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Critical Casimir effect and wetting by helium mixtures

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We have measured the contact angle of the interface of phase-separated ^{3}He-^{4}He mixtures against a sapphire window. We have found that this angle is finite and does not tend to zero when the temperature approaches T_t, the temperature of the tri-critical point. On the contrary, it increases with temperature. This behavior is a remarkable exception to what is generally observed near critical points, i.e. "critical point wetting". We propose that it is a consequence of the "critical Casimir effect" which leads to an effective attraction of the ^{3}He-^{4}He interface by the sapphire near T_t.

In 1977, J. W. Cahn predicted that "in any two-phase mixture of fluids near their critical point, contact angles against any third phase become zero in that one of the critical phases completely wets the third phase and excludes contact with the other critical phase" [1]. This "critical point wetting" is a very general phenomenon [1–4]. We found an exception to it by studying helium mixtures in contact with a sapphire window [5].

In fact, de Gennes [6] had noticed that long range forces may prevent complete wetting. Nightingale and Indekeu [7] further explained that if a long range attraction is exerted by the third phase on the interface between the two critical phases, partial wetting may be observed up to the critical point. We propose that, in ^{3}He-^{4}He mixtures near their tri-critical point, this attraction is provided by the confinement of the fluctuations of superfluidity, i.e. a critical Casimir effect [8,7,9–11] in the ^{4}He-rich film between the sapphire and the ^{3}He-rich bulk phase (Fig. 1).

For a solid substrate in contact with a phase-separated ^{3}He-^{4}He mixture, complete wetting by the ^{4}He-rich "d-phase" was generally expected, due to the van der Waals attraction by the substrate [12,13]. However, we measured the contact angle θ of the ^{3}He-^{4}He interface on sapphire, and we found that it is finite. Furthermore, it increases between 0.81 and 0.86 K, close to the tri-critical point at $T_t = 0.87$ K [14]. This behavior is opposite to the usual "critical point wetting" where θ decreases to zero at a wetting temperature T_w below the critical point. In this letter, we briefly recall our experimental results before explaining why the "critical Casimir effect" provides a reasonable interpretation of our observations.
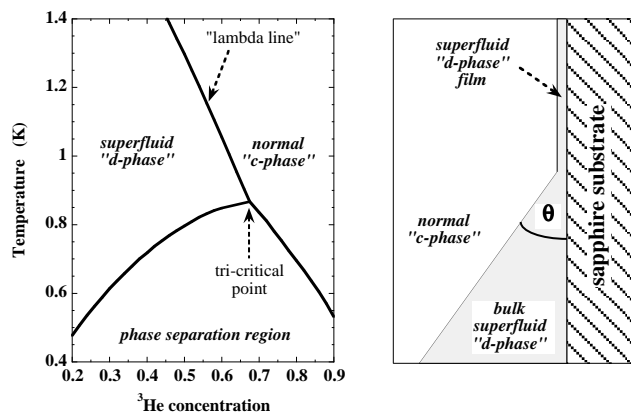

FIG. 1. The phase diagram of ^{3}He-^{4}He mixtures (left graph). On the right, a schematic view of the contact angle θ. There is a superfluid film of ^{4}He rich "d-phase" between the substrate and the c-phase. Its thickness being finite, θ is non-zero.

We use a dilution refrigerator with optical access [14]. Our liquid sample is at saturated vapor pressure, and confined between two sapphire windows which form an interferometric cavity. The inside of the windows is treated to have a 15% reflectivity. The cell is made of pure copper and neither the windows nor the helium absorb any light, so that a very good thermal homogeneity is achieved. From fringe patterns, we analyze the profile of the c-d interface near its contact line with one of the windows [14,15]. A fit with a solution of Laplace's equation gives the interfacial tension σ_i and the contact angle θ. As T approaches T_t, the capillary length vanishes so that the region to be analyzed becomes very small. However, our typical resolution is 5 μm, significantly smaller

