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To cite this article: D. Quéré et al 1989 EPL 10 335

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15 October 1989

Europhys. Lett., 10 (4), pp. 335-340 (1989)

Making van der Waals Films on Fibers.

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(received 20 April 1989; accepted in final form 7 August 1989)

PACS. 68.10C – Surface energy. PACS. 68.10G – Interface activity, spreading. PACS. 68.15 – Liquid thin films.

Abstract. – The liquid layer coating a solid fiber drawn at constant velocity V_0 out of a bath of liquid is all the thicker since V_0 is large. We discuss in this letter the limit of very low capillary numbers: if the liquid wets the fiber, the thickness e of the liquid layer should not depend any longer on V_0 below a critical value of the velocity ($V_0 < \tilde{V}_0$) and should be equal to $a^{2/3} b^{1/3}$, where a is a microscopic length related to the wetting interactions (which are supposed to be van der Waals ones) and b is the radius of the fiber. This thickness is in the 100 Å range. Then, a new experiment is presented: it consists of making such very thin films of dodecane on polymeric fibers and measuring their average thicknesses by gas chromatrography titrations. The results are promising: this technique could be an interesting alternative for detecting or measuring very thin films on curved surfaces for which more usual methods like ellipsometry are not suited.

1. Wetting films on fibers in contact with a reservoir.

Coating a fiber—*i.e.* a thin solid cylinder of radius equal to a few tens of microns—with a liquid is a practical problem of considerable importance (lubrication of textile fibers, optical fiber processing, fibers-reenforced resins, ...) but generally destined for failure: the liquid sheath breaks up into a periodic array of droplets, in order to minimize its interfacial energy (Rayleigh instability) [1].

Actually such a liquid film may be stabilized by attractive interactions, for example van der Waals ones, between solid and liquid. Its equilibrium thickness e has been calculated [2] for a fiber in a saturated atmosphere of a wetting [3], volatile liquid or in contact with an infinite reservoir of a nonvolatile, wetting liquid.

In this latter case the calculation of the equilibrium thickness can be done using a simple pressure argument. For a fiber of radius to be covered by a liquid film of thickness e in contact with a reservoir (for example a huge drop put on the fiber), both film and drop may coexist if their pressures equilibrate. We take the drop pressure equal to the atmosphere one (the Laplace pressure difference between drop and air is neglected); on the other hand,

two ingredients have to be mixed to describe the internal pressure of the film: one is due to curvature (*i.e.* the pressure difference across the free interface, equal to $\gamma/(b + e)$ where γ is the surface tension of the liquid), the other to its microscopic thickness: to maintain it at thickness *e*, the pressure $\pi_d(e)$ (the so-called disjoining pressure) is required [4]. For non-retarded van der Waals interactions

$$\pi_{\rm d}(e) = \frac{-A_{\rm SLV}}{6\pi e^3}.$$
 (1)

In eq. (1), A_{SLV} is the Hamaker constant related to the interaction of vapour (V) and solid (S) separated by liquid (L). A_{SLV} is negative in wetting conditions, which allows the film to exist. In the pressure balance the disjoining pressure must be counted negatively, since it contributes to thicken the film. The equilibrium condition between the drop and the film can now be written ($e \ll b$)

$$0 = \frac{\gamma}{b} + \frac{A_{\rm SLV}}{6\pi e^3}.\tag{2}$$

It is convenient to introduce a length a defined by

$$a^2 = \frac{-A_{\rm SLV}}{6\,\pi\gamma}.\tag{3}$$

For usual liquids and solids, a is about 1 Å. From eqs. (2) and (3) the equilibrium thickness of the film is

$$e = a^{2/3} b^{1/3}.$$
 (4)

