Boundary conditions and critical Casimir forces in helium

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Abstract

If a fluid near its critical point is confined between two interfaces, the long-ranged critical fluctuations in the order parameter will mediate a force. This force, known as the critical Casimir force, is a direct analog of the Casimir force in electromagnetism. Dielectric constant measurements of helium films adsorbed on Cu electrodes provide evidence for the existence of the critical Casimir force near the superfluid transition in ^{4}He and near the tricritical point in ^{3}He-^{4}He mixtures. In pure ^{4}He, we find the force is attractive but near the tricritical point the force appears repulsive, a change due to the extraordinary boundary conditions at the tricritical point.

Key words: critical Casimir force; specific heat; helium

1. Introduction

When a fluid undergoing a phase transition is confined between two flat surfaces, there is a correction $E(d)$ to the free energy per unit area that depends on the separation d between the surfaces. This correction affects the specific heat, a second derivative of the free energy, and also manifests itself in an effective force per unit area $F = -\left(\partial E/\partial d\right)_T$ between the surfaces confining the film. Such effects can be readily verified near a critical point when the diverging correlation length ξ of the fluctuations in the order parameter becomes comparable to the film thickness d. Fisher and deGennes[1,2] propose a universal form for the finite-size correction near a critical point

$$E(d) = \frac{k_B T_c}{d^2}\Theta\left(d/\xi\right) \tag{1}$$

where $\xi = \xi_{o\pm}\left|t\right|^{-\nu}$ and the reduced temperature $t = T/T_c - 1$. Θ is a scaling function that is predicted to depend on the universality class and the boundary conditions of the order parameter[2,4–7]. The corresponding

$$F = \frac{k_B T_c}{d^3}\vartheta\left(d/\xi\right) \tag{2}$$

where $\vartheta\left(d/\xi\right) = 2\Theta - d\partial\Theta/\partial d$[4] is called the critical Casimir force due to a formal analogy with the Casimir force in electromagnetism[3,4]. While the Casimir force is due to the confinement of zero point fluctuations in the electromagnetic field, the critical Casimir force is due to confinement of fluctuations in the order parameter.

Evidence for Eq.1 is found, for example, in the observed finite-size correction to the specific heat of helium films. The maximum of the film specific heat occurs when the scaling variable $x = td^{1/\upsilon} = \left(\xi_o d/\xi\right)^{1/\upsilon} \simeq 9$[4,8], consistent with finite-size scaling(Eq.1). Evidence of the critical Casimir force has also been reported in certain adsorbed binary fluid mixture films[9].

In our experiments, we have sought to observe the effect of the critical Casimir force on liquid helium films adsorbed on Cu substrates near the lambda point. In this case, superfluid fluctuations are confined between the film-substrate and film-vapor interfaces. An experiment by Dionne and Hallock in 1989 shows an anomaly in the helium film thickness suggestive of such a force[10]. Our measurements have found an attractive critical Casimir force in ^{4}He films near the superfluid transition[11] and a repulsive Casimir force near the tricritical point TP of ^{3}He-^{4}He mixtures[12].

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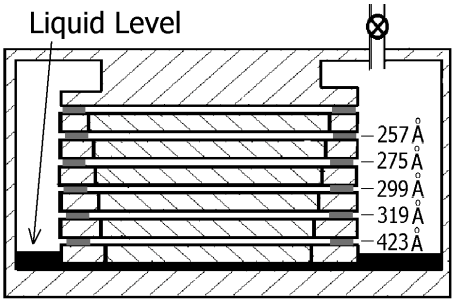

Fig. 1. A schematic of the cell used to study films of pure ^{4}He and ^{4}He with small amounts of ^{3}He added. The adsorbed film thickness decreases the higher up in the cell we go. The bulk liquid helium at the bottom of the cell is shown as a black layer. The height h above the bulk liquid for the various capacitors ranges between 2 mm and 14 mm, giving adsorbed film thicknesses between 423 and 257Å.

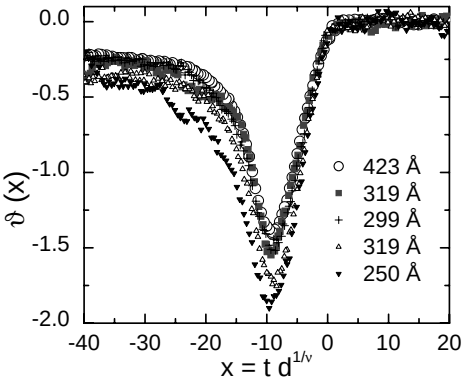

Fig. 2. The scaling function ϑ vs the scaling variable $x = td^{1/\upsilon} = (\xi_o d/\xi)^{1/\upsilon}$ where $\nu = 0.6705$[14]. The 5 different curves correspond to the 5 different h in Fig. 1. The uncertainty in ϑ is about 20%.

