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New Measurements of Wetting by Helium Mixtures

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We have measured the contact angle of the ^{3}He–^{4}He interface on a sapphire window in the temperature range from 50 to 845 mK. Contrary to what had been found by Ueno et al. in two successive experiments, we have found complete wetting by the ^{4}He-rich phase. Our new results have two consequences: first, we suspect that there were some artefacts in the experiments by Ueno et al. Secondly, we now believe that the critical Casimir forces are dominated by the van der Waals force in this experimental situation.

KEY WORDS: wetting; Casimir forces; helium mixtures.

1. INTRODUCTION

Two successive experiments by Ueno *et al*. recently suggested that when a phase separated liquid mixture of ^{3}He and ^{4}He is in contact with a wall, the ^{3}He–^{4}He interface does not touch the wall with zero angle: according to these two experiments, the ^{4}He-rich phase does not completely wet solid walls. The first experiment was done in 2000 in Kyoto with a magnetic imaging technique.[1] According to its analysis, the contact angle was found to vary from about 20° at low temperature to $40° \pm 40°$near the tri-critical point at 0.87 K. The second one[2] was done in Paris in 2003 with an optical interferometric technique. Measurements were restricted to the critical region below the tri-critical point, and the contact angle was found to increase from about $15° \pm 15°$ at 810 mK to $55° \pm 15°$ at 860 mK. This increase appeared contradictory to "critical point wetting," the general phenomenon which had been predicted by J. W. Cahn[3] and observed in all systems up to now.[4–6]

In a third article,[7] Ueno *et al*. invoked the existence of long range forces to interpret their experimental results. Indeed, P. G. de Gennes had pointed out the importance of long range forces in Cahn's situation and he had opened the possibility of exceptions to critical point wetting if such long range forces were present.[8] In this third article,[7] Ueno *et al.* explained that "critical Casimir forces" had the right sign and magnitude to explain the anomalous wetting behavior which had been observed with He mixtures. These forces originate in the confinement of critical fluctuations between two surfaces.[9–11] In the case of He mixtures, Ueno *et al.* considered the fluctuations of superfluidity in a ^{4}He-rich superfluid film which might exist between the wall and the bulk ^{3}He-rich phase.

Given the interest of a first exception to critical point wetting, and its possible relation to the critical Casimir effect, it appeared worth checking Ueno's results by repeating his experiment in a different geometry. In this article, we present the results of this new experiment which, as we shall see, does *not* confirm Ueno's results: we now believe that the ^{4}He-rich phase completely wets the sapphire wall of our cell in the temperature range from 50 to 845 mK. The geometry change allowed us to make measurements in a much larger temperature domain than in Ref. 2, because the fringe pattern was much less sensitive to refraction effects. We were interested in making measurements at low temperature because of the prediction by Kardar and Golestanian[10] that the confinement of Goldstone modes contributes to the Casimir force in the whole temperature domain where the liquid is superfluid, not only close to the critical point. If this last contribution was large enough, it could explain a non-zero contact angle at low temperature, as was observed in the Kyoto experiment by Ueno *et al.*[1]

The present article is organized as follows. In Sec. 2, we describe our new experimental setup and our interferometric method before explaining how we analyzed fringe patterns and how we measured contact angles and interfacial energies; we also discuss possible sources of artefacts in the two previous experiments by Ueno *et al.* In Sec. 3, we present our new results and their implications for the magnitude of the Casimir forces. In conclusion, we make a few proposals for future work on this problem.

2. EXPERIMENTAL METHODS

As in ref. 2, we used an optical interferometric method to measure the profile of the ^{3}He–^{4}He interface near a sapphire wall. In Ref. 2, the sapphire wall was tilted by 10° with respect to vertical and the angle of incidence of the laser beam on the interface was large. As a consequence, large refraction effects occurred at this interface as soon as the difference in index δn between the two liquid phases was large. This restricted Ueno's analysis to a small temperature domain where δn was small, just below the tri-critical temperature $T_t = 0.87\,\mathrm{K}$. In order to avoid such problems, we rotated the cell geometry. As can be seen in Fig. 1, the sapphire window is now tilted by 21.2° with respect to horizontal. In this new geometry, the incidence angle of the laser beam on the interface is always less than 21.2° except if the contact angle is larger than 21.2° (we found it to be zero, so that the incidence angle was between 0° and 21.2°). A typical recording of fringe patterns is shown in Fig. 2. In the absence of interface [top image (a)], the pattern shows a set of parallel fringes because the two sapphire windows limiting the interferometric cavity are slightly tilted with respect to each other. In fact they are not strictly plane either, because they are pressed against indium seals—the cell needs to be leak tight—and this introduces stresses which are not strictly homogeneous. As a consequence, the fringes themselves are weakly curved.

When filling the cell, the ^{3}He–^{4}He interface appears in the cell and the fringe pattern is bent in the contact region [Fig. 2(b) and 3]. In order to obtain the interface profile, one needs to analyze this bending. The

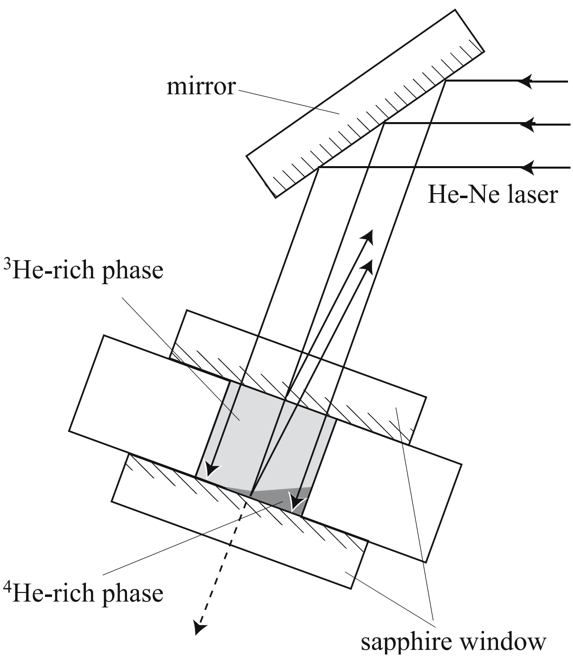

Fig. 1. Schematic drawing of the experimental setup. The diameter of the mirror is 25 mm. The sample space is $11 \times 11 \times\ 10$ mm and it is tilted by 21.2 ± 0.2 from horizontal. The cell is completely filled with liquid. For the ^{4}He–^{3}He interface to meet the lowest window, dead volumes were added above and below the interferometric cavity.

