Wetting near Triple Points

K. G. Sukhatme, J. E. Rutledge, and P. Taborek

Department of Physics and Astronomy, University of California, Irvine, California 92697-4575

(Received 14 August 1997)

The quartz microbalance technique has been used to study the coverage of argon and methane films in the vicinity of the bulk triple point. In contrast to previous measurements, close to the triple point, the discontinuities in the coverage indicate first-order surface phase transitions. A thermodynamic model shows that argon forms a layered solid-liquid film in a range around the triple point, but is liquid both above and below this range. Methane films make a transition directly from solid to liquid. These observations are examples of the rich phase behavior near bulk triple points predicted by Pandit and Fisher [Phys. Rev. Lett. 51, 772 (1983)]. [S0031-9007(97)04948-X]

PACS numbers: 68.35.Rh, 68.45.Da, 68.45.Gd

At the triple point of a one component system, bulk solid, liquid, and vapor can coexist, but even a small thermodynamic perturbation will break this degeneracy. The interfaces at the substrate and the vapor of an adsorbed film provide such a perturbation. For this reason, the phase of the film is not uniquely determined by the bulk phase diagram. The consequences of interfacial effects are surprisingly subtle and determine phenomena such as nonwetting of solid films [1,2], surface melting [3], nucleation, and triple-point-induced wetting [4-8] and dewetting [9]. Pandit and Fisher [10] have discussed a number of possible surface phase diagrams. They show that, typically, surface phases are separated by first-order phase transitions at temperatures distinct from the bulk triple temperature $T_t$. Nevertheless, experiments near solid-liquid-vapor triple points have never revealed transitions except at $T_t$. Previous experiments have relied on two types of techniques. The first utilizes thermodynamic measurements on exfoliated graphite substrates [11]. Recently, it has become clear that multilayer adsorption on these substrates is always accompanied by capillary condensation, so it is very difficult to determine surface phases near coexistence [12]. Another class of experiments, including the one reported here, utilizes microbalances [5-9,13] which do not suffer from this complication. All previous microbalance experiments have identified a single particularly simple type of triple-point wetting scenario in which a thin liquidlike film is stabilized on the substrate below $T_t$, and the thickness $d$ diverges as a power law $d \sim (-t)^n$, with $t = (T - T_t)/T_t$. The exponent $n$ is approximately $-1/3$, which reflects the fact that the chemical potential of the liquid below $T_t$ is larger than the chemical potential at solid-vapor coexistence by an amount proportional to $t$. This must be compensated by the decrease in the chemical potential due to the van der Waals interaction with the substrate, which is proportional to $1/d^3$. The experiments we describe below provide evidence for a distinctly different type of surface phase behavior. In particular, for Ar on gold, we find that, near bulk coexistence, a layered solid/liquid film structure is stabilized in an approximately 3 K interval which brackets $T_t$. The layered phase melts for temperatures both above and (surprisingly) below this interval. The thickness of the low temperature liquid film obeys a power law in $-t$. For methane on gold, films below $T_t$ are always solid, and the thickness is almost independent of $t$.

The quartz microbalance technique used to monitor the adsorbed coverage is conventional [5-7,9]. Adsorption takes place on the gold electrodes of the microbalance, which were used as received from the manufacturer. The main experimental challenge in these studies is to provide a uniform thermal environment. The microbalance was mounted in a cell inside two concentric radiation shields. The cell and the inner shield were made of gold-plated copper to minimize thermal gradients. Our thermometers were calibrated by measuring the saturated vapor pressure to locate the bulk triple point, using a cell connected to a heated fill line. The data reported here, however, were obtained using a cell which was loaded with gas at room temperature and then sealed to entirely eliminate the heated fill line. The amount of gas was sufficient to ensure that several mm$^3$ of bulk phase formed near $T_t$.

