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## CONTACT ANGLE HYSTERESIS ON SINUSOIDALLY GROOVED HYDROPHILIC SURFACES

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**ABSTRACT.** The main goal of the theoretical description of wetting on non-ideal rough solid surfaces is the prediction of the macroscopic behavior in terms of the roughness parameters, defined on a much smaller length scale. The results of a numerical study are presented here of the contact angle hysteresis, appearing in both the static and the dynamic quasi-static case (in Wenzel's wetting regime). The system geometry studied is that of a vertical plate partially immersed in a liquid. The vertical plate has a chemically homogeneous but rough solid surface with the shape of horizontal sinusoidal grooves, so that the solid interface has horizontal translation symmetry. We find the apparent contact angle as a function of the meniscus contact line height. In the dynamic case we apply the contact line dissipation model to describe the quasi-static motion of the contact line. The effective, time independent, contact angle is determined. We present preliminary results on the influence of the value of the Young angle and the Wenzel roughness parameter on the contact angle hysteresis.

**KEY WORDS:** wetting, contact angle, rough surfaces, hysteresis

### 1. Introduction

The spreading/receding of liquids on rough solid surfaces is still an open problem of general interest [1]. Characteristic property of the equilibrium of the liquid meniscus on rough solid surfaces is the existence of a numerous meta-stable states with different apparent contact angles (CA). Various industrial applications are based on the behaviour of the apparent CA on hydrophilic and hydrophobic rough surfaces. While in the first case, the Wenzel's regime of wetting is typical for the liquid/solid contact, in the second – Cassie's regime [1]. The sets of metastable sets are different depending on whether the solid surfaces are smooth and/or rough or both. Since this is a very complicated problem, a big part of the theoretical and numerical studies are concerned with the static contact angle hysteresis (CAH) on regular (periodic) 2-D micro-textured surfaces [2-5]. We study here the effect of a chemically homogeneous but rough sinusoidal micro-textured hydrophilic surface, using a 2-D model, on the static and dynamic CAH in the framework of the standard capillary model [6] and the Contact Line Dissipation Approach (CLDA) [7].

## 2. Problem formulation

We are interested here in the meniscus, which forms when a vertical chemically homogeneous but rough solid plate is partially immersed in a tank of liquid. One of the plate faces  $\Sigma_s$  is described with a Cartesian coordinates  $\Sigma_s = \{a \sin(b\pi z), y, z\}$  where the y-axis is horizontal and the z-axis is directed upwards. The liquid free surface is denoted by  $\Sigma$ , and the contact line (CL), which the liquid meniscus forms with the solid surface by  $L$ . The plate might be immobile or moving vertically (immersing/withdrawing) at a constant velocity  $\mathbf{u} = u\mathbf{z}$ . The considered speeds of the plate are sufficiently small so that the motion the shape of the meniscus can be considered quasi-static. Therefore, at any time moment the well known equilibrium relation between the CL height and the CA is used which follows from the Laplace equation [6]. Since the solid plate is chemically homogenous (and the grooves are parallel to the y-axes) the problem reduces to the study of the 2D projection  $\partial\Sigma = \{x, z(x)\}$  of the meniscus interface in the  $(x, z)$  plane.

The origin of the coordinate system is chosen so that the following conditions hold for the meniscus at infinity:

$$(2.1) \quad z(\infty) = 0.$$

The 2D projection  $\partial S = \{X, Z(X)\}$  of the stationary liquid free surface is described by the following equation [6]:

$$(2.2) \quad \gamma \frac{d^2 z / dx^2}{(1 + dz/dx)^{3/2}} = (\rho - \rho_0) g z,$$

where on the left hand side is the capillary pressure difference across the curved interface, and on the right hand side is the gravitational pressure. The liquid meniscus forms with the solid plate a CA  $\theta$ . In equilibrium this CA is equal to the Young CA  $\theta_{eq}$ . When the solid surface is rough, the apparent CA  $\theta_{ap}$  is of interest, which is related to the macroscopic characteristics of the shape of the liquid meniscus [8]. For the case, under study, this angle is determined by the capillary rise height  $h$  through the relation:

$$(2.3) \quad \cos \theta_{ap} = l_c h \sqrt{4 - l_c^2 h^2} / 2.$$

Here  $l_c$  is the capillary length ( $l_c = \sqrt{\gamma / (\rho - \rho_0) g}$ ,  $\gamma$  is the surface tension of the liquid interface with air, the density of the ambient air is  $\rho_0$ ,  $\rho$  is the liquid density, and  $g$  is the gravity acceleration). The height  $h$  of the CL, relative to the equilibrium level of the liquid bath far from the vertical plate, is equal to z-coordinate of the point of the CL  $\mathbf{R} = \Sigma_s \cap \partial\Sigma$ .

*Static case.* The static CAH is determined as the difference between the biggest and the smallest values of the apparent CA among all equilibrium metastable states of the

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system. We denote these angles by  $\theta^a, \theta^r$ , respectively. First, for all heights  $|h| \leq l_c \sqrt{2}$  the possible meta-stable states are determined, using the analytical solution [6] of Eq. (2.2).