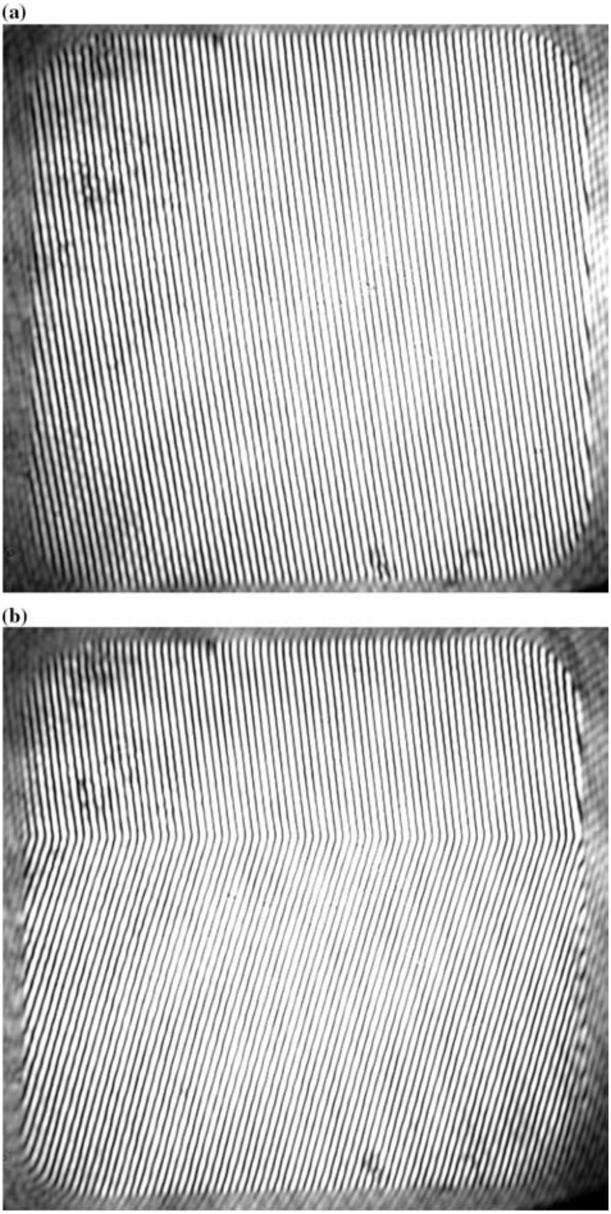

Fig. 2. The profile of the ^{3}He–^{4}He interface between phase separated liquid helium mixtures is calculated from the difference in optical path between a pattern with an interface [bottom image (b)] and a pattern without interface [top image (a)]. The top pattern was recorded at 520 mK and the bottom one at 730 mK.

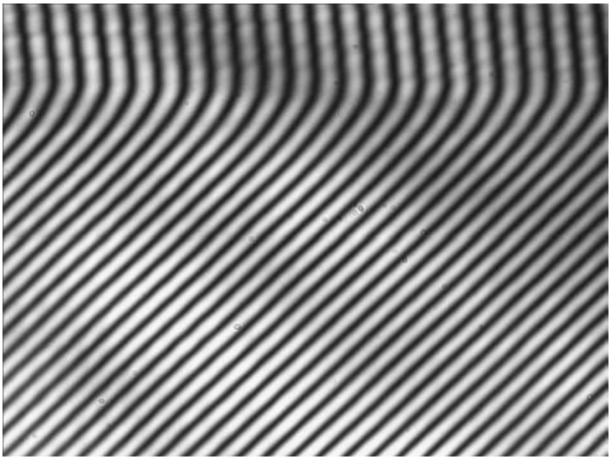

Fig. 3. An enlargement of the fringe pattern at 100 mK in the region of the contact line: the size of this image is 3425 × 2563 μm.

thickness of the ^{4}He-rich phase is obtained by measuring the difference in optical path between the situation with the interface and the one without the interface.

In order to obtain the difference in optical path, we fitted the phase of the light intensity with a sinusoidal function as done in Ref. 2. The relation between the thickness h of the ^{4}He-rich phase and the phase ϕ is:

$$h(d) = \frac{\lambda}{4\pi\,\delta n}(\phi(d)_{\text{with}} - \phi(d)_{\text{without}}), \tag{1}$$

where $\phi(d)_{\text{with}}$ is the phase profile of the fringe pattern with interface which was directly obtained by fitting the image, $\phi(d)_{\text{without}}$ is the one without interface, d is a distance measured perpendicularly to the contact line along the back window, δn is the difference in refractive index between the ^{3}He-rich phase and the ^{4}He-rich phase and λ is the wavelength of the He–Ne laser light.

In order to obtain a fringe pattern without interface that is to say $\phi(d)_{\text{without}}$, we used two methods. At low temperature, we could record the pattern before and after a change in level which was obtained by filling the cell with a little more helium mixture, but this took a long time during which the cell drifted slightly with respect to the optical setup. Instead, it was sufficient to calculate the fringe pattern without interface by extrapolating the upper part of a pattern with interface. This extrapolation was made with a second order polynomial, as was done previously by Ueno in Ref. 2. It was important to check that, by doing this, we obtained

