20]. This $B'(T)$ makes the film thickness approximately temperature independent above and below T_λ for all the capacitors. The $B(T)$ from Ref. [20] is calculated from higher temperature data ($2.6 < T < 27$ K).

We find according to Eq. (3) that the film thicknesses for $T \gg T_\lambda$ are 575, 514, 588, 391, and 298 Å, for capacitors 1 to 5, respectively. These thicknesses exceed the prediction of Eq. (1) by 36%, 52%, 97%, 42%, and 16%, respectively. These discrepancies with theory cannot be explained completely by the expected enhancement of the surface area due to roughness. AFM measurements of similarly prepared surfaces suggest an enhancement of the surface area of 2–10% and hence an increase of 2–10% in d and Δd as computed from Eq. (3).

By contrast, there are other sources of error that we expect will shift d from its true value but which will *not* affect Δd. While the corrections for these effects are very small, 10^{-5} in dielectric constant, they translate to shifts in the apparent film thickness as large as what we have observed. Micron-size scratches and dust particles, for example, can lead to localized capillary condensation on the surface. Capacitor 3, which shows the greatest discrepancy, visually also shows the most scratches. There also is the contribution of edge effects and stray capacitances. In our subsequent analysis, to estimate the true film thickness, we subtract a *temperature independent* constant from the result of Eq. (3) so that $d = d_0$ for the normal fluid film away from the transition region. This is equivalent to assuming that DLP theory is correct in this regime. d_0 is the film thickness predicted by Eq. (1).

In Fig. 2(a), we show the film thickness d for capacitor 1 calculated in this manner. We note that the superfluid film away from the transition region is noticeably thinner than the normal fluid film. This is consistent with a recent prediction that away from the transition region a thinning of the superfluid film is expected due to the Goldstone modes [21]. The most prominent feature and the main result of this Letter is the thinning centered just 2.6 mK below T_λ.

Figure 3(a) shows that both the magnitude of the thinning Δd and the temperature of the minimum decrease systematically for the various capacitors with increasing h. According to Eq. (2), the minimum of the film thickness should coincide with the minimum of $\vartheta(x)$ and therefore should happen at a particular value of $x = td^{1/\nu}$. Indeed, this is what we find. If we use the corrected thickness as described above, the film thickness minimum occurs at the same value of x for all the films, i.e., $x_m = -9.2 \pm 0.2$, as seen in Fig. 3(b). If we use the uncorrected d from Eq. (3), however, the minima of the curves occur for x values ranging between 12 and 25.

The temperature of the maximum of the specific heat of the films confined between two solid walls has also been observed to decrease as the thickness of the film

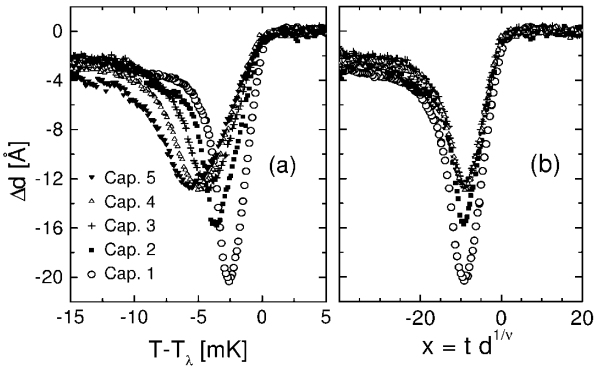

FIG. 3. (a) Fluctuation-induced film thinning Δd vs temperature, showing a systematic trend for films on the five capacitors. (b) The same data plotted vs the scaling variable x, showing the minimum of all five films occurs at $x = -9.2 \pm 0.2$. For clarity, only every fourth point is shown for the various data sets in panels (a) and (b). The uncertainty in Δd is 2%–10%, based on AFM measurements of similar substrates.

decreases and occurs at $x \approx -10$, for films between 500 and 7000 Å [22]. It is intriguing that this x value is quite close to the film thickness minimum in this experiment.