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than the capillary length (from 84 μm at 0.81 K to 33 μm at 0.86 K). Here, we present results only in this temperature range because, closer to the tri-critical point, we would need a better resolution and, below 0.80 K, refraction effects distort the fringe patterns [14].
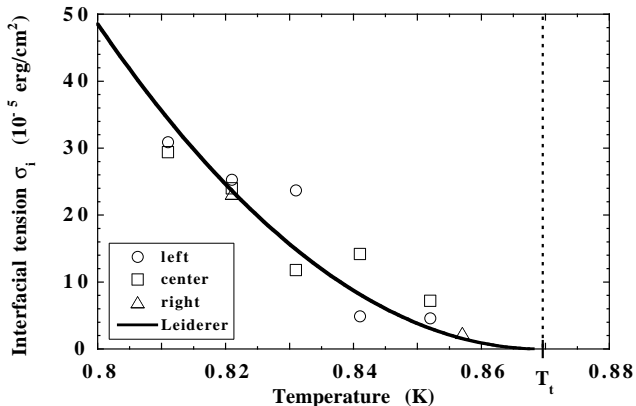

FIG. 2. Our measurements of the interfacial tension agree with Leiderer's results (solid line). Different symbols correspond to three different positions along the contact line.
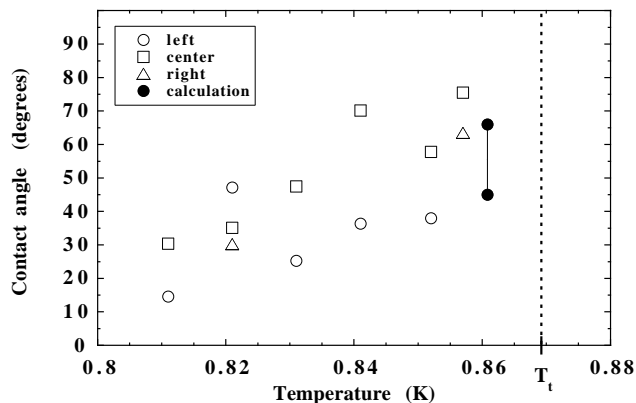

FIG. 3. Temperature dependence of the contact angle θ. Black symbols correspond to the present calculation.

For each temperature, we analyzed three pictures at different positions along the contact line. As shown in Fig. 2, our measurements of σ_i agree well with Leiderer's result $\sigma_i = 0.076 \, t^2$ erg/cm^2 ($t = (1-T/T_t)$ is the reduced temperature) [16]. As for the contact angle θ (Fig. 3), we found that it is non-zero and that it increases with T. On these measurements, the typical error bar is $\pm$ 15 °. It originates in several experimental difficulties such as the precise location of the contact line and a slight bending of the windows which are under stress [14].

When cooling down a homogeneous mixture with concentration higher than the tri-critical value X_t, J.P. Romagnan et al. [12] found that a superfluid film formed between the bulk mixture and a metallic substrate. As

they approached T_{eq} where separation into "c-" and "d-" phases occurred, they observed a film thickness diverging as $(T - T_{eq})^{-1/3}$. This behaviour is characteristic of the van der Waals attraction by the substrate, which is stronger on the densest phase [13]. One used to believe that van der Waals forces were the only long range forces in this problem, so that the film thickness should diverge to infinity, and complete wetting by the superfluid d-phase should occur. However, Romagnan et al. only measured this thickness up to about 20 atomic layers (60 Å). If other forces act on the film near the tri-critical point, its thickness can saturate at a value larger than 60 Å. R. Garcia and M. Chan [10] have shown that superfluid films of pure ^{4}He get thinner near T_λ, due to the critical Casimir effect. Our situation is similar: our d-phase film is just below its superfluid transition, and we have calculated that Casimir forces limit the film thickness to a few hundred Å .

An increasing variation of $\theta(T)$ is also surprising. Young's relation writes:

$$\cos(\theta) = \frac{\delta\sigma}{\sigma_i} = \frac{\sigma_{sc} - \sigma_{sd}}{\sigma_i} \qquad (1)$$

As the critical point is approached, both σ_i and $\delta\sigma$ tend to zero. It is often assumed that $\delta\sigma$ is proportional to the difference in concentration between the two phases. If this was always true, the critical exponent of σ_i would always be larger than that of $\delta\sigma$ [3]. Consequently, θ would always decrease to zero at a wetting temperature T_w below the critical point. Our observations show that this reasoning does not apply to helium mixtures.