In some cases, gravity has to be taken into account. If we consider a vertical fiber partially immerged in a flat bath of liquid, the pressure balance between the microscopic film and the reservoir becomes

$$0 = \frac{A_{\rm SLV}}{6\pi e^3} + \frac{\gamma}{b} + \rho gh , \qquad (5)$$

with ρ the volumetric mass of the liquid, g the gravity constant and h the height of the liquid above the reservoir. Hence the effect of gravity is to make e smaller, following the law

$$e = \frac{a^{23} b^{1/3}}{\left(1 + h/h_0\right)^{1/3}},\tag{6}$$

where $h_0 = x - 2/b$, x^{-1} being the capillary constant: $x^{-1} = \sqrt{\gamma/\rho g}$. The influence of gravity can be neglected if

$$h \ll \frac{x^{-2}}{b}.$$
 (7)

The dynamics of spreading of such thin films (e is of the order of 100 Å) has been calculated: it should be very slow [5]. Therefore, instead of waiting for the film to spread, we undertook to make it by entraining a fiber through an interface.

2. Making liquid films by entraining a fiber through an interface.

2'1. Landau-Deryaguin's formula. – The elaboration of such films is pictured in fig. 1: a fiber is withdrawn through an oil/air interface at constant speed V_0 and carries out a film of wetting oil. The quantity of liquid, *i.e.* the thickness of the film, depends on V_0 . The following simple argument may convince that the faster the fiber is moved, the thickness is the



Fig. 1. – Fiber drawn with velocity V_0 out of a reservoir of oil. $\Delta \varphi$ is the Laplace pressure difference across the free interface.

film: the Laplace pressure difference across the oil film/air interface is $\Delta p = \gamma/b$ ($e \ll b$), while the unperturbated part of the meniscus is defined by: $\Delta p = 0$. This pressure difference between the film and the bulk causes the drainage of the film (we are in a case where Laplace pressure is larger than the gravitational one): this thinning process takes place continually, while the fiber moves, carrying the liquid: the final thickness of the film results from this competition.

The exact variation of $e vs. V_0$ was first calculated by Landau and Levich for a plane withdrawn from a reservoir [6] and their theory was adapted to fibers by Deryaguin [7]

$$e = 1.3 b \left(\frac{V_0}{V^*}\right)^{2/3},\tag{8}$$

where $V^* = \gamma/\eta$ is characteristic of the liquid: γ is the surface tension and η the oil viscosity. The 1.3 constant is an integration constant. For (8) to be valid, the capillary number (*i.e.* V_0/V^*) and the Goucher number (*i.e.* b/x^{-1}) have to be smaller than unity.

2.2. Small capillary number limit. – Equation (8) indicates that when V_0 tends to zero, so does *e*: the disjoining pressure has to be taken into account. Under a certain speed \tilde{V}_0 the pressures in the film and in the bulk are equal: the thickness does not decrease any more,

and it fixes on the value given by eq. (1). Equation (8) becomes

$$\begin{cases} e = a^{2/3} b^{1/3}, & V_0 < \tilde{V}_0, \\ e = 1.3 \cdot b \cdot \left(\frac{V_0}{V^*}\right)^{2/3}, & \tilde{V}_0 < V_0 \ll V^*, \end{cases}$$
(9)

and

$$\tilde{V}_0 \sim \frac{a}{b} \cdot V^*. \tag{10}$$

This crossover speed can be estimated: for a = 2 Å, $b = 20 \,\mu\text{m}$ and $V^* = 2000 \,\text{cm/s}$, we get $\tilde{V}_0 = 200 \,\mu\text{m/s}$ which is easy to realize in the laboratory.

3. Experimental results.

3.1. Set-up. – All the previous experiments of withdrawal of a fiber through an interface were made at relatively high speed $(V_0 > \tilde{V}_0)$: the purpose was either to check Landau's regime (eq. (8)) [8] or to study Rayleigh instability [9]. The film was generally made at an oil/air interface [8, 10] but in one case at an oil/water interface [9]. We have studied this latter situation in order to avoid problems related to oil evaporation, and to reduce gravity effects (the density of oil is about 0.75).