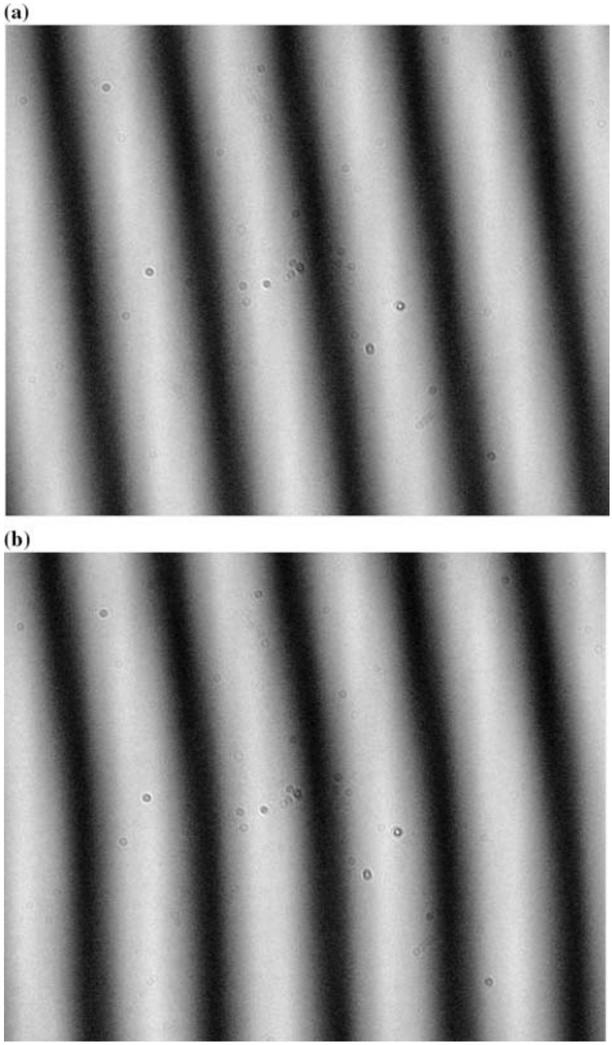

Fig. 4. A set of images at 840 mK: (a) without interface; (b) with an interface in the field of view. The size of these images is 738 × 602 μm. From an analysis of the slight difference between (a) and (b), the profile of the ^{3}He–^{4}He interface near the wall was obtained (see Figs. 5 and 7).

an interface which was horizontal far from the contact region; this was a strong constraint on the coefficient of the second order term in the polynomial and the profile shape was sensitive to it.

At higher temperature, the index difference is very small so that the interface induced very small changes in the fringe pattern (see Fig. 4). We had to divide very small phase differences by the vanishingly small quantity δn, and the previous method was not accurate enough; this is probably the origin of the artefacts in Ueno's previous results. We found a different and more accurate method after realizing that a small increase in temperature δT of order 5 mK was sufficient to shift the interface down below the region of analysis without significantly changing the concentration of the ^{3}He-rich liquid. As a consequence, we could obtain the difference in phase between one real image at T and another real image at $T + \delta T$. No extrapolation was necessary, and if any small defect in the reference pattern existed, for example a small dust particle or a weak additional fringe pattern superimposed on the main one, we were certain to account for it. As can be seen in Fig. 5, such defects existed, and at 840 mK, the phase difference due to the ^{4}He-rich phase appearing in the field of view has an amplitude comparable to the distortion in the reference phase pattern due to defects.

Before recording an interferometric image of the contact region, we waited for about one hour, in order to be sure that equilibrium had been achieved. Fig. 6 shows the result of an analysis at $T = 100$ mK. At this temperature the index difference δn is large and our method has a good accuracy. The experimental line has very little noise and it is almost indistinguishable from the calculation of the interface profile using Sato's value for the interfacial tension[12] and zero contact angle. The same calculation with a non-zero contact angle significantly deviates from the experimental profile, indicating that the contact angle is zero within a small error bar. Another result is shown in Fig. 7, which now corresponds to 840 mK. Since $\delta n = 0.00037$ at this temperature (about 20 times less than at 100 mK), the profile measurement is much more noisy than at 100 mK. In fact, as shown in Fig. 4, the contact region is not easy to see on the fringe pattern, it only appears when comparing phases as done in Fig. 5. Furthermore, the capillary length is now as short as 55 μm, which makes the determination of the contact angle even more difficult.

In order to obtain these interface profiles, several parameters needed to be adjusted. The tilt angle of the sapphire window was adjusted to the value 21.2° from horizontal, the same value for all measurements and we estimated that the error on this angle was ± 0.2. We also had to correct slightly our temperature calibration, otherwise the interface was not found horizontal away from the sapphire wall with the same tilt angle for the sapphire window. This was a small but crucial correction. (we shifted our temperature scale down by about 10 mK from the calibration which had been provided to us by LakeShore when we bought our Ge thermometer from them).

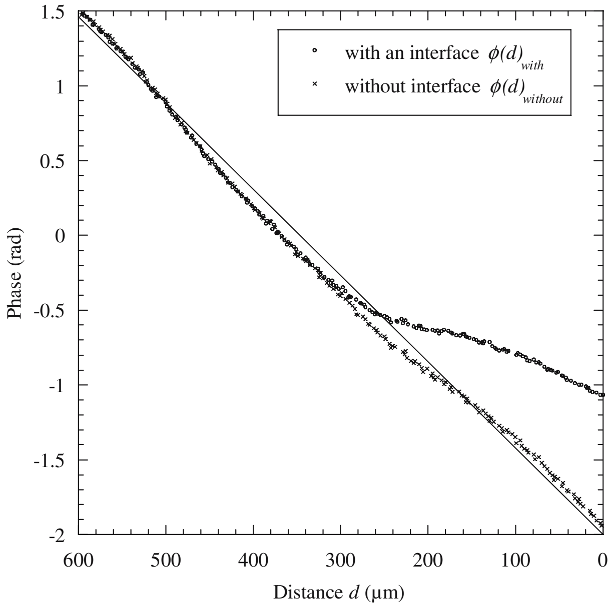

Fig. 5. The fringe patterns are described by a sinusoidal function of position, whose phase is represented here. The two sets of data correspond to 840 mK, respectively with an interface and without interface. The solid line is to show the deviation from a straight line. At this temperature, there are defects inducing phase distortions in the pattern without interface, which are not negligible compared to the phase change introduced by the interface. For an accurate and reliable determination of the contact angle in this temperature range, these distortions need to be taken into account, so that it is necessary to use real images in the contact region, not extrapolations.