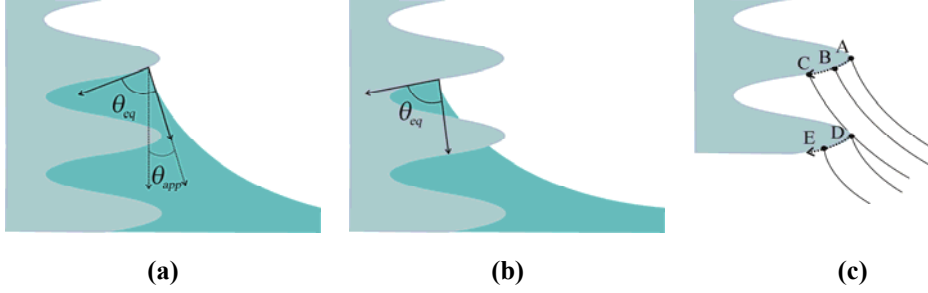


Fig. 1. Examples of a **(a)** physical; **(b)** non-physical solution of Eq. (2.2); **(c)** Schematic drawing of the model for the receding motion of the meniscus.

From all the solutions only the physically feasible solutions are retained (a solution is physically feasible if it does not cross the surface  $x = a \sin(b\pi z)$ ). Examples of physically possible and unfeasible solutions are shown in Figs. 1a and 1b respectively. Then we choose only solutions which have CA equal to  $\theta_{eq}$  with the surface  $x = a \sin(b\pi z)$ . Thus we have the set of all possible equilibrium menisci. Then, among these solutions we find those, for which the apparent CA has the smallest and biggest possible values.

*Dynamic case.* The existence of non-physical solutions of Eq. (2.2) leads to certain specificity (peculiarities) in the quasi-static meniscus dynamics. Since we are studying here the motion of hydrophilic fluids, the meniscus CL remains in contact with the solid surface and there are no air pockets between the fluid and the solid surface. However, during the CL motion in a quasi-static regime it is possible that a state is reached where the meniscus touches solid surface at a particular point. We show such a case in Fig. 1c. When the CL slides down on the solid surface from point A in the shown direction, then it passes through point B and reaches point C, after which a next smooth motion of the CL is not possible. In a quasi-static regime the next physically feasible state would be where the CL touches the solid surface at point D, after which the CL smooth motion will continue towards point E. In the parts of the solid surface, where the CL moves smoothly, we assume that its motion is described in the framework of the contact line dissipation approach (CLDA) [7].

In this approach the energy dissipation is considered as localized *at* the CL and the dissipation rate per unit CL length is proportional to the squared local CL velocity -  $\xi v^2 / 2$ , where the friction coefficient  $\xi$  has the same dimensionality as the liquid viscosity. According to the CLDA, the following differential equation for the height

(capillary rise)  $h(t)$  of the CL follows:

$$(2.4) \quad \frac{dh(t)}{dt} = u + \frac{\gamma}{\xi} (\cos \theta_{eq} - \cos \theta(t)) (\mathbf{z} \cdot \mathbf{n}),$$

where  $\mathbf{n}$  is a unit vector, normal to the contact line, tangent to the liquid-solid interface, and directed outwards the liquid domain.

When the plate is moving, the apparent CA (and so does the CL height  $h(t)$ ) varies with time. Since the rough surface is periodic in  $z$ , the capillary rise  $h$  and the apparent CA angle become periodic functions of time with a period  $P = 2/(b|u|)$  after the elapse of some transient time. The periodic solution (2.2) for the capillary rise  $h$  is especially important since it is independent of the initial height. Averaging of the periodic solution for apparent CA over long time is equivalent to averaging over one period  $P$ . One can thus define an effective (time independent) contact angle  $\theta_{eff}$  by

$$(2.5) \quad \cos \theta_{eff} = \frac{1}{P} \int_0^P \cos \theta_{ap} (h(t)) dt,$$

$\theta_{eff}$  is, of course, dependent on the plate velocity  $u$ , i.e.,  $\theta_{eff} = \theta_{eff}(u)$ . The dynamic CA hysteresis can be defined as a difference in  $\cos \theta_{eff}(u)$  for of the same modules of the velocity  $u$  but for opposite directions of motion. Our goal in this case is to obtain numerically  $h(t)$  at different plate velocities  $u$ , and after then to obtain also the dependence  $\theta_{eff}(u)$ .

### 3. Results and discussion

*Static case.* For various combinations of values of the parameters  $a$  and  $b$  (characterizing the grooved surface) we obtain numerically the CAH. In order to characterize the roughness of the solid surface Wenzel introduced a parameter, called the roughness factor  $r$ , defined as the ratio of the true interfacial area to the area projected on the planar envelope of the surface. We show in Fig. 2a our preliminary results for the cosines of the advancing and receding CAs  $\theta^a, \theta^r$  as functions of the roughness factor  $r$ , (expressed through  $a$  and  $b$ ) for two values of the Young CA of the homogeneous surface:  $\theta_{eq} = 30^\circ, 60^\circ$ .

