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Critical radius of holes in liquid coating

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Abstract. — In this paper, we focus our interest on the stability of a thin liquid film deposited on a non-wetting surface. The film is metastable and dewets by nucleation and growth of dry patches. Dry patches grow only if the radius is greater than a critical value, R_c . We measured R_c in the case of polythene terephthalate coated by glycerol or di-iodomethane as a function of e , the thickness of the film. The experimental results agree well with the predicted formula [5, 6] $R_c = \frac{e}{\ell \sin \theta_e}$ where θ_e is the equilibrium contact angle and ℓ a logarithmic function of R_c .

Introduction.

A sizeable quantity of liquid deposited on a non-wetting surface forms a puddle with an equilibrium thickness e_s . This thickness results from the competition between the capillary and gravitational forces in accordance with the formula : $e_s = 2 \kappa^{-1} \sin \frac{\theta_e}{2}$, where $\kappa^{-1} = \sqrt{\frac{\gamma}{\Delta \rho g}}$ is the capillary length, γ the superficial tension of the liquid, $\Delta \rho$ the difference of density between liquid and air, g the gravitational acceleration and θ_e the equilibrium contact angle. For example, a water puddle has an equilibrium thickness of about 3 mm on polythene terephthalate. However, in coating experiments, a film of liquid is often required to be thinner ; it is then metastable and evolves *via* nucleation and growth of a dry patch. The liquid film then « dewets ». Various aspects of the stability of liquid films have been studied in the last ten years. Srolovitz *et al.* [1] have studied the instability of a thin liquid film as regard to a periodic perturbation creating several dry holes. Sekimoto *et al.* [2] have developed independently a general model describing the morphological stability of a liquid on a solid surface. They apply this model to different shapes of liquid interface like a ridge or a hole. The last one is the one we are interested in this paper. Experimentally, Padday *et al.* [3] noticed the existence of a critical rupture thickness of thin films on low-energy substrates (non-wetting situation).

We show experimentally that the break-up of a thin liquid film deposited on a non-wetting solid surface depends on the size of the nucleated dry hole. This has been seen in soap films by

previous work of Taylor and Michael [4]. As in every nucleation-growth phenomenon, the size of the nucleated dry patch has to be sufficient to induce dewetting (growth of the dry patch). Indeed, if the dry patch of size R is too small, the hole vanishes and the liquid film heals over. If the hole is large enough, the liquid dewets. The critical radius of nucleation, R_c , has a value between the radius of healing over and the radius of dewetting. By making controlled dry holes in liquid films of various thicknesses, we obtained both situations (healing over and dewetting) and then derived an estimation of R_c . We found that R_c varies with the thickness of the liquid film in agreement with a simple model we proposed previously [5] and that was proposed independently by Sharma recently [6]. The experiments were carried out with different liquids on a surface of polythene terephthalate.

Description of the experiments.

A liquid film punctured by a hole corresponding to the critical radius of nucleation is, by definition, in unstable equilibrium. We estimate this critical radius of nucleation by measuring, for a given thickness of liquid, a dewetting hole and a vanishing hole. The polythene terephthalate was stretched on a silicon wafer to ensure a plane surface and tightened with adhesive tape on the edges. The experiments were conducted first with glycerol. The high viscosity of glycerol ($\eta = 954$ cP) enabled us to follow easily the dewetting or the healing of the liquid film after nucleation of the dry zone with a classical video camera using a magnification ratio of X 30 recording 25 images per second. We then measured radii between 200 and 1 200 μm . We produced films of various thickness in order to determine how the radius of nucleation varied with the thickness of the liquid film. We made a second series of experiments with diiodomethane (CH_2I_2) on polythene terephthalate. The viscosity of diiodomethane ($\eta = 3.043$ cP) is much less than that of glycerol, so dewetting or healing over were much faster than in the previous case.

Polythene terephthalate is a non-wetting surface for glycerol and di-iodomethane. For both liquids, the advancing and receding contact angles have been measured. In the following, the given contact angle is the average of the advancing and receding values. The uncertainty takes into account this hysteresis. It can be noted that the hysteresis is relatively small. The equilibrium contact angle of glycerol on this surface is $\theta_e^G = 66 \pm 4^\circ$. The surface tension of glycerol is $\gamma^G = 63.4$ dyn cm^{-1} and the density $\rho^G = 1.26$ kg l^{-1} . This gives rise to a puddle thickness of $e_s^G = 2.46$ mm. For di-iodomethane, $\theta_e^D = 23 \pm 2^\circ$, we measured $\gamma^D = 50.1$ dyn cm^{-1} , $\rho^D = 3.33$ kg l^{-1} and then $e_s^D = 0.49$ mm. It is impossible to make a liquid film of thickness $e < e_s$ by depositing a drop of liquid and letting it spread, because the thickness thus reached is e_s . In order to make a thin liquid film, therefore, we had to force the liquid to spread. There are various ways of forcing thin films to spread on a non-wetting surface : by spin-coating (the substrate rotates very fast and expels the liquid away from the centre) or by drawing the substrate out of a liquid bath. Here we chose to deposit a puddle of liquid and to flatten it by stretching it with a long pipette. To avoid the retraction of the liquid, we retained it by means of a porous crown. This porous crown was made by attacking the surface with sulfochromic acid. Such a liquid film of thickness $e < e_s$ is metastable and thus very sensitive to any external disturbance. We covered the film of glycerol with a Petri box for 1 or 2 minutes to let the thickness become more homogeneous. We describe below how we measured the thickness of the film and how we created a dry zone to induce either dewetting or healing of the liquid film.