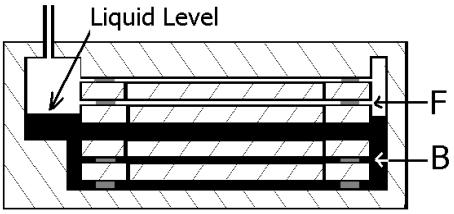

Fig. 3. A schematic of the cell used to study the adsorbed films near the tricritical point TP. Cap. B is submerged in the bulk liquid. Cap. F is 2mm above the liquid level.

2. ^{4}He films near the superfluid transition

In Fig. 1, we show a schematic of the experimental cell we used for films of pure ^{4}He and dilute mixtures. There are six capacitor plates forming 5 capacitors at different heights h above the bulk liquid. In accord with the theory of wetting films[13] and finite-size scaling[2,5], the thickness of a helium film wetting a Cu substrate a height h above the bulk liquid is given by

$$Mgh = \alpha/d^3 + Vk_BT_c\vartheta/d^3 \quad (3)$$

In the first term, g is the gravitational acceleration, h the height above the bulk liquid, and M the mass per atom of the bulk liquid. In the second term, $\alpha = 2600\text{K}\text{Å}^3/(1 + d/193\text{Å})$ is a coefficient characterizing the van der Waals attraction of the helium atom to the Cu substrate[13]. The last term is the predicted chemical potential difference between the film and bulk due to the critical Casimir force, where V the specific volume per atom in the bulk liquid[2,4,5,11].

Far from the superfluid transition, it is expected that $\vartheta \to 0$[2,4,5,7] and the film thickness d at a given h, according to Eq.3, is determined only by a competition between the van der Waals attraction of the liquid to the substrate and gravity which pulls the liquid to the bottom of the cell. The film is progressively thinner on surfaces higher up in the cell. Close to T_c, the critical Casimir force modifies the effective interaction with the substrate, so that if $\vartheta < 0$, the liquid film will thin, producing a dip.

We, indeed, do observe a dip in measured thickness of ^{4}He films near the superfluid transition. In Fig. 2, we show ϑ calculated from the measured thickness for films at different h using Eq. 3[11]. Evidently, $\vartheta < 0$ so that the critical Casimir force is attractive. Such an attractive Casimir force occurs whenever the boundary conditions are the same at both of the confining interfaces[4–7,15]. For pure ^{4}He this makes sense because the order parameter vanishes at the boundaries, consistent with Dirichlet boundary conditions at both the film-vapor and film-substrate interfaces. In Fig. 2, the minimum of ϑ occurs at the same value of d/ξ for films of different thickness. This is expected due to the d/ξ dependence of ϑ. However, the curves do not fall perfectly upon each other. Various explanations have been proposed for this lack of collapse[7,11,15], including a systematic error in the determination of d, but it is interesting that the specific heat of films, also a measure of ϑ, similarly show a lack of collapse[8]. Further work, both experimental and theoretical, is needed to clarify this issue. The measured ϑ is consistent with an ϵ expansion calculation of ϑ for Dirichlet boundary conditions in the small region above T_c[4,11]. However, no appropriate calculations exist for below T_c. A recent calculation of ϑ has been made for T above and below T_c[16]. Since periodic boundary conditions are assumed, it is not directly pertinent to our experiment.

3. ^{3}He-^{4}He mixture films near the tricritical point

In Fig. 3, we show the cell used for measurements near TP, with only two capacitors F and B. The ad-

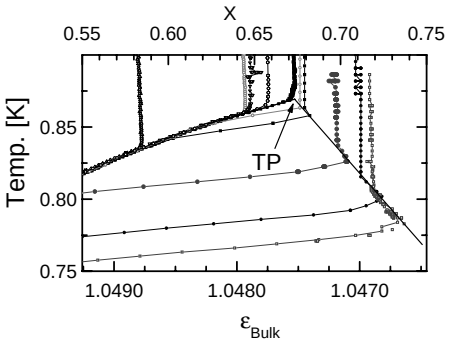

Fig. 4. The temperature T vs. the dielectric constant ε_{bulk} measured by Capacitor B at some point within the bulk liquid. Along the upper axis we show the X corresponding to the measured ε_{bulk}. The first deviation from a straight line marks the onset of phase separation.