Let us now follow D. Ross et al. [17] to calculate θ. We first calculate the "disjoining pressure" $\Pi(l)$ as a function of the thickness l of the d-phase film (Fig. 1). For this we consider three long range forces: the van der Waals force, the Casimir force and the "Helfrich" force [20]. At the equilibrium film thickness $l = l_{eq}$, $\Pi(l)$ has to cross zero with a negative slope. If l_{eq} was macroscopic, the substrate (s) to c-phase interface would be made of an s-d interface plus a c-d interface. Its energy per unit area would thus be $\sigma_{sc} = (\sigma_{sd} + \sigma_i)$. If l_{eq} is small, a correction to the above formula has to be added, which is the integral of the disjoining pressure from infinity to l_{eq}. Finally, Young's relation imply

$$\cos(\theta) = \frac{\sigma_{sc} - \sigma_{sd}}{\sigma_i} = 1 + \frac{\int_{l_{eq}}^{\infty} \Pi(l)dl}{\sigma_i} \qquad (2)$$

Let us start with the van der Waal contribution $\Pi_{vdW}(l)$ to $\Pi(l)$. The net effective force on the interface is the difference between the respective van der Waals attractions on the d- and c-phase. For helium on copper, Garcia found that this attraction is A_0/Vl^3, with $A_0 = 2600$ K.Å^3 (V is the atomic volume) [10]. For our window with its insulating coating, we expect a smaller value. Sabisky [18] found $A_0 = 980$ K.Å^3 for liquid ^{4}He on CaF$_2$.

We thus estimate $A_0* \approx 1000$ K.Å^3 in our case. As for the coefficient of the differential force, it is now

$$A = A_0 * \left(\frac{1}{V_d*} - \frac{1}{V_c*} \right) \quad (3)$$

where $V_{c,d}$ are the respective atomic volumes in the two phases [19]. We included the retarded term in the van der Waals potential [10] and finally found

$$\Pi_{vdW}(l) = \frac{A}{l^3(1 + l/193)} = \frac{14.72t - 2.82t^2 + 2.29t^3}{l^3(1 + l/193)} \quad (4)$$

in K/Å^3 with l in Å.

Let us now consider the Casimir force. Following Garcia [10], the confinement of superfluid fluctuations inside a film of thickness l gives a contribution to the disjoining pressure

$$\Pi_{Cas} * (l) = \frac{\vartheta(x)\, T_t}{l^3} \quad (5)$$

where $x = tl$ and the "scaling function" $\vartheta(x)$ is negative, with a minimum of about -1.5 at $x \approx 10$. The sign of $\vartheta(x)$ depends on the symmetry of the boundary conditions on the two sides of the film [11,9]. In Ref. [10] as in our case, the whole film is superfluid except near both interfaces where the order parameter vanishes on a distance ξ, the correlation length. Consequently, the boundary conditions are symmetric for this order parameter and $\vartheta(x)$ is negative, meaning an attractive force. Note that in Garcia's second experiment [11] on mixtures, the film was separated into a superfluid subfilm near the wall and a normal one near the liquid-gas interface; Garcia considered this as an anti-symmetric situation leading to a repulsive force between the wall and the liquid-gas interface. This second experiment is different from ours because it measures a Casimir force on a liquid-gas surface while ours has to do with the c-d interface. As a result our experiment is paradoxically more similar to Garcia's first experiment [10] with pure ^{4}He which has also symmetric boundary conditions than with Garcia's second experiment on mixtures [11].

In order to evaluate $\vartheta(x)$, and in the absence of any other determination, we have taken Garcia's curve labelled "Cap. 1" in Ref. [10]. It corresponds to a film thickness of about 400 Å , as found below for $t = 10^{-2}$. Fig. 4 shows that, at this temperature, the resulting Casimir contribution dominates the van der Waals one above about 100 Å. This is because the coefficient A in Eq. 4 vanishes with t, so that, for $t = 10^{-2}$, it is about 0.15, ten times less than the maximum amplitude of $\vartheta(x)$. We still need to discuss our approximations further. We are dealing with a tri-critical point instead of the lambda transition in Garcia's case [10]. According to Krech and Dietrich [9] the Casimir amplitude is twice as large for tri-critical points compared to ordinary critical points.

