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A DYNAMIC STUDY OF THE CONTACT ANGLE HYSTERESIS ON SINUSOIDALLY GROOVED SURFACES*

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We consider the quasi-static motion of the liquid contact line when a homogeneous solid plate with non-ideal rough surface is moving vertically in a bath of liquid in Wenzel's wetting regime. The vertical plate has a chemically homogeneous but rough solid surface with the shape of horizontal sinusoidal grooves, so that the solid surface has horizontal translation symmetry. We apply a model which takes into account explicitly the dissipation due to the moving contact line. The effective, time-independent, contact angle is determined. We present here the results of a numerical study of the contact line dynamics, effective advancing and receding contact angles. We present results on the influence of the plate velocity and roughness factor on the effective advancing and receding contact angles. We find that roughness leads to a nonlinear dependence of the effective advancing and receding contact angles on the plate velocity and two regimes in the behavoiur of the dependence of receding contact angles on the plate velocity.

1. Introduction. The main goal of the theoretical description of spreading/receding 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. Two regimes of the contact between the fluid and the solid surface are found when roughness is taken into account. These are Wenzel's regime and Cassie's regime, depending on whether there is absence or presence of air pockets between the fluid and the solid surface, respectively. Here we are going to focus on Wenzel's regime. Since this is a very complicated problem, studies are insufficient and mostly 2D models are considered. In [1, 2] the dependence of the effective slip coefficient in Navier boundary condition on roughness is analyzed. In [3–4] the motion of the three-phase contact line (CL) on rough surface was studied using a lattice Boltzmann model. In [5] the authors study experimentally the stick-jump movement motion of a drop on periodic rough structures consisting of parallel strips. In this work we study the influence of the roughness on the relation between the dynamic contact angle and the velocity of the contact line motion. Such a relation for smooth surface is obtained both experimentally and in the main models describing the quasistatic dynamics of the contact line for very small velocities [6]. Here we study this relation numerically using the contact line dissipation approach (CLDA) applying the Blake and Haynes model [6].

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Key words: spreading, contact angle, rough surfaces, hysteresis.

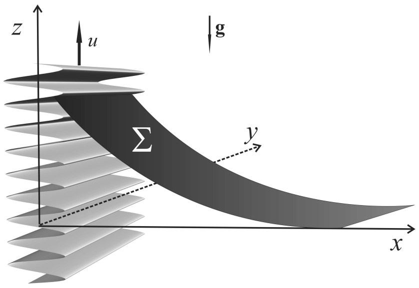


Fig. 1. Schematic image of the considered system

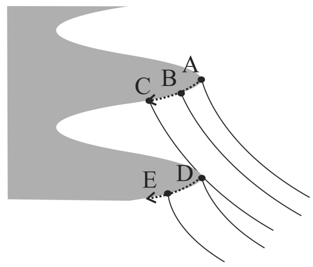


Fig. 2. Schematic drawing of the model for the receding motion of the meniscus

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 (we do not consider the other) Σ_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 as shown in Fig. 1. The liquid free surface is denoted by Σ, and the CL, which the liquid meniscus forms with the solid surface, by L. The plate is 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 of the shape of the meniscus can be considered quasi-static. Therefore, at any moment the well known equilibrium relation between the CL height and the CA is used, which follows from the Laplace equation [7]. 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:

$$z(\infty) = 0. \tag{1}$$

The 2D projection $\partial S = \{x, z(x)\}$ of the stationary liquid free surface is described by the following equation [7]:

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

where the density of the ambient air is ρ_0, ρ is the liquid density, γ is the surface tension of the Σ and g is the gravity acceleration. The liquid meniscus forms a CA θ with the solid plate. In equilibrium this CA is equal to the Young CA θ_{eq}. When the solid surface is rough, the apparent CA θ_{ap} is of interest, which is related to the macroscopic characteristics of the shape of the liquid meniscus. For the case under study, this angle is determined by the capillary rise height h through the relation:

$$\cos\theta_{ap} = l_c h \sqrt{4 - l_c^2 h^2}/2. \tag{3}$$

Here l_c is the capillary length ($l_c = \sqrt{\gamma/(\rho - \rho_0)\, g}$). When the plate is moving, the apparent CA and the CL height $h(t)$ vary with time. Since the rough surface is periodic in $\mathbf{z}$, the capillary rise h and the apparent CA become periodic functions of time with a period $P = 2/(b\,|u|)$ after the elapse of some transient time. The periodic solution for the capillary rise h is especially important since it is independent of the initial CL height.