As shown in Fig. 4(a) and its inset, the *magnitude* of $\vartheta(x)$ calculated using Eq. (2) shows an almost linear increase with height h. We do not a have an explanation of this effect. It has been suggested that ϑ can depend on an additional "off-coexistence" scaling variable $y = hd^{\Delta/\nu}$, where for the superfluid transition $\Delta/\nu = 2.47$ [4,12,23]. If we correct ϑ for a linear dependence on y, the resulting deviation in the curves is reduced tenfold. Alternatively, we find just as good an improvement if we attribute the deviation to a predicted enhancement $[1 + 3(R/d)^2]$ to the prefactor of ϑ in Eq. (2) [21], where R, the roughness of the Cu surface, is assumed to be $R = 127 \pm 15$ Å. However, the same roughness enhancement has been predicted for the van der Waals term [24] in Eq. (2). If the roughness correction is applied to both

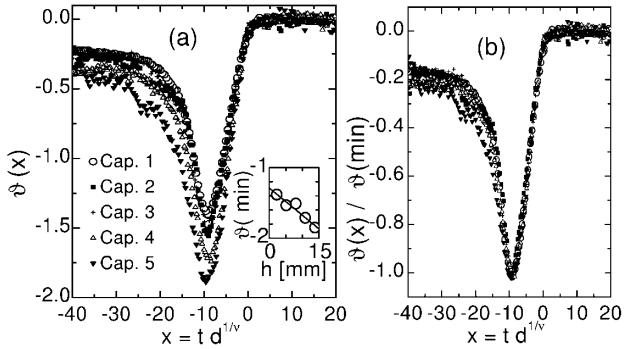

FIG. 4. (a) The scaling function ϑ vs x. The magnitude of the minimum increases systematically with height h of the capacitor. The inset shows the value of ϑ at the minimum vs height. A 10% uncertainty in Δd implies an uncertainty of 10% in ϑ. (b) ϑ normalized by the value at its minimum vs x. As in Fig. 3, every fourth data point is shown.

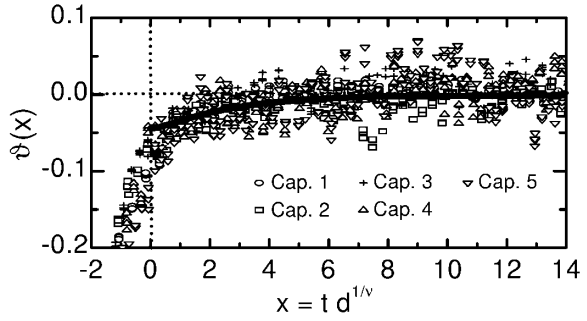

FIG. 5. Blowup of the region for $x > 0$ in Fig. 4(a). Every other data point is shown. The dark line shows a prediction from Fig. 9 in Ref. [5].

terms, a negligible net correction to ϑ results. As a third possibility, the observed trend may be related to a "lack of scaling" observed in the magnitude of the specific heat scaling function [22]. In Fig. 4(b), we show ϑ for each of the curves normalized by the value at its minimum. The collapse of the curves shows that, regardless of the precise cause of the trend in Fig. 4(a), there is a "universal" temperature dependence in the thinning of the film which is consistent with finite-size scaling.

While quantitative prediction does not exist for ϑ over the entire range of x, we show in Fig. 5 a blowup of Fig. 4(a) in the region $x \gtrsim 0$ (i.e., $T \gtrsim T_\lambda$) where predictions do exist. The data are in reasonable agreement with the prediction of Ref. [5]. The experimental value $\vartheta(0) = -0.070 \pm 0.030$ agrees with theoretical estimates of $\vartheta(0)$ which range between -0.044 to -0.06 [4,5]. These theoretical predictions assume the superfluid order parameter vanishes at both the film-vapor and film-substrate interfaces.

In summary, we have shown evidence of the critical Casimir effect in ^{4}He films near the superfluid transition. If the correctness of DLP theory is assumed away from the transition region, the temperature dependence of the thinning and the position of the film thickness minimum, in particular, are consistent with finite-size scaling.

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