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ON THE QUASI-STATIC RELAXATION OF THE CONTACT LINE IN THE WILHELMY-PLATE GEOMETRY: ASYMPTOTIC SOLUTIONS OF A CONTACT LINE DISSIPATION MODEL*

Stanimir Iliev, Nina Pesheva
Institute of Mechanics, Bulgarian Academy of Sciences,
Acad. G. Bonchev St., Bl. 4, 1113 Sofia, Bulgaria,
e-mails: stani@imbm.bas.bg, nina@imbm.bas.bg

Dimitar Iliev
Department of Mathematics and Informatics, Sofia University,
5, J. Bourchier St., 1164 Sofia, Bulgaria,
e-mail: diliev@fmi.uni-sofia.bg

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Abstract. The quasi-static motion of straight contact lines is considered in the context of the "Wilhelmy plate" geometry: a vertical homogeneous solid plate is withdrawn at constant velocity from a bath of liquid. We apply a model, which takes into account explicitly the dissipation due to the moving contact line. Asymptotic solutions are derived of the differential equations describing the capillary rise height of the contact line and the contact angle relaxation. We find that the time relaxation of the height and the cosine of the contact angle are given by sums of exponential functions. The asymptotic solutions are compared with experimental results and with numerically obtained solutions which are based on lubrication theory with a correction factor for finite contact angles.
Key words: relaxation, dissipative system dynamics, dynamic contact angles.

1. Introduction

Many industrial processes involve spreading of liquid on solid surface and respectively motion of the contact line and that has stimulated numerous studies employing different experimental and theoretical approaches [1–3]. The testing of the theoretical approaches modelling the dynamic phenomena

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in close vicinity of the contact line against the experimental data and determination of the range of validity of the approximations made is indispensable part of the research process. The validation of these theoretical approaches is their ability to reproduce correctly the existing experimental data. There are several important questions concerning the relaxation process which need to be answered and the answers to be compared with the experiment for the different models suggested in the literature. It is important to know what kind of function describes best the relaxation process, what is the relaxation time, how it depends on the velocity of the plate, what are the critical velocity and the critical height up to which the relaxation occurs and above which the entrainment of a liquid film starts etc. Here we will try to answer some of these questions for the relaxation of the contact line which forms when a solid plate is withdrawn vertically from a bath of liquid in the partial wetting regime (Wilhelmy plate geometry).

Recently, for this geometry in the framework of a lubrication theory (with a correction factor for finite contact angles) the relaxation rate of the relaxing straight contact line as function of the velocity of the withdrawing plate was obtained [4]. These results were compared with the experimental results for a specific system – that of a fluorinated silicon plate withdrawn from a vessel filled with PolyDiMethylSiloxane (PDMS). It was found that the predictions of this model are in general agreement with the experimental results.

We will address here some of the questions raised above within the contact line dissipation approach [2] applying the Blake and Haynes model [5]. This model which we call Contact Line Dissipation Model (CLDM) reduces the dissipation that occurs in the vicinity of the moving contact line to the dissipation T localized at the contact line L, where the dissipation T is given by:

$$T = \int_L \frac{\xi v_n^2}{2} dL. \tag{1}$$

Here v_n is the contact-line speed measured in the direction normal to the contact line and ξ is a constant "dissipation coefficient". The following equation, relating the local contact line velocity v_n to the local dynamic contact angle θ [2, 5, 6] holds in this model:

$$v_n = \frac{\gamma}{\xi} \left(\cos\theta_{eq} - \cos\theta \right), \tag{2}$$

where γ is the liquid/vapour surface tension, and θ_{eq} is the equilibrium contact angle. In this work we obtain the asymptotic solution of equation (2) for the relaxation of the contact line in the quasi-static regime for the Wilhelmy plate geometry for velocities below the entrainment transition and for arbitrary finite contact angles. In a recent paper [7] it is shown numerically that in the CLDM (2) the relaxation for finite contact angles is well described by an exponential decay function. Here we find that the asymptotic solutions are sums of exponential decay functions. We also compare the asymptotic results with the experimental results in Ref. [4] and also with the results of a lubrication theory with a correction factor for finite contact angles [4].