3. RESULTS AND ANALYSIS

We analyzed the profiles in different ways. We first fitted them with two adjustable parameters: the surface tension and the contact angle on the window. The height of the horizontal surface away from the wall was found from an independent fit of the profile at large distance from the wall. Similarly, the position of the window surface was obtained from a fit of the data points above the contact line. This gave us values of the contact angle which were close to zero and values for the surface tension which were in reasonable agreement with previous measurements by Sato *et al.*[12] and by Leiderer *et al.*,[13] but which had rather large error bars.

A better accuracy on the surface tension value was obtained when we then assumed that the contact angle was zero. As shown in Figs. 8 and 9 for the vicinity of the tri-critical point at T_t, we obtained precise agreement with previous measurements.

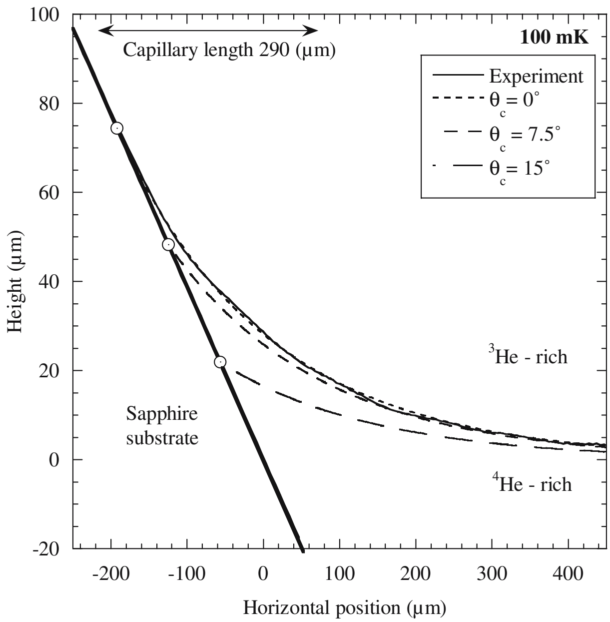

Fig. 6. A profile extracted at 100 mK and three calculations with Sato's value for the interfacial tension[12] and various possible values of the contact angle on the window. The experimental recording is almost indistinguishable from the calculation with zero contact angle. The horizontal arrow indicates the magnitude of the capillary length at this temperature (290 μm).

In a further step, we then calculated the profile by using Sato's value for the interfacial tension σ_i far from T_t[12] and Leiderer's value close to T_t.[13] We chose successive values for the contact angle, and compared calculated profiles with the measured ones (see Figs. 6 and 7). In these two figures, the various lines are thus calculations, not fits. These comparisons with data allowed us to estimate error bars on the measurement of contact angles at each temperature.

Figure 10 shows our results for the contact angle in the whole temperature range. Within an error bar of order 10°, it is zero. Figure 11 shows the temperature domain from 800 mK to 860 mK only, where we again found that the contact angle is zero. This means that, contrary to what was claimed in Refs. 1 and 2, the ^{4}He-rich phase completely wets the sapphire wall.

We already discussed a possible origin of artefacts in the optical measurement by Ueno *et al.* In their MRI experiment, the profile position was obtained after averaging on a finite thickness. Could this mimic a finite contact angle?

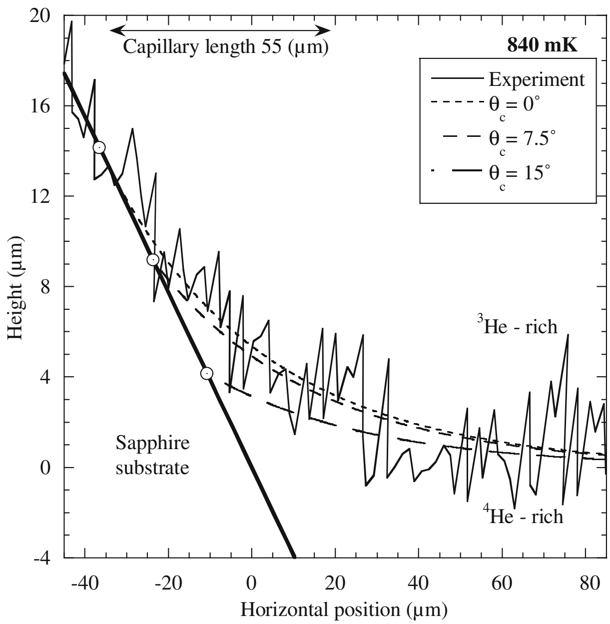

Fig. 7. A profile extracted at 840 mK and three calculations with Leiderer's value of the interfacial tension[13] and three different contact angles. Within an error bar of order 10°, the contact angle is shown to be zero. The horizontal arrow indicates the magnitude of the capillary length at this temperature (55 μm).

especially since the profile could not be measured very close to the wall? Could it be that the van der Waals attraction by an epoxy wall is significantly smaller than by our sapphire window for a mysterious reason? A new MRI study, hopefully with better accuracy, needs to be done in order to answer these questions and confirm that the ^{4}He-rich phase completely wets walls.

4. DISCUSSION

4.1. Critical Casimir Forces

In ref. 7, Ueno *et al.* explained that their experimental results were consistent with the existence of so called "critical Casimir forces" in the system under study. Let us start with a critical review of this effect. The existence of forces between two surfaces confining a critical system was first predicted by Fisher and de Gennes[9] and later[14] written as:

$$F(l, T) = \frac{k_B T}{l^3} \vartheta(l/\xi), \tag{2}$$

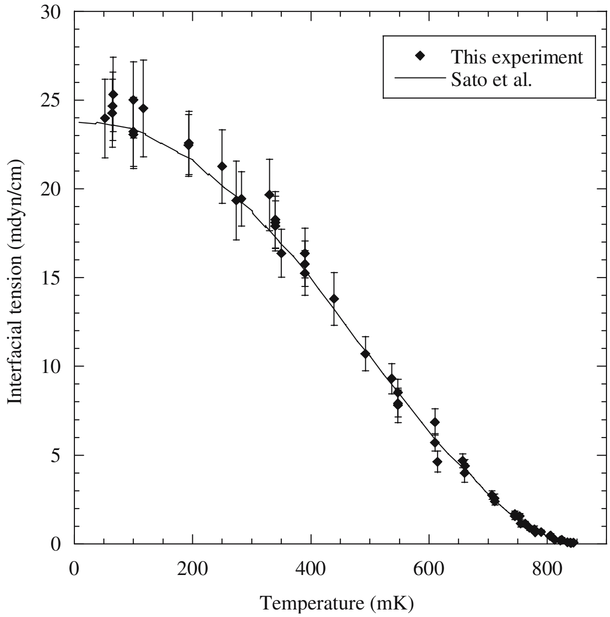

Fig. 8. Assuming that the contact angle is zero, we find precise agreement between our measurements of the interfacial tension and previous measurements by Sato *et al.*[12]

where the "scaling function" $\vartheta(l/\xi)$ depends on temperature and on the thickness l through its ratio to the bulk correlation length ξ. Near T_c, ξ diverges proportionally to $t^{-\nu}$ where $t = (T/T_c - 1)$ is the reduced temperature and $\nu = 0.67$ for ordinary critical points ($\nu = 1$ for tri-critical points). Following the seminal paper by Fisher and de Gennes,[9] several theoretical authors have brought important information about the critical Casimir force:

1. The sign of the force is given by the sign of the scaling function, and it depends on the symmetry of the boundary conditions. If they are symmetric, ϑ is negative and the force is attractive; on the opposite, if the boundary conditions are antisymmetric, ϑ is positive and the force is repulsive.
2. The magnitude of the force is generally considered as universal, in particular at the bulk critical temperature T_c, where its value is twice the "Casimir amplitude" Δ, which is the universal value of Θ (the similar scaling function appearing in the singular contribution to the free energy) at T_c. Furthermore the Casimir amplitude depends on the dimension N of the order parameter. From the

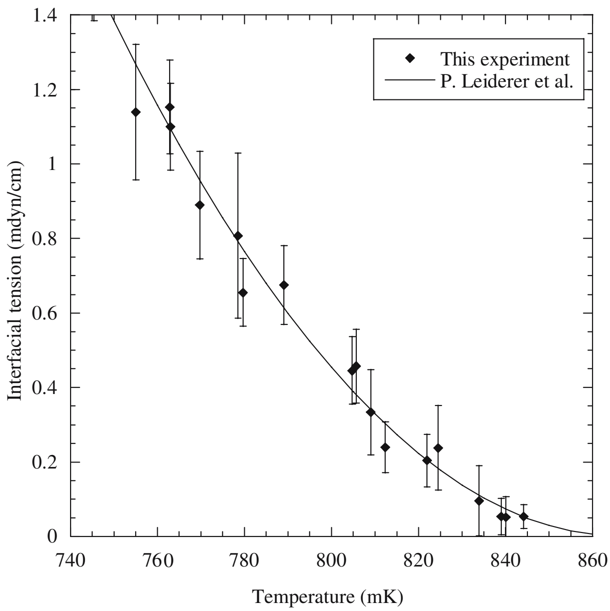

Fig. 9. Measurements of the interfacial tension σ_i between the c- and the d-phase in the vicinity of the tri-critical temperature T_t = 0.87 K. Within the error bars, all data agree with the quadratic critical behavior measured by Leiderer *et al.* in 1977.[13]

work of Nightingale and Indekeu[15–17] and Krech and Dietrich,[14] it appears that Δ is roughly proportional to N. For example, it is expected to be twice as large for a superfluid transition ($N = 2$) as for the phase separation of a usual liquid mixture ($N = 1$). It also depends on the boundary conditions, more precisely on their nature, not on the exact details of surfaces.[14] These conditions can be periodic, or the order parameter can vanish at the boundary ("Dirichlet" boundary conditions) or its derivative can vanish ("von Neumann" conditions).

3. With Dirichlet boundary conditions, the critical temperature in the film is significantly displaced with respect to the bulk critical temperature T_c, and the maximum of the scaling function $\Theta(l/\xi)$ is expected to be rather different from the Casimir amplitude Δ. In fact, as far as we know, there exists no calculation of the scaling functions both below and above T_c for Dirichlet boundary conditions. According to Krech and Dietrich,[14] Δ is much smaller for Dirichlet boundary conditions than for periodic ones, but it does not mean that the maximum amplitude of ϑ is also much smaller,

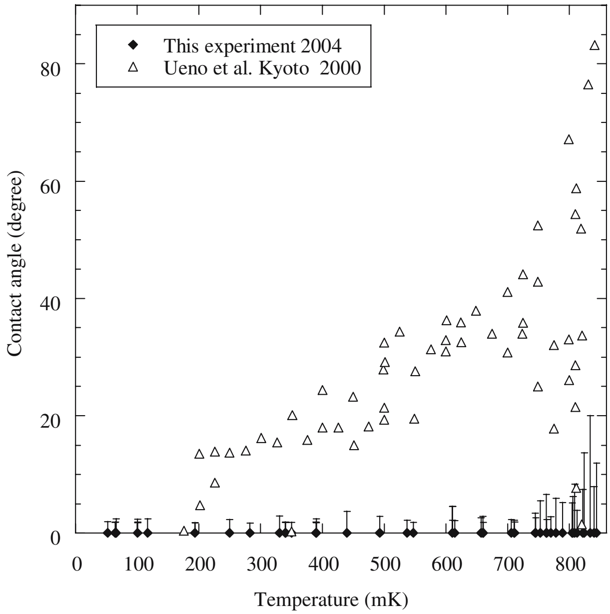

Fig. 10. The contact angle θ of the ^3He–^4He interface with a wall was found non-zero in Ueno's experiments in Kyoto in 2000 (open triangles). They used a magnetic resonance imaging (MRI) technique whose accuracy was not good near the tri-critical point, in view of the large scatter of data points in this temperature region. Agreement with this anomalous behavior was found in a later experiment by Ueno *et al.* in Paris (see Fig. 11). However, the present experiment shows that $\theta = 0$ both at low temperature and near the critical point.

since the temperature at which this maximum is reached is displaced.

