Capillary Condensation between High-Energy Surfaces. An Experimental Study with a Surface Force Apparatus.

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Abstract. - We study the capillary condensation of an undersaturated vapour between high-energy surfaces with a surface force apparatus. The adhesion force shows a large hysteresis cycle when the surfaces are quasi-statistically brought to contact and moved apart, revealing an asymmetry between the condensation and evaporation processes. The condensation of a liquid bridge between the surfaces is associated with a force discontinuity, and occurs at distances which increase with the vapour pressure. The adhesion force is consistent with the classical theory of capillarity, and reveals the presence of wetting films. A mechanism for condensation is proposed based on the instability of the wetting films under their mutual attraction. We predict a condensation distance which grows linearly with the wetting film thickness, in good agreement with the experimental observation.

Introduction. - The adhesion properties of surfaces in the presence of a condensable vapour is known to be strongly affected by capillary condensation. A liquid bridge may form between two solid surfaces separated by a small distance, even if the vapour pressure $P_V$ is lower than the saturated pressure $P_{sat}$, provided that the gain in free energy due to the disappearance of the solid-vapour interfaces balances the cost of creating the unfavourable liquid phase. In the frame of classical capillarity, the equilibrium curvature $r_{eq}^{-1}$ of the fluid interface is given by Kelvin’s law:

$$kT \ln \left( \frac{P_V}{P_{sat}} \right) = v_L \left( -\frac{\gamma}{r_{eq}} + P_V - P_{sat} \right),$$

which expresses the equality of the chemical potential in the vapour phase and in the liquid phase, whose pressure $P_L$ obeys the Laplace law of capillarity: $P_L = P_V - \gamma/r_{eq}$ ($\gamma$ is here the liquid-vapour surface tension and $v_L$ the liquid molecular volume). Under ambient conditions, Kelvin’s radius is very small: a typical value is less than 10 nm. The corresponding Laplace pressure is large ($< -10$ atm) and leads to strong attractive forces between the surfaces. This explains the importance of capillary condensation in many dispersed systems, such as powders, particles, granular flows, porous media, etc.

Early studies of capillary condensation between atomically smooth mica surfaces with a
surface force apparatus (SFA) have shown that small liquid bridges of light alkanes and water obey Kelvin's law up to radii of curvature of some molecular size [1-3]. The "pull-off" force needed to separate the surfaces initially in contact through the condensed liquid has also been measured. However in these experiments the mechanical instabilities inherent in the force measurements prevent continuous variation of the distance between the surfaces. This work reports an experimental study of the adhesion between surfaces of high energy in the presence of vapour, with a SFA of enhanced mechanical stability [4]. The force between the surfaces is measured for distances varying continuously from 100 nm apart up to mechanical contact. The results give new insight into the mechanisms of capillary condensation and evaporation in the case where the liquid phase wets the solid substrates.

Experiment. – Our experimental system consists of a sphere of radius \( R = 3.29 \) mm, made of fire-polished pyrex coated with a 50 nm thick platinum layer, and a plane made of fire-polished pyrex. These solid substrates are a good compromise between high rigidity (giving a negligible elastic deformation under the capillary forces) and low roughness (less than 1 nm measured by an atomic-force microscope). The sphere and the plane are mounted on the SFA and placed in a sealed chamber, in the presence of a desiccator (powder of P_2O_5) and of \( n \)-heptane vapour. The partial pressure of \( n \)-heptane vapour is varied by introducing in the chamber a liquid mixture of \( n \)-heptane and non-volatile polydimethylsiloxane whose saturating vapour pressure at room temperature is less than 0.1 Pa. The partial pressure of \( n \)-heptane vapour in the chamber is then related to the heptane concentration of the liquid mixture by Raoult's law.

We outline here the main characteristics of the SFA only; a detailed description is given in [4, 5]. The sphere can be displaced normal to the plane by a piezoelectric ceramic with a resolution better than 1 Å. We use displacements at constant velocity ranging usually between 0.2 Å/s and 5 Å/s. The relative displacement \( D \) between the sphere and the plane is measured by a capacitive sensor. A feedback loop between this sensor and the piezoelectric element monitoring the displacement confers the system a great mechanical stability. The force between the two substrates is obtained from the displacement of the plane relative to a rigid frame to which it is elastically attached. In the reported experiments we used values of the elastic constant ranging between \( 10^4 \) N/m and \( 2.5 \cdot 10^6 \) N/m. In this case the resolution of the force measurement was always better than 0.5 µN. The absolute distance \( h \) between the surfaces is measured from the relative displacement \( D \) after determining the displacement of the origin \( D_0 \). Reference [5] describes the different methods, electrical and mechanical, to determine the origin. In these experiments we used a mechanical origin, determined from the elastic repulsion between the substrates beyond mechanical contact.