The primary data of our experiment consist of the frequency shift of the microbalance as a function of temperature; data for Ar and CH$_4$ are shown in Figs. 1 and 2, where the frequency shift has been converted to thickness in layers. Data were collected by changing the temperature of the cell by approximately 20 mK and waiting for the microbalance frequency to settle. As has been noted previously [8], we found that the time constant for mass transport in the cell was surprisingly long, and more than 24 h of settling time was typically required per data point. Figure 1 shows data for Ar as a function of $t$. For $t > 0.02$, corresponding to temperature more than 1.6 K above the triple temperature ($\sim$83.31 K), there are approximately 32 layers of adsorbed liquid; this value is determined by the competition between van der Waals forces, which tend to thicken the film, and gravity, which tends to thin it. At low temperatures, e.g., $t = -0.06$, or 5 K below $T_t$, the film is approximately 5 layers thick.
As can be seen in Fig. 1 the transition from the thick high temperature state to the thin low temperature film is not a smooth function of temperature. There are two significant temperatures in addition to \( T_t \); at \( t = -0.007 \) there is a small hysteretic step and a change in slope, and at \( t = 0.02 \) there is a discontinuity. The thermodynamic model discussed below identifies the region \(-0.007 < t < 0.02\) as a layered phase with solid adjacent to the substrate and a liquid layer on top. At both boundaries of this region, there is a first-order transition to a film which is entirely liquid. At high temperatures, the film is a wetting liquid film with a thickness that is essentially independent of temperature, while at low temperature, the liquid film thickness has a power law dependence on \( t \) with an exponent of \(-0.38\). The layered film thickness for \(-0.007 < t < 0.02\) obeys a power law dependence on \(-t\) with an exponent of \(-0.28\).

Figure 2 shows that the temperature dependence of the film thickness for \( \text{CH}_4 \) is distinctly different from Ar. Above \( T_t \) (\(-90.68 \text{ K}\)), the film has a constant temperature independent thickness of approximately 47 layers and shows no evidence of any phase transitions. At the triple point, the film thickness abruptly thins to 21 layers. It is noteworthy that in \( \text{CH}_4 \) both the bulk phase transition and the film thinning are hysteretic with a width of approximately 0.10 K, while in Ar the hysteresis in the bulk transition was undetectable. For \( \text{CH}_4 \), below \( T_t \), the film thickness is a smooth, slowly varying function of \( t \) having a finite slope at \( t = 0 \).

Pandit and Fisher [10] pointed out that the stability of various surface phases depends critically on the relative size of the surface tensions \( \sigma_{lv}, \sigma_{sw}, \sigma_{sl}, \sigma_{lw}, \) and \( \sigma_{sv} \) (where \( l \) = liquid, \( s \) = solid, \( v \) = vapor, and \( w \) = wall), and that a large number of surface phase transitions are possible in the vicinity of the triple point. Pettersen, Lyssek, and Goodstein [14] have constructed a simple phenomenological model in which the film is regarded as a slab or slabs of bulk phase with the surface tension, van der Waals potentials, and other effects treated as perturbations. We have used this type of model to interpret our data. The basis of the method is to write the grand free energy \( \Omega(\mu, T; z) \), for a film of arbitrary thickness \( z \) and minimize \( \Omega \) with respect to \( z \). Near the triple point, there are three free energies \( \Omega_l, \Omega_s, \) and \( \Omega_{lay} \), for the liquid, solid, and layered film, which need to be considered; the stable phase is of course the one with the lowest value of \( \Omega \). For example, the free energy of the layered phase for arbitrary values of the thickness of the liquid and solid slabs \( z_l \) and \( z_s \) is

\[
\Omega_{lay}(\mu, T; z_l, z_s) = (\rho_s - \rho_l) \frac{\Delta C_3^{lw}}{2z_s^2} + \rho_l \frac{\Delta C_3^{ls}}{2z_l^2} + \rho_l \frac{\Delta C_3^{lw}}{2(z_s + z_l)^2} - \rho_l (\mu - \mu_l(T)) z_l - \rho_s (\mu - \mu_s(T)) z_s + mgh(\rho_l z_l + \rho_s z_s) - \frac{\beta \rho_s}{z_s},
\]

where \( \rho_l \) and \( \rho_s \) are the densities, \( \mu_l(T) \) are the bulk chemical potentials, and \( \Delta C_3^{ij} \) are differences of van der Waals \( C_3 \) coefficients for the various bulk phases. The terms proportional to \( \mu - \mu_l(T) \) express the cost of forming a phase away from bulk coexistence. The term containing the surface tensions \( \sigma_{ij} \) accounts for the energy...
required to form solid-wall, solid-liquid, and liquid-vapor interfaces. The term proportional to \( mgh \) accounts for the gravitational potential energy of the film, while the last term proportional to \( \beta \) accounts for the strain energy in the solid part of the film [1,2]. Similar terms appear in \( \Omega_s \) and \( \Omega_l \). See Ref. [14,15] for further details.