To measure the thickness of the liquid film, we used a relatively classical experimental method that we adapted to meet our needs : two parallel stainless-steel rods, one of them being bent at one end (Fig. 1). The film thickness was measured by making the bent rod touch first the liquid surface and then the solid surface. A micrometer was used to measure the vertical

Fig. 1. — a) Measurements of the film thickness with two parallel rods. b) Contact of the bent rod on the liquid surface and formation of a meniscus. c) Contact on the solid surface : the bent rod ceases to be parallel to the straight one.

displacement of the rods. Contact with the liquid surface was indicated by the formation of a meniscus, and the contact with the solid surface was visualized by projecting the two metallic rods on a screen, the rods becoming non parallel when the bent one touched the solid surface. The liquid-film thickness was then measured with an error of $\pm 20 \mu\text{m}$.

To create a circular dry hole the dimensions of which are reasonably accurate is no easy matter. Putting a cylinder (a silicone fibre, for example) of radius 1 or 2 mm on the surface covered by the liquid film is not sufficient to create a dry hole, because some liquid is trapped between the fibre and the surface, and this zone cannot be dried completely. Accordingly we decided to use a smooth hydrophobic material in order to draw all the liquid out of the contact region between the material and the solid. We used a silicone fibre of radius 2 mm, to the end of which we affixed a drop of polydimethyl siloxane melted with a cross-linking reagent and a catalyst. The drop was solidified in an oven at about 100°C . After this heating process, the drop was elastic, flexible and very hydrophobic. When this fibre reaches the surface (Fig. 2), the drop is squashed and hence drives the liquid outwards. The fibre is then withdrawn rapidly, leaving the dry hole, which either vanishes or grows, depending on the size of the hole and the thickness of the film. Actually, the dry zone did not correspond exactly to the contact area between the solidified PDMS drop and the solid surface. As can be seen in figures 2b and 2c, the reorganization of the liquid interface slightly modifies the size of the dry patch. However, the nucleated dry hole was all the larger as the hydrophobic reticulated drop was squashed more strongly on the surface. This method was used exclusively using glycerol. In the case of di-iodomethane, which is much less viscous than glycerol, the velocity of dewetting is much more rapid (the velocity of dewetting is proportional to viscosity [7]). It was impossible to withdraw the fibre fast enough to follow the beginning of the dewetting or the healing of the

Fig. 2. — How to create a dry hole by : a) approaching a fibre with a dry drop of reticulated PDMS on its end, b) squashing it on the solid surface, c) the hole is formed.

liquid film with the video camera. For liquid films of di-iodomethane, we used a more classical technique which consisted in blowing air with a pipette in the centre of the film. The solid surface was then dried on a small circular zone. In both cases (glycerol and CH_2I_2), the radius R of the dried zone was measured on the video image immediately after removing the fibre or after blowing air.

Results.

The curves in figures 3 and 4 show the thickness, e , of the liquid film as a function of the radius R of the nucleated dry patch, respectively for glycerol and di-iodomethane. It will be seen that the points corresponding to the healing case are mainly on the left part of the graph (small radii), whereas those corresponding to the dewetting case are on the right side of the graph (larger radii). This is in agreement with the simple idea that the thicker the liquid film, the more stable. The two zones of dots are very distinct and the delimitation between them is noticeable. This delimitation represents the critical radius of nucleation as a function of the thickness e of the liquid film. In some experiments using glycerol, we saw very distinctly the dry hole remaining stationary for a few seconds and then choosing to grow or vanish. This is probably due to a local reorganization of the contact angle (because of hysteresis) around the dry hole. In the following paragraphs, we will see how these experiments fit in a theoretical model giving $e(R_c)$.

Here we present briefly a model, which is described in more details in reference [5]. We consider the thin liquid film of thickness e . As we wrote above : if a hole of radius $R > R_c$ is created, the liquid dewets ; if $R < R_c$, the hole is filled up with the liquid. The critical radius R_c thus corresponds to an unstable equilibrium. The shape of the liquid-air interface

Fig. 3.

Fig. 4.

Fig. 3. — Thickness e of the liquid film as a function of the radius, R , of the dry patch for glycerol. The symbol (●) represents the dry patches healing, the symbol (◇) represents the dry patches growing. The solid line represents equation (3) in the case of glycerol.