Figure 1 shows the force measured between the surfaces as a function of their distance \( h \), for different values of \( P_V \). The surfaces are initially located more than 100 nm apart, far enough so they do not interact. They are brought toward each other at a constant slow velocity of 1 Å s\(^{-1}\). The condensation of a liquid bridge between the surfaces is revealed by a large discontinuity in the force, which jumps from an (almost) zero value toward a finite attraction. The maximum attraction is about two orders of magnitude larger than the maximum attractive force measured when the solid surfaces are immersed in a macroscopic liquid drop. This strong attraction is due to the capillary force exerted by the liquid bridge. The discontinuity of the force shows that capillary condensation corresponds to a first-order transition [6]. Some distance beyond the mechanical contact, the relative motion of the surfaces is reversed at the same velocity. The force has a strong hysteresis and remains negative until much larger distances than in the forward motion. The limits of the hysteresis give the range of distance over which the system has two metastable states, one unbridged, and one with a liquid bridge.
Fig. 1. – Variation of the force $F/R$ between the sphere and the plane as a function of their distance $h$, for two different values of the $n$-heptane vapour pressure. The arrows on the curves show the direction of the surfaces relative motion, at a constant velocity of 1 Å/s. The number of arrows increases with the vapour pressure. When the surfaces advance toward each other, the force undergoes a discontinuity, due to the condensation of a liquid bridge. The abscissa $h_c$ of the discontinuity, marked by an arrow on the $h$-axis, increases with the vapour pressure. The dashed line parallel to the $h$-axis corresponds to the ordinate $4\pi \gamma$. Each curve corresponds to a single run, and is reproducible when the system is cycled.

Figure 1 also shows the effect of the vapour pressure on the adhesion force. The range of distances for which the receding force has a non-zero value increases with $P_v$. This range gives an order of magnitude for the meniscus curvature; in this set of experiments it varies typically between 8 nm and 80 nm. The distance $h_c$ at which condensation occurs, which does not depend on the drift velocity in the range 0.2 Å/s to 2 Å/s, is also growing with the vapour pressure but at a smaller rate. On the contrary, the maximum attraction between the surfaces decreases with increasing vapour pressure. Such an effect has been reported by Christenson [2] in his measurements of the pull-off force between mica surfaces in the presence of alkane vapour.

Discussion. – For a quantitative analysis of the data we introduce the radial extension $\varepsilon$ of the bridge, its axisymmetric curvature $r^{-1} = r_{eq}^{-1} + \varepsilon^{-1}$, the height $z$ between the surfaces at the distance $z$ from the axis, and the thicknesses $e_1$ and $e_2$ of the wetting films coating each substrate far from the bridge (fig. 2). In the frame of classical capillarity, and in the limit $r_{eq} \ll R$, the attractive force exerted by the liquid bridge is [2]:

$$F_{cap} = 4\pi \gamma R \left( \frac{z - h}{2 r_{eq}} \right) \left( 1 + o\left( \frac{r_{eq}}{z}, \frac{z - h}{R} \right) \right).$$

The height $z$ depends on the shape of the meniscus. If this shape is a simple circle cutting the film tangentially, then $z = 2r + e_1 + e_2$. However, in the region close to the film, the meniscus shape is affected by the surface forces responsible for the film adsorption [7-9]. In the case of van der Waals forces, and if the radius $r$ is larger than the film thickness, one can show that $z = 2r + (3/2)(e_1 + e_2)$ [9-11]. Thus, the equilibrium force given by classical capillarity, in the case of wetting by van der Waals forces is, to the leading order in $r_{eq}/\varepsilon$,

$$F_{cap} = 4\pi \gamma R \left( 1 - \frac{h - (3/2)(e_1 + e_2)}{2 r_{eq}} \right).$$

(2)
Equation (2) does not take into account long-range solid-solid interactions. This is justified in the experiment, since these interactions are separately measured by immersing the surfaces in a macroscopic liquid droplet, and are found to be two orders of magnitude smaller than the maximum capillary force. A more serious approximation is the neglect of the radial curvature (i.e. the higher-order terms in \( r_{eq}/\beta \)). However, with the order of magnitude of the menisci curvature obtained in this experiment, this approximation should not lead to a relative error \( \Delta F/F_{\text{max}} \) higher than 2%.

