Critical Casimir Effect and Wetting by Helium Mixtures

T. Ueno, S. Balibar, T. Mizusaki, F. Caupin, and E. Rolley

Laboratoire de Physique Statistique de l’Ecole Normale Supérieure, associé aux Universités Paris 6 et Paris 7 et au CNRS, 24 rue Lhomond 75231 Paris Cedex 05, France

(Received 13 July 2002; published 20 March 2003)

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 tricritical 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 $T_t$.

DOI: 10.1103/PhysRevLett.90.116102 PACS numbers: 68.35.Rh, 64.60.Fr, 67.60.–g

In 1977, 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. Then Nightingale and Indekeu [7] 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 tricritical point, this attraction is provided by the confinement of the fluctuations of superfluidity, i.e., a critical Casimir effect [7–11] 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 $^3$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 $\theta$ 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 tricritical point at $T_t = 0.87$ K [14]. This behavior is opposite to the usual critical point wetting where $\theta$ 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.

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 $\sigma_i$ and the contact angle $\theta$. 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 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 tricritical point, we would need a better resolution and, below 0.80 K, refraction effects distort the fringe patterns [14].

For each temperature, we analyzed three pictures at different positions along the contact line. As shown in Fig. 2, our measurements of $\sigma_i$ agree well with Leiderer’s result $\sigma_i = 0.076 i^2$ erg/cm$^2$ [$i = (1 - T/T_t)$ is the reduced temperature] [16]. As for the contact angle $\theta$ (Fig. 3), we found that it is nonzero and that it increases with $T$. On these measurements, the typical error bar is ±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 tricritical value $X_t$, Romagnan et al. [12] found that a superfluid film formed between the...
As the critical point is approached, both \( \sigma_s \) 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 \( \sigma_s \) would always be larger than that of \( \delta \sigma \) [3]. Consequently, \( \theta \) 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 Ross et al. [17] to calculate \( \theta \). 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 [18]. 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 \( \sigma_{sc} = (\sigma_{sd} + \sigma_j) \). 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 implies

\[
\cos(\theta) = \frac{\sigma_{sc} - \sigma_{sd}}{\sigma_j} = 1 + \int_{l_{eq}}^{\infty} \Pi(l)dl. \tag{2}
\]

Let us start with the van der Waals 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 \( A_0/V^2 \), with \( A_0 = 2600 \text{ K} \cdot \text{Å}^3 \) (\( V \) is the atomic volume) [10]. For our window with its insulating coating, we expect a smaller value. Sabisky [19] found \( A_0 = 980 \text{ K} \cdot \text{Å}^3 \) for liquid \(^4\text{He} \) on CaF\(_2\). We thus estimate \( A_0 = 1000 \text{ K} \cdot \text{Å}^3 \) in our case. As for the coefficient of the differential force, it is now

\[
A = A_0 \left( \frac{1}{V_d} - \frac{1}{V_c} \right), \tag{3}
\]

where \( V_{c,d} \) are the respective atomic volumes in the two phases [20]. We included the retarded term in the van der Waals potential [10] and finally found

\[
\Pi_{vdW}(l) = \frac{A}{l^3(1 + l/193)} = \frac{14.72r - 2.82r^2 + 2.29r^3}{l^3(1 + l/193)}, \tag{4}
\]

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

\[
\Pi_{Cas}(l) = \frac{\vartheta(x) T_l}{l^3}, \tag{5}
\]

where \( x = tl \) and the “scaling function” \( \vartheta(x) \) is negative, with a minimum of about \(-1.5\) at \( x = 10 \). The sign of \( \vartheta(x) \) depends on the symmetry of the boundary conditions on the two sides of the film [9,11]. In Ref. [10] as in our case, the whole film is superfluid except near both
interfaces where the order parameter vanishes on a distance \( \xi \), the correlation length. Consequently, the boundary conditions are symmetric for this order parameter and \( \theta(x) \) 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 antisymmetric 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 \( \theta(x) \), and in the absence of any other determination, we have taken Garcia’s curve labeled “Cap. 1” in Ref. [10]. It corresponds to a film thickness of about 400 Å, as found below for \( t = 10^{-2} \). Figure 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, which is 10 times less than the maximum amplitude of \( \theta(x) \). We still need to discuss our approximations further. We are dealing with a tricritical 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 tricritical points compared to ordinary critical points. Doubling Garcia’s scaling function enforces consistency 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 antisymmetric 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.

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 [18], \( \langle z(0) \rangle = l^2 / 6 \) and, following Ross et al. [17]  

\[
\Pi_{H}(l) = \frac{T}{2L^2 l},
\]

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

\[
L = \frac{\xi}{\exp \left( \frac{2\pi \sigma_i l^2}{6k_B T} \right)}.
\]

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

\[
\Pi_{H}(l) = \frac{3\pi \sigma_i}{2l} \exp \left( -\frac{2\pi \sigma_i l^2}{3k_B T} \right).
\]

The disjoining pressure and the equilibrium film thickness are now obtained by adding the three above contributions and by looking for \( l_{\text{eq}} \) such that \( \Pi(l_{\text{eq}}) = 0 \). Figure 4 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 repel 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. Figure 4 shows that, for \( t = 10^{-2} \), \( l_{\text{eq}} = 400 \) Å. This is larger than \( \xi = 100 \) 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 \( \theta = 45^\circ \), 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°, in even better agreement with our data.

The most important result is that \( \theta \) is finite. Its exact magnitude depends on the many approximations made above, especially on the value of \( \theta(x) \) which is known only through Garcia’s measurement in a slightly different situation. We repeated the same calculation for \( t = 5 \cdot 10^{-2} \), i.e., \( T = 0.83 \) K, and we found \( \theta = 30^\circ \). However, at this temperature, we found a thinner film.
for which the value of $\theta(x)$ is less accurately known. It is reasonable to find that the contact angle vanishes away from $T_\text{f}$, because the Casimir force vanishes while the van der Waals force increases. Clearly, there is a temperature region where $\theta$ increases with $T_\text{f}$, as found experimentally. As for very close to $T_\text{f}$, a crossover to a different regime should occur when $l_{\text{eq}} = \xi$ 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 $\theta$ and a calculation of the scaling function for a more accurate theoretical prediction.

We are grateful to C. Guthmann, S. Moulinet, M. Poujade, D. Bonn, J. Meunier, D. Chatenay, and E. Brezin for very helpful discussions. T. Ueno acknowledges support from the JSPS and the Kyoto University Foundation during his stay at ENS.

*Present address: Research Laboratory of Electronics and MIT-Harvard Center for Ultracold Atoms, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139.

Permanent address: Department of Physics, Graduate School of Science, Kyoto University, Kitashirakawa-Oiwake-cho, Sakyo-ku, Kyoto 606-8502, Japan.

[5] We believe that this is the first experimental evidence for an exception to critical point wetting. S. Ross and R.E. Kornbrekke [J. Colloid Interface Sci. 99, 446 (1984)] claimed that they had found such an exception with binary liquid solutions against glass, but M.R. Moldover and J.W. Schmidt [Physica (Amsterdam) 12D, 351, 1984] explained that this was an artifact due to their observation method. Our results are consistent with preliminary indications obtained with the same helium mixtures against an epoxy resin and with a magnetic resonance imaging technique by T. Ueno, M. Fujisawa, K. Fukuda, Y. Sasaki, and T. Mizusaki [Physica (Amsterdam) 284B–288B, 2057 (2000)]. However, in the latter work, the evidence was weaker since the error bar on the contact angle $\theta$ was as large as the value of $\theta$ itself near the critical point.