Averaging of the periodic solution for the apparent CA over a long time is equivalent to averaging over one period P. One can thus define an effective (time independent) contact angle θ_{eff} by

$$\cos\theta_{\text{eff}} = \frac{1}{P}\int_0^P \cos\theta_{ap}\left(h\left(t\right)\right)dt, \tag{4}$$

θ_{eff} is, of course, dependent on the plate velocity u, i.e., $\theta_{\text{eff}} = \theta_{\text{eff}}(u)$. The dynamic CA hysteresis can be defined as a difference in $\cos\theta_{\text{eff}}(u)$ for the same modules of 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 then to also obtain the relation $\theta_{\text{eff}}(u)$. The height h of the CL is equal to the z-coordinate of the point of the CL $\mathbf{R}(t) = \Sigma_s(t) \cap \partial\Sigma(t)$. Thus, we are going to obtain the time evolution of the point $\mathbf{R}(t)$, where $\mathbf{R}(0) = \mathbf{R}_0$. The motion of $\mathbf{R}(t)$ is determined by: *1.* The motion of $\mathbf{R}$ with respect to the plate; *2.* The motion of the plate; *3.* The possibility of the existence of a solution of (2) which doesn't intersect with the surface; *4.* The possibility of a formation of air pockets between the fluid and the solid surface.

1. We assume that when the CL moves smoothly, its motion on (with respect to) the plate is described in the framework of the Blake and Haynes model. The model is based on the idea [6] that the velocity-dependence of the dynamic contact angle is due to the disturbance of the adsorption equilibrium and hence to changes of the local surface tensions as the wetting line moves across the solid surface. Taking into account that the driving force for the contact line to move in a given direction is equal to the out-of-balance surface tension force, they obtain a relation for the contact line relative velocity $\mathbf{v}_s$, $\mathbf{v}_s = v_n\mathbf{n}$, with respect to the solid plate

$$\xi v_n = \gamma\left(\cos\theta_{eq} - \cos\theta\left(t\right)\right), \tag{5}$$

where $\mathbf{n}$ is a unit vector, normal to the contact line, tangent to the liquid-solid interface, and directed outwards the liquid domain. The coefficient ξ has the same dimensionality as the viscosity of the liquid.

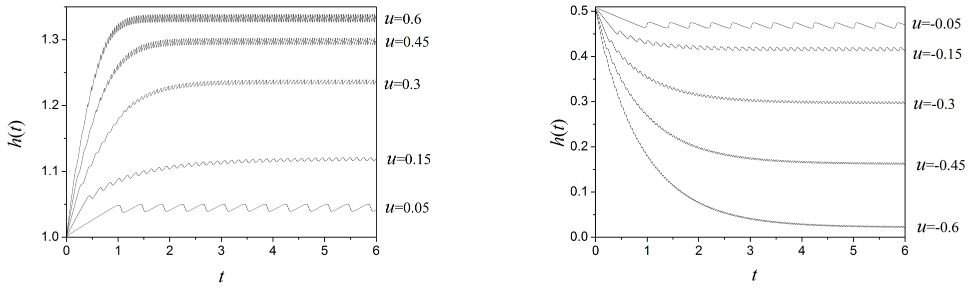
2. The contact line velocity $\mathbf{v}$ with respect to the used coordinate system is

$$\mathbf{v} = \mathbf{v}_s + \mathbf{u}. \tag{6}$$

3. However, during the CL motion in a quasi-static regime it is possible that a state is reached where the meniscus touches the solid surface at a particular point. We show such a situation in Fig. 2 for the case of a withdrawing plate. 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.