2. Problem formulation

We consider here a partially immersed homogeneous solid plate moving vertically with constant speed u in a bath of liquid as shown in Fig. 1. The liquid forms with the air free surface Σ. The considered velocities of the plate are sufficiently small so that the motion of the meniscus can be considered quasi-static. One of the plate faces (we do not consider the other) is described with a Cartesian coordinates (y, z) where the y-axis is horizontal and the z-axis is directed upwards as shown in Fig. 1. The liquid meniscus forms with the solid plate a contact line L and a dynamic contact angle θ. Since we consider homogeneous plate we assume that the meniscus Σ and the contact line L do not depend on y: $\Sigma\{x, y, z(x)\}, L \equiv \{0, y, z(0)\}$. The contact line L is defined by its rise height $h(\mathrm{t}) = z(0)$ above the surface of the meniscus sufficiently away from the plate (see Fig. 1). The velocity v_n of the contact line is:

$$v_n = \dot{h} - u. \tag{3}$$

We assume that initially the liquid meniscus is not in a stationary state. Under the action of the surface tension and the gravity the incompressible liquid relaxes towards the stationary state dissipating energy. In the quasi-

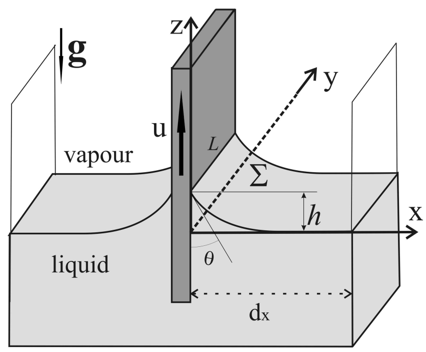

Fig. 1. Schematic drawing of the Wilhelmy plate geometry

stationary regime the liquid meniscus Σ is a Laplacian surface at any instant of time t. The linear sizes of the container are considered sufficiently big as compared to the capillary length l_c ($l_c = \sqrt{\gamma/\rho g}$, ρ is the liquid density, g is the gravity acceleration), so that the following conditions hold for the meniscus at infinity: $z(\infty) = 0$, $dz/dx|_\infty = 0$. Based on the quasi-stationarity assumption one can utilize the expression known from equilibrium [8] relating the instantaneous height and the contact angle of the meniscus at the moving plate:

$$h = l_c\sqrt{2(1 - \sin\theta)}. \tag{4}$$

One can study without a loss of generality only the case:

$$0 \le h < l_c\sqrt{2}, \tag{5}$$

which corresponds to contact angles $0 < \theta \le 90°$ (since the following symmetry holds $h, \theta \Leftrightarrow -h, 180° - \theta$).

Taking into account the (2), (3), (4) one arrives at the following differential equation for h:

$$\dot{h} = u + \frac{\gamma}{\xi}\left(\cos\theta_{eq} - \frac{h}{2l_c^2}\sqrt{4l_c^2 - h^2}\right). \tag{6}$$

Our goal is to find asymptotic solution $h(t)$ of equation (6) for small initial deviations of the capillary rise height from the final stationary height h_{st}. Equation (6) can be made dimensionless by expressing the height in terms of the capillary length l_c and the time in terms of the characteristic time $\tau_0 = l_c\,\xi/\gamma$, i.e., $\tilde{h} = h/l_c$, $\tilde{t} = t/\tau_0$:

$$\dot{\tilde{h}} = \tilde{u} + \cos\theta_{eq} - \tilde{h}\sqrt{4 - \tilde{h}^2}\Big/2, \tag{7}$$

where

$$\tilde{u} = \xi u/\gamma \tag{8}$$

is the dimensionless velocity.