Our numerical studies show that for all equilibrium Young 's CAs, the advancing and receding CAs  $\theta^a, \theta^r$  depend on the roughness factor  $r$ , and not on the parameters  $a$  and  $b$  separately. More precisely, for different combinations of values of the parameters  $a$  and  $b$ , such that the roughness factor  $r$  is one and the same, one gets also the same values for  $\theta^a, \theta^r$ . One can observe from Fig. 2a, that both,

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$\cos \theta^a, \cos \theta^r$  are non-linear functions of the roughness factor  $r$ . The same holds true also for the magnitude of the CAH, defined by their difference  $\Delta \cos = \cos \theta^r - \cos \theta^a$ .

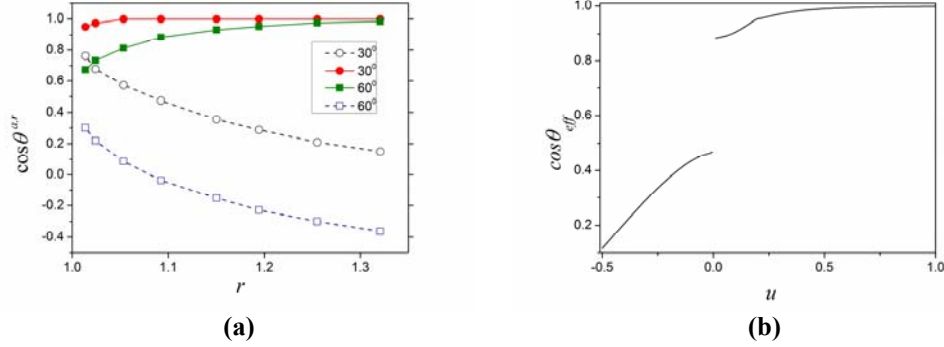


Fig. 2. (a)  $\cos \theta^a, \cos \theta^r$  as functions of the  $r$ ; (b) Effective CA as function of the plate velocity.

*Dynamic case.* We obtain numerically the CL dynamics for the following set of parameters, characterizing the rough solid surface:  $a = 0.001$ ;  $b = 100$  ( $r = 1.024$ ); and for  $\theta_{eq} = 45^\circ$ . For plate velocities  $-0.6 \leq u \leq 2$  we find that for an initial dimensionless CL height in the interval between 0 and  $\sqrt{2}$ , the CL height variation in time reaches the same periodic regime and therefore the same values of the effective CAs.

*Withdrawing plate.* For withdrawing plate we find two regimes in the behaviour of the dependence of CL height on the plate velocity. At small values of the magnitude  $|u|$  of the velocity the change is smooth. However, at velocity  $u = 0.2$ , a small jump of the CL height appears. With increasing the plate velocity the amplitude of the jump in the CL height increases and at velocity  $u = 0.4 - 0.8$ , the variation with time of the CL height is saw-tooth like where one of the sides is almost vertical.

*Immersing plate:* When the plate is immersing, i.e., when  $u < 0$  and the magnitude of the velocity, for which the apparent  $CA > 0$ , the CL height variation with time reaches a smooth periodic regime of change. In this case there are no jumps observed of the CL height variation with time. In Fig. 2b we show the cosine of the effective CA  $\cos \theta_{eff}(u)$  as function of the plate velocity for  $-0.5 \leq u \leq 1$ . When the plate is withdrawing, a specific dependence of  $\cos \theta_{eff}(u)$  on the plate velocity  $u$  is observed. Up to velocity 0.19 (where the CL height variation with time is a smooth function), the dependence of  $\cos \theta_{eff}(u)$  is a convex function of  $u$ , and

for higher velocities it becomes a concave function. For immersing plate ( $u < 0$ ) it is again a concave function. With increasing the magnitude  $|u|$  of the plate velocity the function  $\cos\theta_{eff}(u)$  becomes practically linear in  $u$ . For small values of  $|u|$ , one can clearly observe the non-linear character of the function  $\cos\theta_{eff}(u)$ . The numerical studies show that as plate velocity  $u \rightarrow \pm 0$ ,  $\theta_{eff}(u)$  coincides with  $\theta^r, \theta^a$ , respectively.

#### **4. Conclusion**

The results of a numerical study are presented here of the CAH, appearing on rough sinusoidally grooved surface, in both the static and the dynamic quasi-static case (in Wenzel's wetting regime). In the static case the Young-Laplace equation is used to obtain the meniscus shape. The apparent contact angle is obtained as a function of the meniscus CL height. In the dynamic case the contact line dissipation approach is used to find the quasi-static motion of the CL. Our numerical studies show that the advancing and receding CAs  $\theta^a, \theta^r$  depend on the roughness factor  $r$ , and not on the parameters  $a$  and  $b$  separately. Also for withdrawing plate we find two regimes in the behaviour of the dependence of CL height on the plate velocity.

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