The experimental set-up is pictured in fig. 2: a fiber (either nylon or polyester of diameter $2b = (19 \pm 1) \,\mu$ m) runs successively across three layers of liquid: first pure dodecane, then triply-distilled water, finally carbon-tetrachloride. The whole is held in a glass U-tube. As soon as the fiber is entrained (by a stepping motor), a film forms at the dodecane/water interface, passes through the water layer, and then dissolves in carbon-tetrachloride: the dodecane fraction is measured out by gas chromatography (GC) using a flame ionization detector. Knowing the volume of tetrachloride and the fiber length that passed through the interface, the mean thickness of the fiber can be derived. The extreme sensitivity of GC



Fig. 2.

Fig. 3.

Fig. 2. – Experimental set-up. The glass tube which contains the liquids and the fiber is 4 cm high. Fig. 3. – Measured thickness e of the dodecane layer as a function of V_0 , the entrainment speed of the fiber (\bullet polyester and | nylon).

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enables to detect 5 Å-thick films for an entrained length of 20 cm. Two different motors were used, allowing V_0 to vary, respectively, from 1 to 100 μ m/s and from 0.7 to 14 cm/s.

3.2. First results. – The interfacial tension between dodecane and water was measured by the pendant drop method: $\gamma_{\rm OW} = 46 \text{ mN/m} (\pm 2)$, the dodecane viscosity is $\eta = 1.40 \pm 0.05$ Poise at 20 °C; hence $V^* = 3300 \text{ cm/s} (\pm 10\%)$.

On the other hand, after calibrating the GC apparatus (for a solution of known concentration, the reproducibility is $\pm 5\%$ around the known value), we have checked that with a zero entrainment speed ($V_0 = 0$) no oil was carried through the water phase.

In fig. 3, the film thickness e is plotted (on a log-log scale) as a function of V_0 (the fiber speed) for two different kinds of monofilament (nylon or polyester) of the same diameter. These results appeal for the following comments:

1) At «high» velocity $(V_0 > \dot{V}_0)$, the thickness *e* increases with the velocity V_0 in accordance with Landau-Deryaguin's predictions (eq. (8)): the experimental behaviour is found to be: $e = \alpha b(V_0/V^*)^{0.69\pm0.05}$ with $\alpha = 1.75 \ (\pm 25\%)$; this value is somewhat larger than the predicted one (1.75 in place of 1.3) but we do not think that this discrepancy is significant, in view of the accuracy on α (25%). In this regime, polyester and nylon fibers follow the same experimental law since they have the same diameter.

2) At «low» speed ($V_0 < \tilde{V}_0$) the thickness of the film seems to be independent of V_0 , as predicted.

Let us compare our *e*-values with literature data. From eq. (3), we compute the microscopic length *a*: A_{SLV} is here $A_{SOLID/DODECANE/WATER}$ (that we name A_N or A_P according to the fiber material) and $\gamma = \gamma_{DOD/WATER}$. From [11] and [12], $A_N = -1.74 \cdot 10^{-21}$ J and $A_P = -2.9 \cdot 10^{-21}$ J and hence: $a_N = 0.45$ Å, $a_P = 0.58$ Å ($a_P > a_N$ because polyester polarizability is larger than Nylon's). Let us note that *a* is very small: this arises from the fact that our system is wetting (*i.e.* oil film can exist on fiber in an aqueous environment), but «in extremis»: the dispersive component of the water tension is slightly smaller than the dodecane tension [11].

The thickness of the van der Waals films can now be calculated in both cases, using eq. (4): the gravity effects on the thickness of the films can be neglected, since the height of the microscopic film above the reservoir of dodecane cannot be larger than the thickness of the layer of water (see fig. 2); this latter is one centimeter high: that ensures that the condition (7) is fulfilled, since $h_0 = 14$ cm for our system. So we find

$$e(N) = 27 \text{ Å}, \quad e(P) = 32 \text{ Å}.$$

So the agreement is good with our experimental values: $e(N) = (24 \pm 4)$ Å, $e(P) = (34 \pm 4)$ Å. The most surprising thing is that it seems possible to measure by this method the difference of wetting behaviour of dodecane towards our two materials, nylon and polyester, which have slightly different polarizabilities.