The relation (4) takes the dimensionless form:

$$\tilde{h} = \sqrt{2(1 - \sin\theta)}, \tag{9}$$

from which follow the expressions for the cosine and sine of the contact angle:

$$\cos\theta = \tilde{h}\sqrt{4 - \tilde{h}^2}\Big/2, \quad \sin\theta = 1 - \tilde{h}^2\Big/2. \tag{10}$$

After a solution is found for the contact line height $\tilde{h}(\tilde{t})$, one can obtain the time evolution of the cosine of the contact angle using equation (10).

3. Asymptotic solution

From equation (7), taking into account (5) one gets the following expression for the stationary height $\tilde{h}_{st}$:

$$\tilde{h}_{st} = \sqrt{2\left(1 - \sqrt{1 - c^2}\right)}, \tag{11}$$

where we have set

$$c = \cos\theta_{eq} + \tilde{u}. \tag{12}$$

When $\dot{\tilde{h}} \neq 0$ we look for the asymptotic solution $\tilde{h}\left(\tilde{t}\right)$ of equation (7) in the case of small initial deviations $\tilde{h}_0 \equiv \tilde{h}\left(0\right)$ from the final stationary value $\tilde{h}_{st}$ in the following form:

$$\tilde{h}\left(\tilde{t}\right) = \tilde{h}_{st} + \tilde{H}(\tilde{t}), \quad \text{where} \quad \left|\tilde{H}(\tilde{t})\right| \ll 1. \tag{13}$$

From (7) we obtain an ordinary differential equation for $\tilde{H}\left(\tilde{t}\right)$:

$$\dot{\tilde{H}}\left(\tilde{t}\right) = c - \left(\tilde{H} + \tilde{h}_{st}\right)\sqrt{1 - \left(\tilde{H} + \tilde{h}_{st}\right)^2 \Big/ 4}. \tag{14}$$

Presenting the right-hand side of equation (14) as a Taylor series one has:

$$\dot{\tilde{H}}\left(\tilde{t}\right) = -A\,\tilde{H} + B\,\tilde{H}^2 + O(\tilde{H}^3), \tag{15}$$

where the constants A and B are given by:

$$A = \left(2 - \tilde{h}_{st}^2\right) \Big/ \sqrt{4 - \tilde{h}_{st}^2}; \tag{16}$$

$$B = \tilde{h}_{st}\left(6 - \tilde{h}_{st}^2\right) \Big/ \left(2\sqrt{4 - \tilde{h}_{st}^2}(4 - \tilde{h}_{st}^2)\right). \tag{17}$$

We will find a solution of equation (15) by the perturbation technique. Considering the initial deviation $H_0 = \tilde{h}_0 - \tilde{h}_{st}$ to be a small parameter, we now seek a solution of equation (15) in the following form:

$$\tilde{H}\left(\tilde{t}\right) = H_0 X_1\left(\tilde{t}\right) + H_0^2 X_2\left(\tilde{t}\right) + \cdots \tag{18}$$

In this work we will obtain only the first two terms in this expansion. It is clear that in the same way one can proceed to obtain the higher order corrections. Inserting (18) into (15), we obtain to a first order in H_0 an equation for $X_1\left(\tilde{t}\right)$:

$$\dot{X}_1\left(\tilde{t}\right) = -AX_1\left(\tilde{t}\right), \tag{19}$$

and to a second order an equation for $X_1\left(\tilde{t}\right)$ and $X_2\left(\tilde{t}\right)$:

$$\dot{X}_2\left(\tilde{t}\right) = -AX_2\left(\tilde{t}\right) + BX_1^2\left(\tilde{t}\right). \tag{20}$$

