Wetting Transition in Liquid Helium

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We have used a vibrating-wire microbalance technique to investigate the wetting of ^{3}He and ^{4}He on solid surfaces. Although superfluid ^{4}He wets solid substrates and forms a thick film, we find that films of ^{3}He and normal ^{4}He are limited to less than thirteen layers. The λ transition appears to be a wetting transition for ^{4}He.

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Recently, there has been considerable theoretical and experimental interest in the growth from the vapor of multilayer films on solid substrates. Condensed phases tend to form on substrates because the free energy in the vicinity of a wall is reduced by the attractive van der Waals potential. If the attractive potential is the dominant thickness-dependent term in the free energy, the chemical potential of the film is a monotonically increasing function of film thickness and approaches the bulk chemical potential from below. In this case, the thickness of a film absorbed on a planar substrate diverges at the bulk equilibrium vapor pressure and the film is said to wet the substrate. If, however, the free energy of the film contains other important terms, it is possible that the film will be stable with respect to formation of the bulk for only a restricted range of thickness.[1] This occurs, for example, in some solid systems where the effects of substrate-induced strain increase the free energy,[2,3] and in systems in which the van der Waals attraction of the adsorbate to itself is comparable or greater than the attraction to the substrate.[4] These effects are not considered to be important for most noble gases in the liquid state, and the theoretical expectation of complete wetting is supported by experiments which show the formation of films at least five layers thick on highly polarizable substrates such as metals.[5]

The helium isotopes are a special case of the noble gases because of the importance of quantum effects on the thermodynamic properties of the bulk phases and the superfluid transition in ^{4}He. There has been a vast amount of work on helium films[6] which implies that the superfluid wets most solids.[7] Since wetting behavior is thought to be controlled by the van der Waals interaction which is identical for the superfluid, normal ^{4}He, and ^{3}He, the standard theoretical models suggest that all phases of liquid helium should completely wet solid surfaces. In contrast, recent experimental results[8,9] suggest that ^{4}He does not wet Au and Ag surfaces at any temperature from below the λ point up to the critical point.

In this paper, we describe experiments on the formation of saturated films of normal and superfluid ^{4}He and of ^{3}He on graphite and platinum wires. We find that normal ^{4}He and ^{3}He films in equilibrium with bulk liquid are an order of magnitude thinner than superfluid films on the same substrate. Our results imply that normal helium does not wet graphite or platinum. For ^{4}He, we find that there is an abrupt wetting transition close to T_λ associated with the onset of superfluidity. These observations rely on two improvements over previous measurements: Our experimental technique is sensitive to the total mass of the adsorbed film, independent of the fluid viscosity, and we have taken special precautions to insure that the temperature in our apparatus is uniform to better than 1 part in 10^4.

The microbalance technique we used to measure the mass of the adsorbed films was originally developed by Bartosch and Gregory.[10] A wire approximately 10 mμ in diameter and 1 cm long is mounted horizontally under compression in a slight bow and is clamped at both ends on sapphire blocks using silver paint. A static magnetic field (~ 2000 G) is applied normal to the wire so that elastic resonant vibrations of the wire can be driven with a small ac current. Since the wire is of order 10^4 atoms thick, the additional mass of a monolayer is sufficient to cause an appreciable shift in the resonant frequency. The data reported here were obtained with graphite fibers grown by pyrolysis of a hydrocarbon vapor and heat treated at 2900 °C. The fibers can be cleaned *in situ* by heating to 600 °C by passing a few milliamperes of current through them in vacuum at low temperatures. Examination of the fibers by scanning electron microscopy shows that there are essentially no surface features with a scale greater than 500 Å. The fibers are not perfectly cylindrical, but rather have flat regions with a characteristic dimension of 1 μm which are facets of crystallites.

Since the fiber is a harmonic oscillator, the frequency is given by an expression of the form $\omega = (k/m)^{1/2}$, where k is an effective elastic constant and m is the total mass. The change in frequency due to a change in the mass is then $d\omega = -\omega dm/2m$. If the fiber is oscillating in a dense gas with mean free path much smaller than the fiber diameter, the effective mass is increased by hydrodynamic effects[11] which are linear in the gas pressure.