Equation (2) has two interesting consequences. First, when the liquid bridge is in equilibrium with the vapour, the force varies linearly with the distance \( h \) between the surfaces. In the experiment, when the surfaces are receding, we observe that the force \( F(h) \) at short and intermediate distances has a constant slope which does not depend on the drift velocity. This behaviour is in agreement with eq. (2) and suggests that the liquid bridge keeps its equilibrium curvature. At larger distances, \( F(h) \) departs from a linear behaviour and becomes slightly velocity dependent. This is due to the loss of liquid-vapour equilibrium, since the evaporation rate needed to ensure a constant curvature increases rapidly with \( h \) and diverges when \( h \approx 2r_{eq} \) [12]. Assuming the validity of eq. (2), we derive the equilibrium radius of curvature \( r_{eq} \) from the slope of the receding force \( F(h) \) at short distances. The values increase with the vapour pressure. In the following we focus on four experiments in which the values of \( r_{eq} \) are: 3.5 nm, 11.5 nm, 17.5 nm and 37.7 nm. The smallest value is about ten time larger than the heptane molecular diameter (\( \approx 4 \text{ Å} \)). A number of works on similar liquids conclude that the surface tension does not deviate significantly from its macroscopic value [1,13,8] for this range of curvature.

Another consequence of eq. (2) is that \( F_{\text{cap}} = 4\pi \gamma R \) at the distance \( h_0 = (3/2)(e_1 + e_2) \), whatever the vapour pressure or the amount of condensed liquid. The experimental observation agrees qualitatively with this property, since all the curves \( F_{\text{cap}}(h) \) obtained for different vapour pressures intersect in a small region, of ordinate around \( 4\pi \gamma R \).

(1) The Hamaker constant pyrex/heptane/vapour is assumed equal to the one of fused-quartz/octane/air, \(-0.7\times10^{-20} \text{ J}[14]\). For platinum/heptane/vapour, we use the approximation

\[
A_{\text{SLV}} = (\sqrt{A_{SS}} - \sqrt{A_{LL}})(\sqrt{A_{VV}} - \sqrt{A_{LL}})
\]

with \( A_{SS} = 33\times10^{-20} \text{ J}[15] \), \( A_{LL} = 4.5\times10^{-20} \text{ J}[14] \), and \( A_{VV} = 0 \), yielding \( A_{\text{SLV}} = -8\times10^{-20} \text{ J} \).
eq. (2), the average thickness of the wetting films can be measured at each vapour pressure, from the abscissae \( h_0 \) such that \( F_\text{eq}(h_0) = 4\pi\gamma R \). It is of interest to compare the results with the theory of van der Waals wetting, since the assumption of van der Waals interactions underlies the \( e \)-dependence of eq. (2). The expected film thickness on each substrate is related to the Kelvin radius by [9]

\[
\frac{A_{i\text{SLV}}}{6\pi\varepsilon_i^3} = -\frac{\gamma}{\tau_{eq}} = \frac{kT}{v_L} \ln \frac{P_V}{P_{sat}} - P_V + P_{sat},
\]

where \( A_{i\text{SLV}} \) is the substrate/liquid/vapour Hamaker constant [14]. Figure 3 shows the plot of \( h_0 \) vs. \( \tau_{eq}^{1/3} \). The error bars come mainly from uncertainty on the determination of the sphere radius (\( \Delta R/R = 1\% \)). The data is in good agreement with the linear dependence predicted by van der Waals wetting. The order of magnitude is compatible with the theoretical values given by (3), based on Hamaker constants estimated from the literature (see (1)). It is remarkable that the van der Waals theory provides a reasonable description of the experimental data, when the average film thickness is not very much larger than the surface roughness. It is also of interest to notice that eqs. (2) and (3) predict an increase of the maximum force with decreasing vapour pressure, as observed in the data.