4. During the motion of the CL we consider the possibility of a formation of air pockets using the method described in [8]. The results shown below are for parameters values of a, b, θ_{eq}, for which there are no air pockets.

Equations (1)–(3) can be made dimensionless by the help of the capillary length l_c, Eq. (5) and by the help of l_c and by expressing the time in terms of the characteristic time $\tau_0 = l_c\xi/\gamma$. In what follows, we will work in dimensionless variables and for simplicity we will use the same symbols as for the dimensional variables, i.e., $h = h/l_c$, $t = t/\tau_0$ and



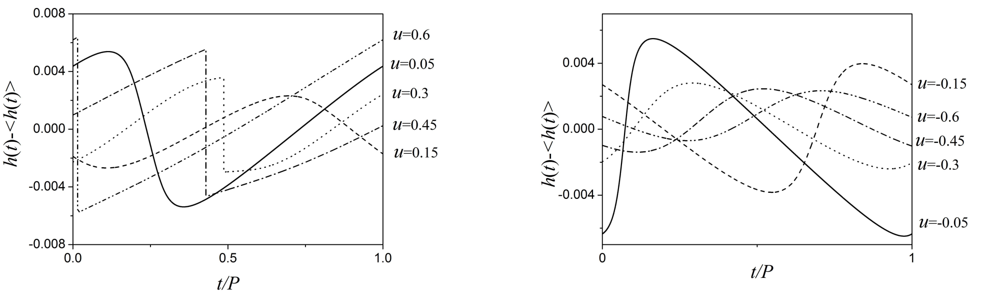
(a) (b)

Fig. 3. CL height variation with time for a set of plate velocities

the dimensionless plate velocity is $u = u\xi/\gamma$. Without loss of generality one can study the case $0 \leq h < \sqrt{2}$ which corresponds to contact angles $0 < \theta \leq 90°$ since the following symmetry holds: $h, \theta \Leftrightarrow -h, 180° - \theta$.

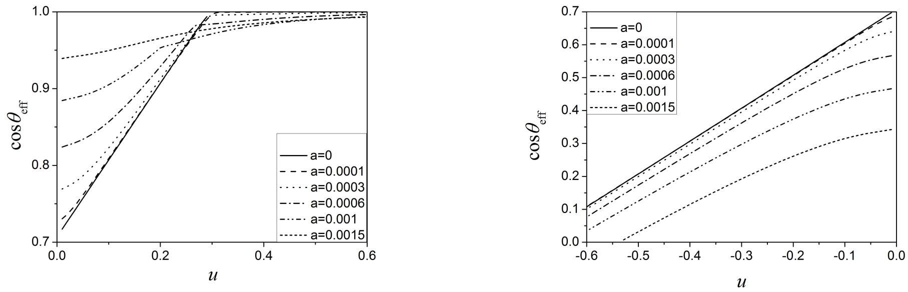
3. Results and discussion. We obtain numerically the CL height dynamics for $b = 100$ and $\theta_{eq} = 45°$ as a function of plate velocities $|u| \leq 0.6$ and amplitude of the sinusoidal waves $0 \leq a \leq 0.0015$. Note that for $a = 0$ we have the case of a flat plate, considered in detail in [9]. 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. First for $a = 0.001$ we present results for $h(t)$.

We show our results for $h(t)$ for different $|u| = 0.05; 0.15; 0.3; 0.45; 0.6$ for a dimensionless time 6 in withdrawing and immersing regime in Fig. 3(a) and 3(b), respectively. In the initial state, the meniscus has height $h(0) = 1$ and 0.5 respectively. Up to time 6 all solutions shown in Fig. 3 reach a periodic regime of change. In Fig. 4, one period of change of the CL height is shown for the solutions, shown in Fig. 3 in periodic regime for the $h(t)$, in time t/P and height $h(t) - \langle h(t) \rangle$, where $\langle h(t) \rangle$ is the mean value of the $h(t)$ for one time period in periodic regime. For all solutions for $h(t)$ obtained in Fig. 4, different initial states with different initial CL heights are probed. We observe that for $h(0)$ in the interval $(0, \sqrt{2})$, the $h(t)$ reaches the same periodic regime and therefore the