The expected thickness of a film adsorbed on the surface of a cylindrical wire can be calculated by equating the chemical potential of the vapor and the film.

In most theoretical treatments of this problem, the chemical potential of the film is approximated by the chemical potential of the bulk phase μ_{liq} modified only by the van der Waals potential, $-\alpha/d^3$. If the film has a curved interface with the vapor, there is an additional term[1] $\sigma v/r$, where σ is the surface tension, v is the volume per atom, and r is the radius of curvature. The equation which determines the film thickness d is

$$\mu_{\text{gas}} = \mu_{\text{liq}} - \alpha/d^3 + \sigma v/r. \tag{1}$$

There should be a term in Eq. (1) which describes the effect of the gravitational potential, but for our experimental apparatus it is more than an order of magnitude smaller than the curvature term, so we neglect it. On a cylindrical wire, the film does not grow infinitely thick even at the saturated vapor pressure, because the vapor pressure of the curved interface is slightly higher than that of the bulk. For a wire of radius r the film thickness at the saturated vapor pressure is given by

$$d = (\alpha r/\sigma v)^{1/3}. \tag{2}$$

These results on the asymptotic film thickness are based on the assumption of a perfectly uniform temperature distribution in the cell. The effect of a nonuniform temperature distribution can be analyzed with Eq. (1) if we assume that the pressure in the cell is uniform and is determined by the saturated vapor pressure at the coldest point. The change in the chemical potential of the vapor with temperature is determined by the latent heat of vaporization L and is given by $\Delta\mu = L\,\Delta T/T$. If the film is at a temperature ΔT above the ambient temperature T, the expression for the film thickness Eq. (2) is modified to

$$d = \left[\frac{\alpha}{L\,\Delta T/T + \sigma v/r}\right]^{1/3}. \tag{3}$$

If we substitute values appropriate for helium at low temperatures, we find that at a ΔT of 10^{-4} K, the film thickness is two-thirds of the isothermal result, while a ΔT of 1 mK reduces the thickness to one-third of the isothermal value. The sensitivity of the film thickness to small temperature gradients implies that a meaningful experimental determination of wetting behavior in the thick-film regime requires control of the temperature of not only the microbalance but also its environment to 1 part in 10^4. This problem is particularly severe at helium temperatures where the thermal conductivity of even good conductors like copper is typically an order of magnitude lower than at high temperatures.

The relatively low thermal conductivity of the cell materials implies that even a slight nonuniformity in the heat flux required to regulate the temperature (typically applied by an electric heater on the surface of the cell) can lead to temperature deviations greater than 10^{-4} K. To avoid this problem, we used a two-stage temperature-regulation scheme. The experimental cell (made of oxygen-free high-conductivity copper, 3 cm diameter by 3 cm high) was supported inside a brass can whose temperature was regulated approximately 20 mK above the bath temperature. The only thermal link from the brass can to the copper cell was through low-pressure helium exchange gas. The fill line and the electrical leads were also thermally regulated. Using this method, we estimate that the maximum temperature differences in the copper cell were less than 10^{-4} K.

Another potential source of thermal inhomogeneity is the temperature rise of the fiber due to the Joule heating of the drive current. We employed currents between 0.06 and 0.2 μA which resulted in power dissipation of between 0.2 and 2 pW in the fiber. Almost all of the heat generated by the drive current is conducted into the surrounding gas. The temperature rise due to the input power can be computed from standard formulas[12]; the estimated ΔT is always less than a microkelvin, and the experimental results showed no dependence on the drive amplitude.