Doubling Garcia's scaling function enlarges θ and improves the agreement with our experiment (see below). Furthermore, in our system, concentration and superfluidity fluctuations are coupled together. Both should be considered in a rigorous calculation which has not yet been done. The boundary conditions are symmetric for superfluidity but they are anti-symmetric for concentration fluctuations since the film is richer in ^{4}He near the substrate than near the c-phase. We thus believe that a rigorous calculation should include two contributions with opposite sign. We assume that the confinement of superfluidity dominates because the Casimir amplitude is roughly proportional to the dimension N of the order parameter [9] ($N = 2$ for superfluidity and $N = 1$ for concentration). We hope that our intuition can be confirmed by further theoretical work.
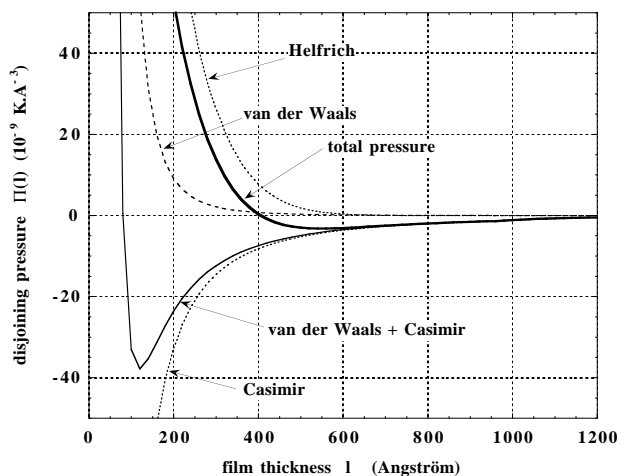

FIG. 4. The three contributions to the disjoining pressure for $t = 10^{-2}$. The total pressure is zero at $l_{eq} = 400$ Å.

The third contribution $\Pi_H * (l)$ originates in the limitation of the amplitude z of the c-d interface fluctuations to a fraction of the thickness l. According to Helfrich [20], $< (z)^2 > \approx l^2/6$ and, following Ross et al [17]

$$\Pi_H(l) = \frac{T}{2L^2 * l} \,, \quad (6)$$

where L is a long wavelength cutoff. L can be calculated from the equipartition theorem as

$$L* = *\xi \exp\left(\frac{2\pi\sigma_i * l^2*}{6k_B * T} \right) \quad (7)$$

The bulk correlation length ξ is related to the surface tension σ_i* by $\xi^2* \approx k_B * T/(3\pi\sigma_i)$, where the factor 3 is consistent with both Refs. [16] and [17]. Finally

$$\Pi_H(l) = \frac{3\pi\sigma_i*}{2l} \exp\left(\frac{-2\pi\sigma_i * l^2*}{3k_B * T} \right) \quad (8)$$

The disjoining pressure and the equilibrium film thickness are now obtained by adding the three above contributions and by looking for l_{eq} such that $\Pi(l_{eq}) = 0$. Fig. 4

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shows the results of a calculation for $t = 10^{-2}$. If we had the van der Waals contribution only, the disjoining pressure would be positive everywhere and it would repell the film surface to infinity (complete wetting). The Casimir contribution is negative and large enough to induce partial wetting. As for the Helfrich repulsion, it is very large at small thickness but it decreases exponentially so that its effect is to shift the equilibrium thickness by a few hundred Å. Fig. 4 shows that, for $t = 10^{-2}$, $l_{eq} = 400$ Å. This is larger than $\xi \approx 100$ Å, so that the superfluidity is well established in the middle of the d-phase film. At this temperature we finally calculated the contact angle with Eq. 2, and found $\theta = 45$ degrees, in good agreement with experimental results (Fig. 3). In order to account for tricriticality, one could double the Casimir amplitude; this would roughly double $(1- \cos \theta)$ and change 45 into 66 degrees, in even better agreement with our data.

The most important result is that θ is finite. Its exact magnitude depends on the many approximations made above, especially on the value of $\vartheta(x)$ which is only known through Garcia's measurement in a slightly different situation. We repeated the same calculation for $t = 5.10^{-2}$, i.e. $T = 0.83$ K, and we found $\theta = 30$ degrees. However, at this temperature, we found a thinner film for which the value of $\vartheta(x)$ is less accurately known. It is reasonable to find that the contact angle vanishes away from T_t because the Casimir force vanishes while the van der Waals force increases. Clearly, there is a temperature region where θ increases with T, as found experimentally. As for very close to T_t, a crossover to a different regime should occur when $l_{eq} \approx \xi$ so that short range forces should dominate; whether the contact angle keeps increasing, or reaches a finite value, or starts decreasing to zero is an additional question to be solved.

Let us finally remark that, if we had an ordinary critical point with van der Waals forces and concentration fluctuations only, the Casimir force would be repulsive [21] and favor critical point wetting. In the case of our helium mixtures, it is the symmetric boundary conditions for superfluidity which lead to a Casimir force acting against critical point wetting. One obviously needs more measurements for a more precise determination of θ and a calculation of the scaling function for a more accurate theoretical prediction.

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