The calculation of $\Theta(l/\xi)$ has been performed above T_c by Krech and Dietrich,[14] using an ϵ-expansion method. For periodic boundary conditions and below T_c, it has been more recently calculated by G. Williams in the frame of his vortex loop-model for liquid helium.[18] According to Williams, his calculation below T_c matches nicely with Krech's calculation above T_c, the Casimir amplitude being about -0.15, close to the maximum amplitude of the scaling function $\Theta(l/\xi)$.

In their first experiment, Garcia and Chan[19] observed the thinning of a pure liquid helium film near the superfluid transition at T_λ. This film was adsorbed on a copper electrode and most of the thinning occurred in a small temperature region near T_λ. They analyzed it in terms of the critical Casimir effect and extracted a scaling function $\vartheta(l/\xi)$ whose shape was very similar to calculations, for example the recent ones by Dantchev

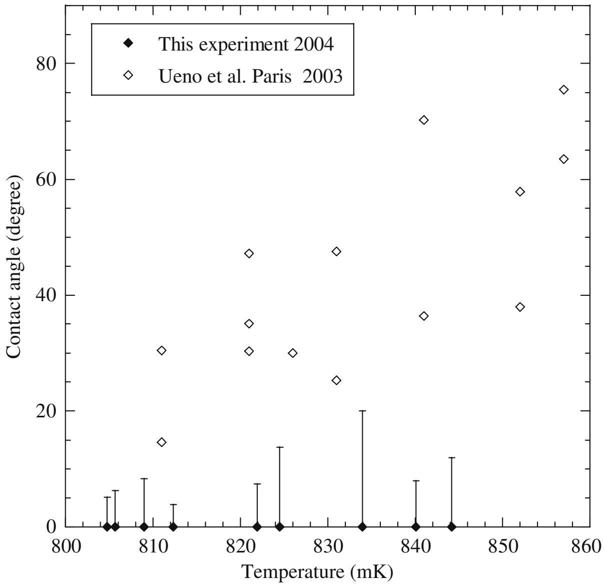

Fig. 11. The contact angle near the tri-critical point. The experiment by Ueno *et al.* in Paris in 2003 (open diamonds) showed that θ increased instead of tending to zero as T approached the tri-critical temperature T_t. However, this anomalous behavior is not confirmed by the present experiment which shows that $\theta = 0$ within an error bar of order 10°.

and Krech.[23] Garcia's scaling function displays important features which deserve several comments:

1. The maximum amplitude of ϑ does not occur at the bulk critical temperature T_c. This was expected because the order parameter for superfluidity vanishes on both sides of the superfluid film (Dirichlet boundary conditions), so that the superfluid transition temperature is depressed in the film: $T_c^{\text{film}} < T_c^{\text{bulk}}$. It occurs significantly *below* T_c, for $x = tl^{1/\nu} \approx -10$ (The reduced temperature is taken negative below T_c. Note also that, in both articles by Garcia and Chan,[19,20] the horizontal coordinate $x = tl^{1/\nu} = (l\xi_0/\xi)^{1/\nu}$ is not dimensionless, but close to $(l/\xi)^{1/\nu}$ since l is taken in Å and the quantity ξ_0 is about 1 Å.[13]). The magnitude of the scaling function *above* T_c is very small, as predicted by Krech and Dietrich.[14] Garcia and Chan claim that their measurement of ϑ agrees with the calculation, but this only concerns the small tail at $T > T_c$, where the signal/noise ratio is poor, while most of the observed effect occurs below T_c.

2. Garcia and Chan found that $\vartheta(l/\xi)$ reaches maximum negative values which vary from -1.5 to -2 as a function of the film thickness l. This is doubly surprising, first because a dependence on l contradicts the predicted universality, secondly because no calculation has ever found such large amplitudes for ϑ. In the various situations which have been calculated, the theoretical results are 5 to 50 times smaller. This is a serious problem which needs further studies: new experiments should identify the origin of the l-dependence, and ϑ should be calculated below T_c with Dirichlet boundary conditions.
3. They also found indications that the scaling function does not tend to zero in the low temperature limit, away from T_c. One possible explanation for this is the confinement of Goldstone modes invoked by Kardar and Golestanian.[10] The amplitude of the Goldstone mode contribution looked too small to explain the rather large negative value of $\vartheta(T \to 0)$ found by Garcia and Chan, but a more recent calculation by R. Zandi *et al.*[21] proposes that, the film surface being mobile, a contribution from third sound modes at the surface of a superfluid film should be added to the one coming from Goldstone modes, so that the total attractive force acting on the film surface is larger than first calculated.[21] It has also been suggested that solvation forces play a role in this situation.[24] One could even imagine that phonons also contribute to the force at low temperature.[22]

It thus seems to us that, despite the evidence that critical Casimir forces exist, which is provided by the remarkable experiment by Garcia and Chan, the exact magnitude of this effect is not accurately known yet.

4.2. Critical Point Wetting in Helium

Below their tri-critical temperature T_t, helium mixtures are separated in two phases which are often called "c-phase" (meaning concentrated in ^{3}He), and "d-phase" (diluted in ^{3}He, consequently rich in ^{4}He). In ref. 7, Ueno *et al.* related partial wetting by the d-phase to the existence of a d-phase film of finite thickness between the wall and the bulk c-phase (see Fig. 12). An infinite thickness would mean complete wetting and for this thickness to be finite, attractive forces have to act between the wall and the cd-interface.