A typical experimental run consists of monitoring the resonant frequency of the fiber as a function of gas pressure at constant temperature. The results of an experiment on the absorption of ^{4}He on graphite below the λ point which shows wetting is shown in Fig. 1(a). The main features of the data are a linear decrease of the frequency with pressure for pressures below P_0 with a rather abrupt drop in frequency as the pressure approaches P_0. The linear background is due to the increasing effective hydrodynamic mass of the gas, while the frequency drop at P_0 is due to the formation of a thick film. P_0 is identified by adding gas to the cell until further additions cause no additional frequency shift. Adding gas when the pressure is close to P_0 causes the vapor to become supersaturated and we observe a large transient frequency drop which is presumably due to the condensation of droplets on the fiber. The transients relax with a time constant of several minutes towards an end point which is stable and reproducible. The total frequency shift due to the adsorbed film is obtained from the difference between the end-point frequency and the extrapolation of the linear hydrodynamic background to P_0. The arrow in Fig. 1(a) shows the frequency drop expected from Eq. (2) assuming a cylindrical fiber geometry. The film thickness computed from Eq. (2) is approximately sixty layers, while the frequency drop we observe corresponds to 110 layers; we attribute this difference to the fact that the cross section of the fiber is not perfectly circular, but rather has flat faceted portions where the local curvature is smaller.

Figure 1(b) shows the results of a similar experiment with ^{4}He on the same fiber at a temperature slightly above the λ point. The parameters in Eq. (2)

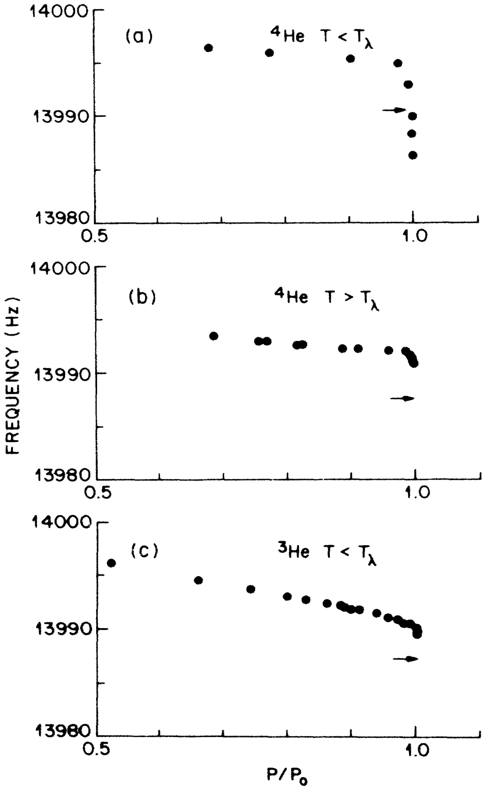

FIG. 1. Resonant frequency of the graphite fiber as a function of gas pressure in units of the saturated vapor pressure P_c. The arrows mark the end-point frequency computed from Eq. (2). (a) ^{4}He at $T = 2.095$ K, (b) ^{4}He at $T = 2.308$ K, (c) ^{3}He at $T = 1.605$ K. 1 Hz ≈ 12 layers.

which determine the film thickness have only a slight temperature dependence and do not depend significantly on the state (superfluid or normal) of the helium, so the predicted frequency drop is essentially the same as in Fig. 1(a). Figure 1(b) shows, however, that the observed frequency drop is approximately one-tenth of the drop observed below the λ point, and one-fifth of the drop predicted from Eq. (2). This frequency shift corresponds to twelve layers, assuming a perfect cylindrical geometry.