Equation (1) and its analog for \( \Omega_s \) and \( \Omega_l \) can be numerically minimized with respect to the \( z_i \). The equilibrium \( \Omega \), the surface phase, and the film thicknesses are then determined by the lowest lying branch at each temperature. The relative positions of the three branches are determined by the magnitudes of the surface tensions. Figure 3 shows three different orderings of the free energies with \( \mu = \) the bulk coexistence value. The orderings correspond to different sequences of surface phase transitions near \( T_t \). The qualitative behavior of each free energy branch is independent of the values of the parameters. The single phase branches have essentially constant values of \( \Omega \) as long as the corresponding bulk phase is stable, with a cusplike rise at the triple point where the bulk phase becomes metastable. \( \Omega_{\text{lay}} \) is \( V \) shaped with a sharp minimum at \( T_t \). Figure 3(a) corresponds to the Ar surface phase diagram obtained from the data in Fig. 1 with a high and low temperature liquid phase separated by a layered phase near \( T_t \). Figure 3(b) shows a direct transition from liquid to solid at a temperature very close to \( T_t \), which we believe is the case for CH\(_4\). Figure 3(c) illustrates the triple-point wetting scenario inferred from all previous experiments in which liquid films coexist with bulk solid over a wide range of temperature.

To compare the model with the experiments, the \( z_i \) given by the equilibrium \( \Omega \) can be compared to the data in Figs. 1 and 2. This requires numerical values for the parameters in the free energy of Eq. (1). Although the densities [16], van der Waals coefficients [17], bulk chemical potentials, and \( \sigma_{ls} \) are known, \( \sigma_{sw} \), \( \sigma_{sl} \), and the elastic strain parameter \( \beta \) are not. If \( \sigma_{sw} \), \( \sigma_{sl} \), and \( \beta \) are treated as temperature independent fitting parameters, we find that the model cannot reproduce the features we observe at \( t = -0.007 \) and 0.02. Both the elastic constants, which determine \( \beta \), and the surface tensions are, in fact, temperature dependent. If we include a linear coefficient of temperature variation for \( \sigma_{sl} \) and \( \beta \) as additional fitting parameters, we obtain qualitative agreement between the model and the data. The parameters resulting from the fitting procedure are physically reasonable. Details will be given elsewhere [15]. Figure 4 shows the coverage as a function of temperature for Ar on Au. The model accurately reproduces the positions of the discontinuities. In the liquid phase, the model predicts that the film thickness obeys a power law with an exponent of \(-0.34\), and an exponent of \(-0.27\) in the layered phase, in reasonable agreement with the data.

A similar analysis of the CH\(_4\) data shows that the free energy diagrams for this case look qualitatively like Fig. 3(b). The fact that the film thickness is independent of temperature above \( T_t \) implies that the liquid branch lies below both the solid and layered branch in this temperature range. The smooth behavior of the thickness below \( T_t \), as well as the nondivergent temperature dependence of the thickness, suggests that the film is entirely solid. As Fig. 3(b) shows, the surface transition can lie extremely close to \( T_t \), even for substantial offsets in the \( \Omega \) vs \( t \) curves. In this scenario, the layered state is never stable.
This may be related to the fact that we observe substantial hysteresis in the bulk phase transition. Without a layered state, formation of the solid requires a nucleation event. For Ar, the solid can grow continuously from the partially solid layered film.

In summary, we have documented two scenarios for triple-point wetting which are distinctly different from those previously reported. They are characterized by first-order surface phase transitions at temperatures close to but not coincident with $T_t$ and by temperature dependence of the coverage which differs markedly from $(-t)^{-1/3}$. The phase behavior of films near the triple point depends critically on rather subtle variations in the surface tensions and their temperature dependence. The thermodynamic model of Ref. [14] provides a useful framework for analysis of these effects.

This work was supported by NSF Grant No. DMR 9623976.