3) By extrapolating Landau's regime we can find a crossover speed \tilde{V}_0 in good agreement with the one calculated from eq. (10): $\tilde{V}_0 = (175 \pm 50) \,\mu\text{m/s}$.

3'3. Discussion. – A recurrent problem related to spreading phenomena over which we passed in silence up to now is the roughness of the solids on which experiments are performed. It is usual for fibers to show axial grooves [5].

A theoretical paper of Andelman et al. has recently been devoted to the statics of wetting on rough surfaces [13]: we recall the main results.

1) Long-wavelength fluctuations of the solid surface are followed by the liquid interface if $q^{-1} \gg \xi$, where q is the wave vector of these fluctuations and ξ a healing length (determined by a balance between surface tension and disjoining pressure) which behaves as

$$\xi \sim \frac{e^2}{a}.\tag{11}$$

For our systems, $\xi \simeq 2000$ Å. On this scale (and down to 1000 Å) it was possible to check that our fibres were smooth by Scanning Electron Microscope observations.

2) Short-wavelength fluctuations are damped (by the surface tension of the liquid for $q^{-1} \ll \xi$ and by averaging the local disjoining pressure for $q^{-1} \ll e$). Especially in this latter case we have no information about the roughness of the fibers. Nevertheless we still believe that these liquid films which form at the dodecane/water interface are continuous films, arguing that:

a) If it were not the case, we should not have a good agreement for the value of V_0 .

b) If a mixture of two alcanes (dodecane and hexadecane) is used instead of dodecane alone, the composition of the thin liquid layer is not the same as the one of the bulk (which was 50%/50%): hexadecane which is slightly more polarizable than dodecane is present with a larger concentration in the film phase. That corroborates the fact that these films are determined by van der Waals interactions. A quantitative analysis of this «chromatrography-like» process (since dodecane and hexadecane are partially separated by the making of the film) is under progress, with the same experimental set-up.

We thank M.-A. GUEDEAU-BOUDEVILLE for introducing us to the joys of gas chromatography and B. CATOIRE for supplying (smooth) fibers. In addition, we thank Atochem for financial support.

REFERENCES

- [1] LORD RAYLEIGH, Proc. London Math. Soc., 10 (1878) 4.
- [2] STAROV V. M. and CHURAEV N. V., Kolloid-Z., 40 (1978) 909.
- [3] BROCHARD-WYART F., J. Chem. Phys., 84 (1986) 4664.
- [4] DERYAGUIN B., Kolloid-Z., 17 (1955) 191.
- [5] QUÉRÉ D., DI MEGLIO J. M. and BROCHARD-WYART F., Rev. Phys. Appl., 23 (1988) 1023.
- [6] LANDAU L. and LEVICH V., Acta Physicochemica USSR, 17 (1942) 42.
- [7] DERYAGUIN B., Dokl. Acad. Nauk USSR, 39 (1943) 11.
- [8] BONDARENKO V., Trans. Groznyy Petrol. Inst. (1948).
- [9] CARROLL B. J. and LUCASSEN J., Chem. Eng. Sci., 28 (1973) 23; J. Chem. Soc. Faraday, 70 (1974) 1228.
- [10] GOUCHER F. S. and WARD H., Philos. Mag., 44 (1922) 1002.
- [11] ISRAELASHVILI J., Intermolecular and Surface Forces (Academic Press, New York, N.Y.) 1985.
- [12] DUHAU P., Thèse, Université de Haute-Alsace (1985).
- [13] ANDELMAN D., JOANNY J. F. and ROBBINS M. O., Europhys. Lett., 7 (1988) 731.