(a) (b)

Fig. 4. CL height variation with time (in dimensionless units) for one time period for solutions presented in Fig. 3



(a) (b)

Fig. 5. Effective CA as function of u for (a) withdrawing and for (b) immersing plate

same values of the effective CAs. For small velocities in withdrawing regime the CL height is smaller than the heights of the solutions, which are not physically feasible. Because of this, for small velocities the CL height changes smoothly. Such solutions in Figs 3(a), 4(a) are these at velocities $u = 0.05$; 0.15. However, in the next solution in Fig. 4, at velocity $u = 0.3$, as can be seen, there is a sharp decrease of the CL height with a small amplitude. With increasing the plate velocity the amplitude of the jump in the CL height increases and at velocity $u = 0.45$, 0.6, the variation with time of the CL height is saw-tooth like where one of the sides is almost vertical. When the plate is immersing, i.e., when $u < 0$ and the magnitude of the velocity $|u| \leq 0.6$, the CL height variation is smooth. In this case there are no jumps of the CL.

The obtained results contribute to analyzing the effective CA θ_{eff} (4) as a function of the velocity of the solid plate u.

In Fig. 5 the numerically obtained relations $\theta_{\text{eff}}(u)$ are shown for $|u \leq 0.6|$ for a range of amplitudes $a = 0; 0.0001; 0.0003; 0.0006; 0.001; 0.0015$. $a = 0$ corresponds to the case of a flat plate. It can be seen from Fig. 5 that there is a linear dependence in $\theta_{\text{eff}}(u)$ on u in this case. In Fig. 5 one can notice the nonlinear dependency in $\theta_{\text{eff}}(u)$ on u for $a \neq 0$ and also see how the function $\theta_{\text{eff}}(u)$ changes when a increases. The fact that there are two regimes observed of periodic variation of the CL height with time when the plate is withdrawing, i.e., smooth variation and with sharp changes, leads to a specific dependence of $\theta_{\text{eff}}(u)$ on the plate velocity. For small velocities, where the CL height variation with time is a smooth function, the dependence of $\cos\theta_{\text{eff}}(u)$ is a convex function of u, and for higher velocities it becomes a concave function. For withdrawing plate it is again a concave function. When the velocity increases the function $\cos\theta_{\text{eff}}(u)$ becomes practically linear in u. For small values of the velocity u, one can clearly observe the non-linear character of the function $\cos\theta_{\text{eff}}(u)$ for all $a \neq 0$. This result does not corroborate earlier results for the quasi-static dynamic case, obtained in the framework of the CLDA [9, 10] for homogeneous and heterogeneous flat solid surfaces, where a linear dependence was obtained. This shows that taking into account the roughness of the surface through a change of the mobility coefficient, suggested in Ref [11], is not sufficient for taking into account the roughness of the solid surfaces since it leads to a linear dependence of $\cos\theta_{\text{eff}}(u)$ on u.

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ИЗСЛЕДВАНЕ НА ХИСТЕРЕЗИСА НА ДИНАМИЧНИЯ КОНТАКТЕН ЪГЪЛ ВЪРХУ ГРАПАВА СИНУСОИДАЛНА ПОВЪРХНОСТ

Павел Илиев, Нина Пешева, Станимир Илиев

Разглежда се квазистатично движение на течен менискус в контакт с движеща се вертикална твърда повърхност. Повърхността е грапава със синусоидален профил, а при контакта ѝ с течността не се образуват въздушни мехури в микроскопичните ями между тях. За описание на движението на течността се използва модела на „дисипация на енергията на контактната линия“. Представени са числени резултати за динамиката на контактната линия, за ефективните настъпващ и отстъпващ контактни ъгли. Изследвано е влиянието на скоростта на движение на пластината и грапавостта на повърхността върху хистерезиса на контактния ъгъл. Показано е, че грапавостта води до нелинейна зависимост на напредващия и на отстъпващия контактен ъгъл. Получени са два режима на поведение на отстъпващия контактен ъгъл.