The way to calculate the contact angle is to integrate the so-called "disjoining pressure" $\Pi(l)$ which is nothing but the sum of the forces

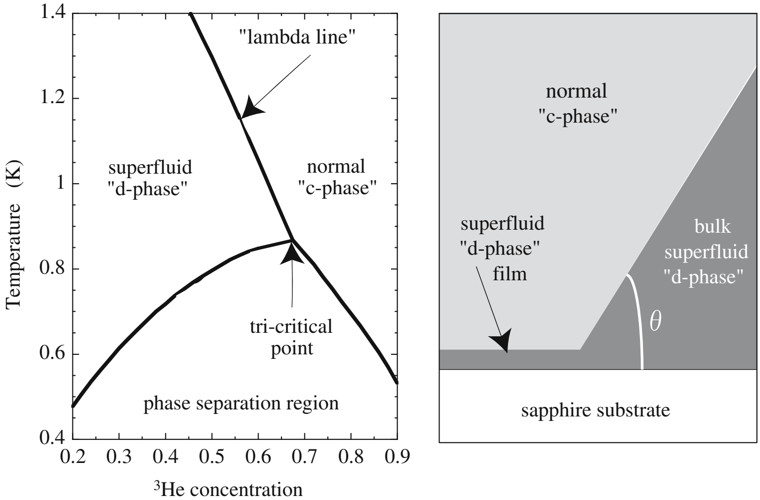

Fig. 12. The phase diagram of liquid helium mixtures (left) and a schematic representation of the partial wetting of a wall by the phase separated mixture (right).

acting on the *cd*-interface:[25]

$$\cos(\theta) = \frac{\sigma_{sc} - \sigma_{sd}}{\sigma_i} = 1 + \frac{\int_{l_{\text{eq}}}^{\infty} \Pi(l)dl}{\sigma_i}. \qquad (3)$$

Ueno *et al.* identified three long range forces contributing to the pressure $\Pi(l)$. The van der Waals force is attractive on atoms and ^{4}He atoms occupy a smaller volume than ^{3}He atoms because their quantum fluctuations are weaker (their mass is larger). As a result, the van der Waals attraction on the *d*-phase is stronger than on the *c*-phase, and a *c*-phase is always separated from a solid wall (in Fig. 12, a sapphire window) by a film of *d*-phase. Being attractive on atoms, the van der Waals field induces an effective force which is *repulsive* on the film surface. In the absence of other long range forces, a finite thickness film would only exist off-equilibrium, but as equilibrium is approached the film thickness would diverge and complete wetting by the *d*-phase would occur. Romagnan *et al.*[26,27] found some experimental evidence for this, but their measurements were limited to thickness up to about 80 Å only. The sketch in Fig. 12 corresponds to a situation where another long range force acts on the film. Being attractive, this other force is assumed to dominate the van der Waals field and to limit the film thickness, so that the macroscopic contact angle is non-zero.

A critical Casimir force exists if a superfluid d-phase film separates the wall from the normal c-phase. The order parameter of superfluidity is nonzero inside the film but it has to vanish on both sides. This symmetric vanishing should produce an attractive Casimir force on the film surface. Since there exists no calculation with such Dirichlet boundary conditions yet, Ueno *et al.*[7] used Garcia's measurement of $\vartheta(l/\xi)$ to calculate the contribution of the critical Casimir effect to the disjoining pressure. They also included the Helfrich force, which is repulsive, due to the cutoff of capillary modes at long wavelength by the presence of the nearby wall.[28] At a reduced temperature $t=-0.01$ below T_t, they found that the critical Casimir force was stronger than the two others in the thickness range from 0 to 400 Å (see Fig. 13). According to this calculation, the equilibrium film thickness was thus 400 Å, and Ueno *et al.* could calculate the contact angle by integration of the disjoining pressure (Eq. (3)). They found 45°, in good agreement with their measurement. Moreover, they argued that, in their experiment, the Casimir force could be twice as large as in Garcia's experiment, because it is a tri-critical point instead of an ordinary critical point such as the lambda point of pure liquid helium 4. According to this further argument, they found that the contact angle was 60° at $t=0.01$, in even better agreement with their experimental results.

However, Ueno's assumption that the magnitude of the Casimir forces could be taken from the measurement by Garcia and Chan[19] is questionable. Garcia and Chan measured the Casimir force between a solid wall and the free surface of pure liquid ^{4}He near the lambda transition. In the present case, it is the force between a solid wall and the interface between a ^{4}He-rich and a ^{3}He-rich liquid phase, near the tri-critical point where phase separation *and* superfluidity occurs. Near this tri-critical point, the fluctuations of concentration are coupled to the fluctuations of the amplitude of the superfluid order parameter, so that one should not, in principle, consider fluctuations of superfluidity without the others. Since no calculation nor any measurement exist in this situation, Ueno *et al.* considered that, according to theory,[11,17] the effect of the fluctuations of superfluidity should dominate. This is because, the amplitude of the Casimir amplitude is roughly proportional to the dimension of the order parameter, which is 2 for superfluidity and 1 for concentration. Ueno *et al.* further assumed that the Casimir amplitude, in fact the whole scaling function ϑ being universal, they were allowed to take Garcia's measurement to estimate the typical magnitude of the Casimir force in their case. In fact, they neglected the effect of concentration fluctuations, despite mentioning that they should act in the opposite way, since the boundary conditions for superfluidity are symmetric (it vanishes in a similar way on both sides of the superfluid ^{4}He-rich film), while they are

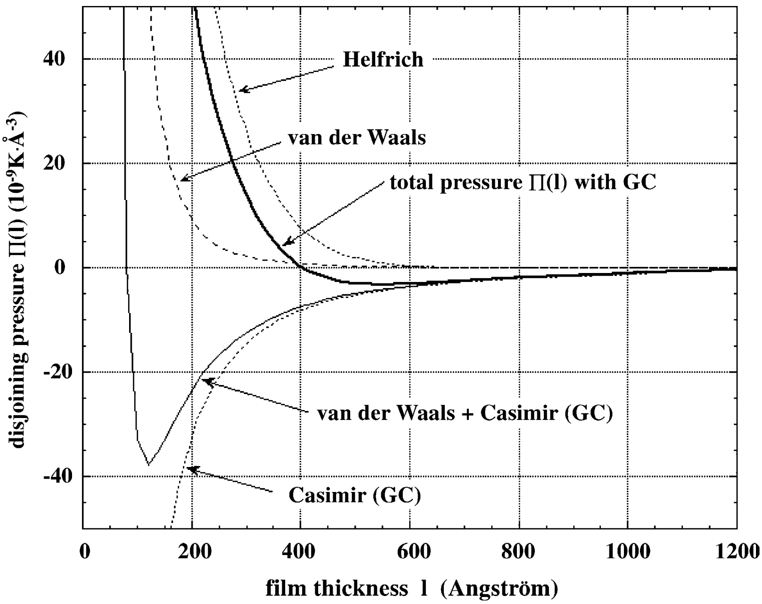

Fig. 13. The 2003 calculation by Ueno *et al.*[7] of the various forces acting on the film surface. The amplitude of the Casimir force was taken directly from the measurement by Garcia and Chan in 1999.[19] It was apparently stronger than the van der Waals effective force which is positive, meaning repulsive on the film surface. After adding the Helfrich force, Ueno *et al.* found a total disjoining pressure crossing zero at l_{eq} = 400 Å, the equilibrium film thickness. A finite film thickness means partial wetting and quantitative agreement was found with the measurements by Ueno *et al.* in 2003.

