DYNAMIC STUDY OF THE CONTACT ANGLE HYSTERESIS IN THE PRESENCE OF PERIODIC DEFECTS*

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ABSTRACT. A modification of the contact line dissipation model is proposed to treat the contact line motion on chemically heterogeneous substrates with sharp borders between the two types of domains with different surface energies. It is applied to the quasi-static motion of the contact lines in the Wilhelmy plate geometry where a solid plate is withdrawn/immersed vertically at constant speed from/into a bath of liquid. The plate surface is a 2D pattern of round spots (defects) of surface energy different from the rest of the plate. The spot pattern is spatially periodic in both horizontal and vertical directions. A numerical code is developed for simulation of the motion of the 3D liquid meniscus including the three-phase contact line for different plate velocities. Critical velocities are obtained beyond which the liquid entrainment or drying thresholds are attained. The average contact angle is obtained from the capillary contribution to the force acting on the plate. It is shown that the chemical heterogeneity leads to a larger then zero value of the average contact angle for the entrainment threshold and smaller than 180° value for the drying threshold.

KEY WORDS: relaxation, dissipative system dynamics, dynamic contact angles

1. Introduction

The spreading/receding of liquid on non-ideal solid surfaces is still an open problem of general interest. This problem is very important since most real surfaces appearing in nature, in the laboratories and in the different technological processes, are rough and/or heterogeneous.

We study here the effect of the substrate chemical heterogeneity on the contact line (CL) motion and in particular on the dynamic contact angle (CA) in the framework of the Contact Line Dissipation Approach (CLDA) [1, 2]. We consider the motion of the contact line in the Wilhelmy plate geometry (a vertical flat solid

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plate is withdrawn/pushed from/into a liquid bath at constant velocity u, see Fig. 1). The heterogeneous surface of the solid plate consists of two types of domains; the surface energy changes sharply on the borders between them.

The effect of the substrate chemical heterogeneity on the CL motion in the framework of the CLDA is studied in a number of previous works. In [3-5] the influence of the heterogeneity is modeled by including in the equation for the CL motion of an additional term: an elastic restoring force. The concept of the elastic force is developed earlier, see e.g. [6]. Nikolayev [7] obtained an analytical CLDA equation describing the CL dynamics and solved it numerically for the CL motion on a substrate with periodic heterogeneity. However, he assumed that the slope of the liquid surface is small, which is not always satisfied.

Our goal here is to extend such an analysis to any interface slope by performing a full-scale 3D dynamic numerical simulation of the CL slow motion on a substrate with periodic heterogeneity within the CLDA.

2. Problem formulation

The classical Wilhelmy plate surface is described with Cartesian coordinates (y, z), where the y-axis is horizontal and the z-axis is directed upward. The plate surface is infinite and consists of regularly spaced identical circular spots with surface energy different from that of the rest of the surface.

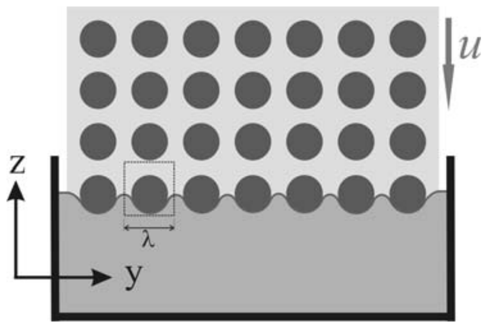


Fig. 1. Schematic drawing of the considered system.

The spot centers form a quadratic lattice with unit cell of size λ. The spot radius is denoted by *a*. Between the spots the surface is homogeneous and is characterized by equilibrium contact angle $\theta_{eq}^{(1)}$ that it forms with the liquid meniscus. The spots are characterized by equilibrium contact angle $\theta_{eq}^{(2)} \neq \theta_{eq}^{(1)}$ so that the surface energy of the plate changes sharply at the borders of the spots. The liquid meniscus forms a contact line L with the moving plate. The dynamic contact angle value $\theta(\mathbf{R})$, where $\mathbf{R} \in L$ denotes a point belonging to the plate surface, varies along the CL. The distance between the plate and the (distant) bath wall opposite to the plate is denoted by d_x. The contact line $L(t)$ at time moment t is described by its height $h(y,t)$ relative to the meniscus level sufficiently far from the plate, where the meniscus is horizontal.