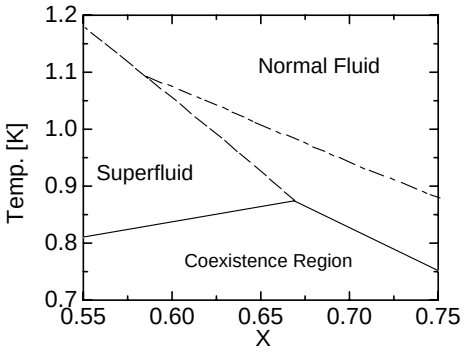

Fig. 5. A schematic drawing of the bulk phase diagram for liquid ^{3}He-^{4}He mixture near TP. X is the mole fraction of ^{3}He in the mixture. The superfluid transition marked by a dashed line, the coexistence region is marked by solid lines[17,18]. The dash-dotted line marks the onset of superfluidity in the ^{4}He rich layer near the walls and the substrate surface[19].

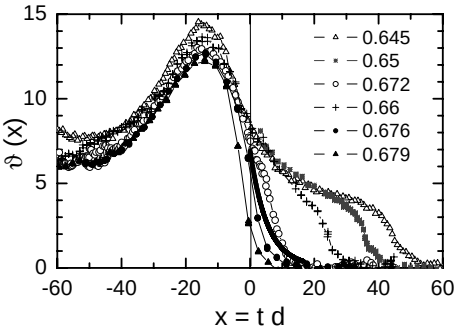

Fig. 6. The scaling function ϑ vs the scaling variable $x = td^{1/\nu}$ where $\nu = 1$ along a path of constant X near TP[18]. The different curves correspond to 5 different mole fractions X close to the tricritical point. For $X < 0.672$, we observe a shoulder-like thickening associated with the superfluid onset in the bulk liquid and a peak associated with phase separation. As $X \sim 0.672$ is approached, the shoulder and peak merge.

sorbed film is measured using cap. F, situated 2 mm above the bulk mixture liquid surface. Cap.B measures the effective dielectric constant ε_{bulk} at specific height inside the bulk liquid. The measured T vs. ε_{bulk} is shown in Fig. 4. The kinks in ε_{bulk} are due to phase separation in the bulk liquid and mark the coexistence region. The mole fraction of ^{3}He in the liquid $X = n_3/(n_3 + n_4)$ where n_3 is the number of moles of ^{3}He and n_4 is the number of moles of ^{4}He. In Fig. 4, we also show the average X within capacitor B, calculated from ε_{bulk}. From this data, we are able to verify our temperature scale and locate TP at X_t =0.672±0.001, T_t =0.8698±0.0001K.

In pure ^{4}He films and in ^{4}He with small amounts of ^{3}He added, the critical Casimir force is observed to be attractive, i.e $\vartheta < 0$, producing a dip in the film thickness centered just below the bulk superfluid transition temperature. As ^{3}He is added, the dip follows the superfluid transition to lower temperature, becoming progressively broader but remaining about the same magnitude as for pure ^{4}He for $X < 0.6$[11].

At $X \sim 0.6$, however, there is a change in the mixture film close to the substrate surface. The liquid mixture within a few layers of the substrate surface is always enriched in ^{4}He. The higher pressure near the substrate due to van der Waals forces favors the denser ^{4}He rich fluid there. ^{4}He is denser due to the smaller quantum zero point motion. Below the dash-dotted line shown in Fig. 5 this ^{4}He rich layer near the substrate surface becomes superfluid, as determined by Laheurte et al.[19]. Because of this superfluid layer, for $X > 0.6$, different boundary conditions are present close to TP and the critical Casimir force there is expected to be repulsive rather than attractive[5,6,20].

In Fig. 6, we show the measured ϑ for a single height (2 mm) above the bulk liquid and various X close to tricritical mole fraction X_t. We use Eq. 3, but are careful to substitute for M and V the corresponding quantities for the bulk liquid mixture[12]. Evidently, $\vartheta > 0$ as expected, consistent with a repulsive force. For $X < 0.672$, we observe a shoulder-like thickening associated with the superfluid onset in the bulk liquid and a peak associated with phase separation. As TP ($X \sim 0.672$) is approached, the shoulder and peak merge. Further work is necessary to study in detail how the critical Casimir force evolves near $X \sim 0.6$ where the bulk superfluid transition line merges with the boundary layer superfluid transition line.

The thick line in Fig. 6 shows a theoretical calculation of ϑ near the tricritical point of the Ginzburg-Landau XY model, where the order parameter is assumed to be zero at one interface and nonzero at the other[20]. While the agreement between the theoretical and measured ϑ seems quite good, this agreement may be fortuitous, considering the 5-20% experimental uncertainty in ϑ[12]. At present, there is no theory

describing how the critical Casimir force evolves as X is varied from X_t.

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