antisymmetric for concentration (the solid side is rich in ^{4}He while the interface side is rich in ^{3}He, due to the van der Waals field from the wall which attracts ^{4}He more strongly than ^{3}He).

In summary, there appears two reasons for the magnitude of the critical Casimir forces in our case to be smaller than previously thought by Ueno *et al.*: it could be reduced by the effect of concentration fluctuations, or perhaps Garcia and Chan have overestimated it. Ueno *et al.* calculated the contact angle at 860 mK from an integration of the disjoining pressure on the ^{3}He–^{4}He interface. As shown in Fig. 13, they found that, if taken from Garcia and Chan, the Casimir force dominates the two other forces for a film thickness less than 400 Å. However, if we now assume that the Casimir force is less by a factor five, Fig. 14 shows that the effect basically disappears: the two repulsive forces dominate and the disjoining pressure is positive everywhere, so that the equilibrium film thickness is infinite and complete wetting by the ^{4}He-rich phase occurs.

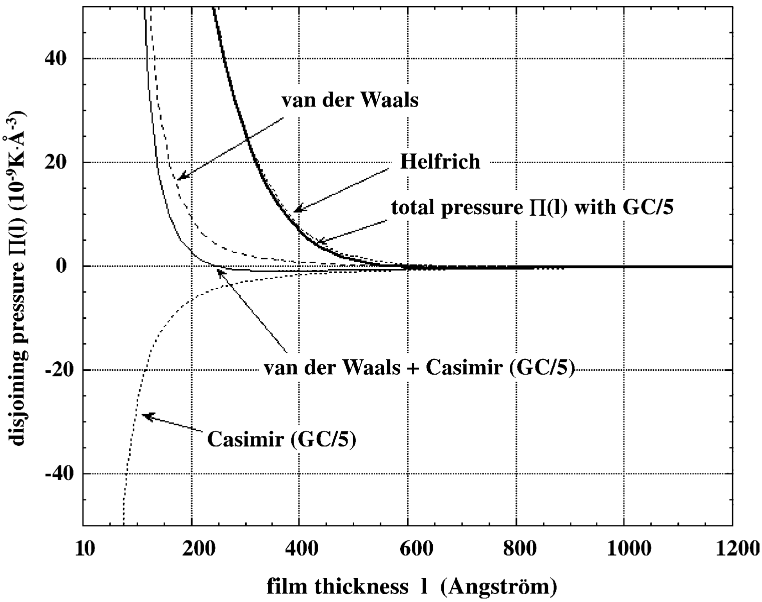

Fig. 14. A modified calculation of the disjoining pressure acting on the film surface, where the amplitude of the critical Casimir force has been taken as one fifth only of the experimental result obtained by Garcia and Cahn. Contrary to what was shown in Fig. 13, one now finds that the repulsive forces always dominate the Casimir force, so that the disjoining pressure is always positive, leading to a macroscopic film thickness at equilibrium, and complete wetting.

Let us finally consider the low temperature limit. The van der Waals effective force acting on a *cd*-interface is repulsive, proportional to the difference in the average volume per atom in each phase $V_c - V_d$:

$$\Pi_{udW} = \frac{A_0}{l^3}\left(\frac{1}{V_d} - \frac{1}{V_c}\right) \tag{4}$$

with $A_0 \approx 1000\ \mathrm{K\,Å^{-3}}$ for an insulating substrate. At low temperature, $V_c = 61.15\,Å^3$ and $V_d = 46.56\,Å^3$,[12] so that, far below $T_t = 0.87\,\mathrm{K}$, the effective van der Waals force is about $5/l^3$ in $\mathrm{K\,Å^{-3}}$ units. For partial wetting to occur in this limit, the contribution of the Goldstone modes to the Casimir force would need to be more negative than $-5/l^3$. In their review article,[10] Kardar and Golestanian propose $-0.048k_BT/l^3$ which looks much too small. Following the recent work of Zandi *et al.*,[21] one should also account for the existence of fluctuations at the film surface, i.e. third sound modes. Their contribution should add to that of Goldstone modes and lead to a total Casimir force which is three times more negative than previously thought, about $-0.15 k_B T/l^3$. However, this looks still too small compared to the van der Waals field. In a sense, it is not surprising that we found complete wetting at low temperature, but in the first experiment done by Ueno *et al.* in Kyoto, partial wetting had been found and, since Garcia's measured value of the Casimir force is much larger than available calculations, it was worth checking that complete wetting occurred at low T.

5. CONCLUSION

We have presented new measurements of the contact angle between the ^{3}He–^{4}He interface and a sapphire wall. We have found that, contrary to previous measurements by Ueno *et al.* in a similar situation, the wall is completely wet by the ^{4}He-rich liquid phase. This means that there might have been some artefacts in the analysis of Ueno's measurements. It also means that the amplitude of the critical Casimir forces in this situation is smaller than proposed by Ueno *et al.* in Ref. 7, consequently dominated by the van der Waals forces.

Given these new results, it appears useful to repeat Ueno's MRI measurements and to confirm that the contradiction between such measurements and the present ones are not due to a difference in the nature of the solid wall. It would also be useful to confirm the magnitude of the Casimir forces as measured by Garcia and Chan, since it seems rather large compared to available calculations.

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