We study the motion of the CL in the framework of the CLDA. In the CLDA one neglects the viscous dissipation in the bulk of the liquid with respect to that occurring in the vicinity of the moving CL. The dissipation is then considered as localized *at* the CL. The dissipation rate per CL length $\Sigma_l = \xi v_n^2/2$ is proportional to the squared local CL velocity v_n (assumed to be positive when the liquid advance). We denote by ξ the friction coefficient, which has the same dimensionality as the liquid viscosity. We assume here that ξ is independent of v_n, which holds, e.g., for the molecular-kinetic model of the contact line motion [8]. For simplicity we assume here that both types of domains have the same ξ value. According to the CLDA, the motion of the point $\mathbf{R}$ of the CL is given by:

(2.1) $$v_n\left(L\left(\mathbf{R},t\right)\right) = \gamma\left(\cos\theta_{eq}(\mathbf{R}) - \cos\theta(\mathbf{R})\right)/\xi,$$

where $\theta_{eq}(\mathbf{R})$ is the equilibrium (Young) contact angle equal to $\theta_{eq}^{(2)}$ or to $\theta_{eq}^{(2)}$ depending on $\mathbf{R}$, γ is the surface tension. When the plate is moving downwards with velocity u, the CL velocity with respect to the solid surface is $v_n = \dot{h} + u$, where $\dot{h}$ is the time derivative of the CL height. Equation (2.1) holds when $\cos\theta_{eq}\left(\mathbf{R}\right)$ is a smooth function in the neighborhood of the point $\mathbf{R}$. However, when $\mathbf{R}$ belongs to the border between two domains where the surface energy changes sharply, one should use the condition obtained by Iliev and Pesheva [9]. According to it, the border point $\mathbf{R} \in L$ remains immobile with respect to the plate while $\theta\left(\mathbf{R}\right) \in \left[\theta_{eq}^{(1)}, \theta_{eq}^{(2)}\right]$ if $\theta_{eq}^{(2)} > \theta_{eq}^{(1)}$ or $\theta\left(\mathbf{R}\right) \in \left[\theta_{eq}^{(2)}, \theta_{eq}^{(1)}\right]$ if $\theta_{eq}^{(2)} < \theta_{eq}^{(1)}$. This phenomenon is at the origin of the „stick-slip" behavior of the CL.Equation (2.1) can be made dimensionless by expressing the lengths in terms of the capillary length $l_c = \sqrt{\gamma/\rho g}$ (ρ: liquid density; g: gravity acceleration) and the time in terms of the characteristic time $\tau_0 = l_c\,\xi/\gamma$, i.e., $\tilde{x} = x/l_c, \tilde{y} = y/l_c, \tilde{z} = z/l_c$, $\tilde{t} = t/\tau_0$ (and therefore the dimensionless velocity is $\tilde{v}_n = \xi v_n/\gamma$):

(2.5) $$\tilde{v}_n\left(L\left(\tilde{R},\tilde{t}\right)\right) = \cos\theta_{eq}\left(\tilde{R}\right) - \cos\theta.$$

Our study here focuses on a specific system studied previously in [7] for which $\theta_{eq}^{(1)} = 70^\circ$, $\theta_{eq}^{(2)} = 110^\circ$, $a = 0.1$, and $\lambda = 0.3$.

3. Numerical algorithm

We employ the following numerical algorithm [2] having three basic steps. *First,* for a given position of the CL at the moving plate the stationary shape of the meniscus of the liquid with fixed volume in the domain enclosed between the surfaces $x = 0$ and $x = d_x$ is determined. We impose periodic boundary conditions in *y*-direction and we set the right contact angle at the container wall opposite to the moving plate. *Next,* velocity at every point of the CL is obtained directly from the equality of variations of the free energy and of the CL dissipation (which is equivalent to using Eq. (2.1) [2]). *Third,* the CL position at the next instant of time is found explicitly from the kinematic condition $\Delta R = v_n \Delta t$. The above algorithm is repeated for the successive time steps.

The main ingredients of this algorithm are the determination of the meniscus shape with given volume of the liquid in the tank and given contact line, and the calculation of the velocity of the contact line. The determination of the meniscus shape is realized by an iterative minimization procedure based on the local variations method and adapted to treat the Wilhelmy plate geometry in [10].

4. Numerical results

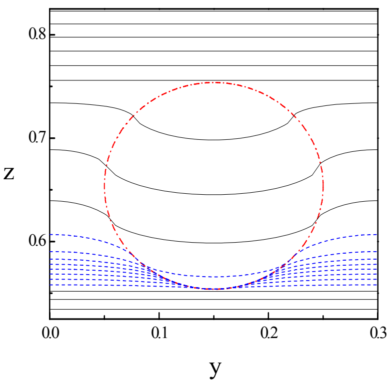
We study the CL motion for different plate velocities. Our numerical simulations show that in a certain interval of (dimensionless) plate velocities $\tilde{u} \in \left[\tilde{u}_r^*, \tilde{u}_a^*\right]$ a double periodic solution (both in t and y) for $h(y,t)$ appears after the CL passes through several rows of defects. Outside this interval the double periodic solutions do not appear. The liquid is entrained by the plate when $\tilde{u} \le \tilde{u}_r^*$ (dynamic complete wetting; Landau-Levich transition). The gas entrainment between the liquid and the plate (dynamic complete unwetting) occurs when $\tilde{u} \ge \tilde{u}_a^*$. In Fig. 2 we show the obtained contact lines (in a reference system immobile with respect to the plate). The dotted line shows the border of the circular defect where the equilibrium contact angle is $\theta_{eq}^{(2)} = 110^\circ$. The successive contact lines are shown with solid lines (going from top to bottom). One can see that, when the CL reaches the upper end of the defect, the CL accelerates since the local CL velocity sharply increases with $\cos 70^\circ - \cos 110^\circ$. The part of the CL which lies outside the defect is also entrained. We observe also that when the contact line reaches the lower end of the defect a part of the contact line remains fixed to the border of the defect. These contact lines which have part stuck to the border of the defect are shown with dashed lines. Thus a stick-slip behavior of the CL in the CLDA is modeled.