A comparison of the results in Figs. 1(a) and 1(b) leads to the surprising conclusion that wetting and superfluidity in ^{4}He are related. The most obvious experimental artifact which could mimic this behavior is a thermal inhomogeneity in the cell which is short circuited by the superfluid film, but leads to thermal gradients and lower mass loading above the λ point. Since experimental tests of wetting are extremely sensitive to thermal gradients, we have devoted considerably effort to ruling out possible thermal explanations of our observations. Using Eq. (3), we estimate that the fiber would have to be at least 1 mK warmer than some other point in the cell to account for the decreased film thickness as a purely thermal effect. This temperature difference is orders of magnitude larger than what we expect from simple Joule heating in the fiber. Even at the highest drive currents employed, the Joule heating raises the temperature of the film by less than a microkelvin, and the results are independent of drive power down to a level of 5 fW where the temperature rise is only nanokelvins. A cold spot in the apparatus could also account for our results, but again, the temperature difference is more than an order of magnitude larger than what we estimate is possible in our thermally isolated high-conductivity cell. Perhaps the most convincing experimental proof that the nonwetting of the normal fluid is not an artifact of thermal inhomogeneities in the apparatus is provided by a comparison of the wetting behavior of ^{3}He and ^{4}He in an identical thermal environment. Figure 1(c) shows the results of a ^{3}He isotherm with the copper cell immersed in a bath of superfluid ^{4}He. The superfluid bath guarantees that the temperature distribution in the cell is highly uniform and is identical to the thermal environment which leads to the wetting observed in Fig. 1(a). The only essential difference between the experiments of Figs. 1(a) and 1(c) is that the adsorbed ^{4}He film is superfluid while the ^{3}He film is not. Despite the isothermal conditions provided by the superfluid bath and the extremely small Joule heating of the fiber, we find that ^{3}He does not completely wet graphite. The ^{3}He results are very similar to the results obtained for ^{4}He above the λ point. Taking the reduced density and surface tension of ^{4}He into account, the frequency shift we observe corresponds to thirteen layers, compared to the predicted asymptotic thickness of 75 layers.

We have determined the temperature of the thick-film–thin-film transition in ^{4}He by the monitoring the frequency as a function of temperature along the liquid-vapor coexistence curve. The results, shown in Fig. 2, demonstrate that the transition takes place in a single sharp step approximately 30 mK below the bulk λ point, which is consistent with estimates for the λ transition temperature in a film approximately fifteen layers thick.[13] We have also verified that the wetting behavior illustrated in Figs. 1 and 2 is not peculiar to graphite; all of the qualitative results have been observed with platinum-wire substrates which are also free of oxide and topographical features which could lead to capillary condensation.

In summary, we have studied the growth of helium films on chemically clean surfaces in a well-controlled thermal environment. In the temperature range we investigated, normal ^{4}He and ^{3}He do not wet solid substrates, and therefore the standard slab model of Eq. (1) does not describe the chemical potential of the adsorbed film accurately enough to predict the correct behavior of thick helium films. Superfluid films wet solid substrates, and therefore superfluidity and wet-

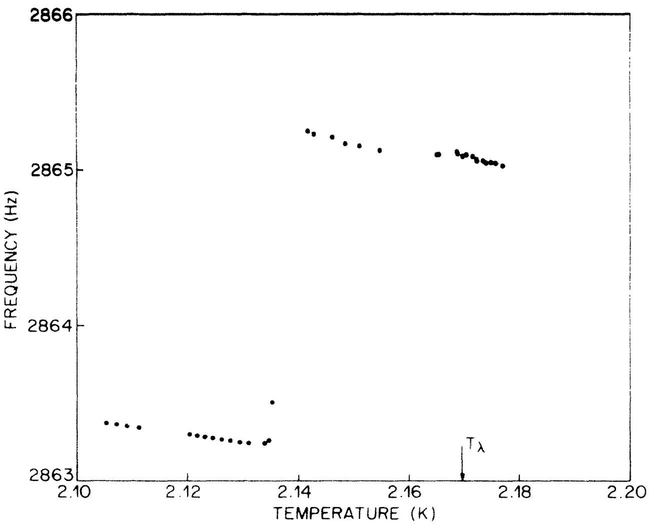

FIG. 2. Resonant frequency of the graphite fiber as a function of (decreasing) temperature. The cell contains a small amount of bulk ^{4}He, so the pressure is the equilibrium vapor pressure at each temperature. A dramatic increase in the mass loading is observed 30 mK below the bulk λ transition. A much smaller frequency drop corresponding to ~ 3 layers is seen at T_λ; this is probably due to a reduction in the residual temperature gradients when the bulk becomes superfluid.

ting are related. Although these results are in qualitative agreement with the well-known properties of superfluid films below the λ point, and with the results of Migone, Krim, and Dash[9] above the λ point, the nonwetting of any fluid adsorbate and the difference in the wetting behavior between the normal and superfluid are difficult to explain with current theoretical concepts.

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