Fig. 4. — Thickness e of the liquid film as a function of the radius, R , of the dry patch for di-iodomethane. The symbol (●) represents the dry patches healing, the symbol (◇) represents the dry patches growing. The solid line represents equation (3) in the case of di-iodomethane.

enables us to calculate R_c . The profile $r(z)$ is deduced from the equilibrium between Laplace and gravity forces :

$$\frac{1}{\left(1 + \left(\frac{dr}{dz}\right)^2\right)^{3/2}} \left(\frac{d^2r}{dz^2}\right) - \frac{1}{r \left(1 + \left(\frac{dr}{dz}\right)^2\right)^{1/2}} - \frac{g \Delta\rho}{\gamma} (e - z) = 0 \quad (1)$$

the boundary conditions being $r(z = 0) = R_c$ and $\frac{dr}{dz}(z = 0) = \frac{1}{\tan \theta_e}$, where g is the acceleration due to gravity, γ the surface tension of the liquid, $\Delta\rho$ the difference of density between liquid and air.

Equation (1) is unsolvable analytically, but can be solved by neglecting gravity near the contact line. The solution is then :

$$r(z) = R_c \left(\operatorname{ch} \left(\frac{z}{R_c \sin \theta_e} \right) + \cos \theta_e \operatorname{sh} \left(\frac{z}{R_c \sin \theta_e} \right) \right). \quad (2)$$

The function $r(z)$ tends towards infinity as z increases. The approximation of neglecting gravity is justified only for a distance less than κ^{-1} . Thus it seems reasonable (as in the case of a meniscus on a fibre [8]) to cut off this solution at the plane $z = e$ for $r = R_c + \kappa^{-1}$. This approximation is in agreement with numerical solutions of equation (1) giving the height of the meniscus on a fibre [9]. In fact, the problem and geometry of the fibre is the same as in our case ; one only needs to replace θ_e by $\left(\frac{\pi}{2} - \theta_e\right)$. We then deduce the variation of e as a

function of R_c .

$$e = R_c \sin \theta_e \ln \left[\frac{2}{(1 + \cos \theta_e)} \left(1 + \frac{\kappa^{-1}}{R_c} \right) \right] = R_c \sin \theta_e \ell \quad (3)$$

where $\ell = \ell(R_c) = \ln \left[\frac{2}{(1 + \cos \theta_e)} \left(1 + \frac{\kappa^{-1}}{R_c} \right) \right]$ is a logarithmic function of R_c . This equation is a generalization of the equation predicted by Sekimoto *et al.* [2] for small θ_e and $R_c \ll \kappa^{-1}$. $R_c = \theta_e \ln \left(\frac{\kappa^{-1}}{R_c} \right)$. Equation (3) has been found independently by Sharma [6] recently.

Discussion.

The curve of e as a function of the critical radius of nucleation (from Eq. (3)) agrees well with our experimental points, either for glycerol or di-iodomethane on a surface of polythene terephthalate. Indeed, it can be seen in figures 3 and 4 that the curve deduced from equation (3) clearly separates the domain where dry holes heal up (●) from the domain where dry holes grow (◇). Other models have been proposed. In one of them [10], the authors derive R_c by comparing the surface energy of the flat film with that of the flat film with a hole. But the area of the liquid surface modified by the presence of a hole is calculated approximately (almost a cone) and this rough approximation renders the function $\ell(R_c)$ meaningless: ℓ becomes a constant equal to 0.5 independant of R_c . This calculation disagrees by a factor of 5 with our experimental measurements. However, it seems that numerical calculations for thin films [11] fit well with equation (13).

Fig. 5. — Unstable equilibrium of a liquid film of thickness $e < e_c$, with a dry patch of radius R_c .

For a given thickness of liquid film, we can thus predict which size of dry hole will break up the liquid film. This can be applied to a non-wetting surface punctured with small defects [5]. In this case, a dry patch can be in stable equilibrium: if the substrate is non-wettable (solid 1 characterized by a contact angle θ_{e1}) and contains a less wettable defect of radius R (solid 2 characterized by a contact angle θ_{e2}), the equilibrium situations depend on the film thickness. Let us call $e_1(R)$ and $e_2(R)$ respectively the thickness defined by:

$$e(R) = R \sin \theta_e \ln \left[\frac{2}{(1 + \cos \theta_e)} \left(1 + \frac{\kappa^{-1}}{R} \right) \right] \quad (4)$$

for solid 1 and 2. If $e > e_2(R)$, the liquid film is stable. If $e_1(R) < e < e_2(R)$, the dry solid 2 is in stable equilibrium with the liquid film of thickness e . If $e < e_1(R)$, the only situation for stable equilibrium is that in which the whole solid is dry.

Conclusion.

We have presented systematic experiments for measuring the critical radius of nucleation of dewetting. These experiments are in agreement with a model giving the dependency of the thickness e of the liquid film as a function of the critical radius of nucleation.

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