Here we are interested in the calculation of the wetting force (or else the capillary restoring force) which the liquid exerts on the solid plate. It can be determined experimentally by tensiometric methods in Wilhelmy plate geometry and is used to study the dynamic CA and its dependence on the CL velocity [5]. When a periodic motion of the CL is attained, the time and space averaged force is (the time period is P=$\lambda / |\tilde{u}|$):

(4.1) $$\langle F \rangle = -\frac{\gamma}{\lambda P} \int_0^P \int_0^\lambda \cos\theta(y)\left(\mathbf{z} \cdot \mathbf{n}(y)\right) dy dt$$

Through this force one can introduce the effective dynamic CA θ_{eff} for the heterogeneous surface, (4.2) $$\cos\theta_{eff} = -\langle F \rangle / \gamma .$$

In Fig 3. we plot the results for $\cos\theta_{eff}$ as function of $\tilde{u}$.



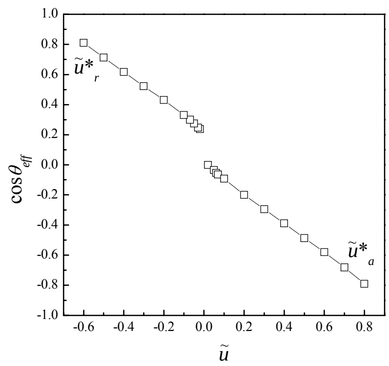


Fig. 2. Unit cell $\lambda x \lambda$ of the plate surface including one of the surface defects. The dash-dotted line is the border of the defect. The CLs positions (in a reference system immobile with respect to the plate) for the double periodical solution are shown with time step $\Delta t = 0.15$ for the plate moving upwards with velocity $\tilde{u} = -0.1$. The CLs are shown with solid lines except for those which are partially stuck to the border of the defect (dashed lines).

Fig. 3. The cosine of the effective contact angle as function of the plate velocity $\tilde{u}$. A contact angle hysteresis $\sim 13^{\circ}$ is observed when $\tilde{u} \to 0$. Critical velocities $\tilde{u}_r^*$ and $\tilde{u}_a^*$ are obtained above which the entrainment transitions occur for receding or advancing motion, respectively.

For the considered type of heterogeneity we obtain a dependence close to linear between the velocity and the cosine of the effective CA. The CA hysteresis is observed both in dynamics and in statics. The static hysteresis (for $\tilde{u} \to 0$) is of the order of 13°. The dynamic hysteresis can be defined as a difference in θ_{eff} for $\tilde{u}$ of the same modules but opposite signs.

Threshold velocities $\tilde{u}_r^*, \tilde{u}_a^*$ (and corresponding critical receding and advancing dynamic contact angles $\theta_{eff}^{*r}, \theta_{eff}^{*a}$) are obtained. Beyond these velocities the entrainment transitions occur. One can see that at the entrainment threshold $\left|\cos\theta_{eff}^*\right| < 1$ (i.e., $\theta_{eff}^{*r} > 0^{\circ}$ and $\theta_{eff}^{*a} < 180^{\circ}$). Note that, within CLDA, the entrainment transitions *for a homogeneous plate* occur when $|\cos\theta| = 1$. This difference appears because, *for heterogeneous plate*, the entrainment threshold is attained first for one of the domains. Such a behavior is similar to that described by the hydrodynamic approach [11]. It shows that the experimentally observed inequality for the Landau-

Levich threshold $\theta_{eff}^{*} > 0$ [11] can be explained by the interaction with the surface heterogeneity within the quasi-static CLDA, without using more complicated hydrodynamic approaches.

5. Conclusion

A quasi-static contact line dissipation approach is applied to simulate the slow motion of the contact line on a chemically heterogeneous substrate with sharp spatial variation of the surface energy. A stick-slip behavior of the CL is observed. The contact angle hysteresis is obtained both in statics and dynamics. Critical velocities and critical effective contact angles are determined beyond which the liquid or gas are entrained by the plate. The finiteness of the dynamic contact angle at Landau-Levich liquid entrainment transition can be explained by the interaction with the substrate heterogeneity.

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