In fig. 3 we also plot the distance of condensation \( h_c \) vs. \( \tau_{eq}^{1/3} \). The distance \( h_c \) is significantly larger than \( h_0 \), but also shows a linear dependence on \( \tau_{eq}^{1/3} \). This suggests that van der Waals forces play a role in the condensation process. A condensation mechanism can be proposed which explains this result qualitatively. We first assume that, for \( h > h_c \), the unbridged state is less stable than the bridged state. Thus condensation may occur either because the energy barrier between the two metastable states is low enough to be overcome by thermal fluctuations, or because the unbridged state becomes unstable. We follow this last possibility and study the stability of the two wetting films coating the substrate in the unbridged state, under the effect of van der Waals interactions. For simplification, we consider two flat and identical substrates, separated by a distance \( h \). The thickness \( \varepsilon \) of the two wetting films is related to the free energy per unit surface \( F_{\text{SLVLS}} \) by the condition of equilibrium with the vapour [5]:

\[
F_{\text{SLVLS}}(h, \varepsilon) = -\frac{2A_{\text{SLV}}}{12\pi\varepsilon^2} + \frac{2A_{\text{SLV}}}{12\pi(h - \varepsilon)^2} - \frac{A_{\text{LL}}}{12\pi(h - 2\varepsilon)^2} - \frac{A_{\text{SLS}}}{12\pi h^2},
\]

\[
\frac{\partial F_{\text{SLVLS}}(h, \varepsilon)}{\partial \varepsilon} = \frac{A_{\text{SLV}}}{6\pi\varepsilon^3} = \frac{kT}{v_L} \left( \ln \frac{P_V}{P_{sat}} - P_V + P_{sat} \right).
\]

Here \( A_{\text{LL}} \) and \( A_{\text{SLS}} \) are the Hamaker constants for the liquid/liquid and solid/liquid/solid interactions. Defining \( \alpha = -A_{\text{LL}}/A_{\text{SLV}} > 0 \), the equilibrium thickness of interacting wetting films is given by the solution of the homogeneous equation

\[
g(\varepsilon, h) = \frac{1}{\varepsilon^3} + \frac{1}{(h - \varepsilon)^3} + \frac{\alpha}{(h - 2\varepsilon)^3} = \frac{1}{\varepsilon^3}.
\]

The condition for relative stability is given by: \( \partial^2 F_{\text{SLVLS}}(h, \varepsilon) / \partial \varepsilon^2 > 0 \). The study of eq. (4) shows that when \( h \) is larger than a critical value \( h_c \), there is only one stable solution \( \varepsilon(h) \) smaller than \( h/2 \). \( \varepsilon(h) \) is a decreasing function of \( h \), and goes to the unperturbed solution \( \varepsilon \) when \( h \) goes to infinity (i.e. when interactions with the opposite substrates are negligible). By continuity, when the surfaces are brought toward each other from a remote position
where the wetting films do not interact, the films take the thickness $\varepsilon(h)$. When $h$ reaches the critical value $h_c$, the solution $\varepsilon(h_c)$ becomes unstable with respect to all positive fluctuations (i.e. fluctuations which make the films thicker). Equation (4) has no solution in between 0 and $h/2$ for $h < h_c$. Thus $h_c$ is a critical distance at which the films become unstable and coalesce under the effect of the attractive interaction with the opposite substrate.

Due to homogeneity of eq. (4), the critical distance $h_c$ varies linearly with the wetting film thickness $\varepsilon$, which is consistent with the experimental data. The ratio $h_c/\varepsilon$ is a slowly varying function of $x$: a good approximation if $x \gg 2 \cdot 10^{-3}$ is $h_c = 2 \varepsilon(1 + (2x)^{1/2}/2)^{4/3}$. For a value of $A_{SLV}$ lying in between the estimated Hamaker constants of our substrates (see (1)), the coalescence distance predicted by this mechanism is $3.5 < h_c/\varepsilon < 4.8$. This result is compatible with the experimental data $h_c/\varepsilon = 3h_c/h_0 = 4.5$. This simplified calculation does not permit us to go further in the quantitative comparison with the experiment, first because the experimental substrates are of a different nature and are not flat, second because we have not considered the kinetic aspects of the instability. However, we believe that this mechanism captures an essential feature of the condensation process and explains the linear relation between the condensation distance and the wetting films thickness.

**Conclusion.**—The adhesion force measured between high-energy surfaces as a function of their separation, in the presence of an undersaturated vapour, reveals some basic features of capillary condensation. The condensation of a liquid annulus bridging the surfaces appears as a first-order transition. The condensation and evaporation processes occur with a strong hysteresis when the surface separation is varied. We find that the adhesion force is compatible with the macroscopic theory of capillarity, and derive from it the radius of curvature $r_{eq}$ of the liquid-vapour interface and the thickness of the wetting films. We also find that the surface separation at which condensation occurs grows like $r_{eq}^{1/3}$, and interpret this result by a mechanism of coalescence of the wetting films induced by van der Waals interactions. We think that these results may be of help in understanding the adsorption of vapour in porous media.

**REFERENCES**