The appropriate boundary conditions are:

$$X_1(0) = 1,\ X_2\left(0\right) = 0. \tag{21}$$

The integration of equation (19) follows trivially. By applying the boundary condition (21) we obtain:

$$X_1 = \exp(-A\tilde{t}). \tag{22}$$

Next, by substituting (22) into (20) we obtain an equation only for X_2. With the help of the (21) we obtain:

$$X_2\left(\tilde{t}\right) = -\exp(-A\tilde{t})\left(\exp(-A\tilde{t}) - 1\right)B/A. \tag{23}$$

Now, by substituting back in equation (18) the solutions found for X_1 and X_2 we finally obtain for $\tilde{h}\left(\tilde{t}\right)$ the following expression (up to a second order of the small parameter H_0):

$$\tilde{h}\left(\tilde{t}\right) = \tilde{h}_{st} + H_0\exp(-A\tilde{t}) - H_0^2\frac{B}{A}\exp(-A\tilde{t})(\exp(-A\tilde{t}) - 1) + O\left(H_0^3\right). \tag{24}$$

By inserting $\tilde{h}$ in equation (10) an exponential time dependence follows also for the cosine of the contact angle, $\cos\theta$, with the same relaxation times:

$$\begin{aligned}\cos\theta\left(\tilde{t}\right) = \cos\theta_{eq} + \tilde{u} + H_0A\exp(-A\tilde{t})\\ - H_0^2B\exp(-A\tilde{t})\left(2\exp(-A\tilde{t}) - 1\right) + O\left(H_0^3\right).\end{aligned} \tag{25}$$

4. Analysis and discussion

The asymptotic solutions found for the quasi-static relaxation of the height of the contact line (24) and of the cosine of the contact angle (25) in the Wilhelmy plate geometry are sums of exponential functions.

In the case of spontaneous relaxation these asymptotic solutions are very similar to the asymptotic solutions found in [9] for the relaxation of the radius and the cosine of the contact angle of sessile drop in the framework of the contact line dissipation approach. The (dimensional) relaxation times found for the relaxation of the meniscus in the Wilhelmy plate geometry and the relaxation of the drop are respectively:

$$\tau = \frac{\xi l_c}{\gamma \tilde{h}_{eq}} \mathrm{cotg}\theta_{eq}, \tag{26}$$

and

$$\tau = \frac{\xi R_{eq}}{\gamma \left(2 + \cos\theta_{eq}\right)\left(1 - \cos^2\theta_{eq}\right)}. \tag{27}$$

The relaxation times in both cases are proportional to the dissipation coefficient and are inversely proportional to the surface tension. The different dependence on the contact angle and the height (respectively the radius) in the relaxation times in the two cases comes from the different relations which exist between the dynamic contact angle and the height of the contact line, in the case of a Wilhelmy plate geometry, and between the dynamic contact angle and the radius of the drop.

The obtained expressions for $\tilde{h}\left(\tilde{t}\right)$ and $\cos\theta(\tilde{t})$ (see equations (24) and (25)) describe a relaxation towards a stable stationary state only for $A > 0$. Note, the coefficient A is actually the dimensionless relaxation rate $\tilde{\sigma}$, which is the inverse of the relaxation time ($\tilde{\sigma} = 1/\tilde{\tau}$). Taking into account equation (10), A (equation (16)) can be written as

$$A \equiv \tilde{\sigma} = \frac{\tilde{h}_{st}}{\mathrm{cotg}\theta_{st}}, \tag{28}$$

and as one can see, it is always positive. A reaches zero at height $\tilde{h}_{st} = \sqrt{2}$ at zero stationary angle.

In the considered model of dissipation of the contact line, we find that the contact line relaxes towards a stationary state up to plate velocities for which the stationary contact angle becomes zero and the stationary height reaches $l_c\sqrt{2}$. These are the critical quantitites for the model. The stationary states corresponding to contact line heights less than $l_c\sqrt{2}$ and respectively non-zero stationary contact angles are stable with respect to symmetrical perturbations of the contact line, i.e., perturbations for which the contact line remains parallel to that of the stationary state but its height is above or below the stationary height.

In what follows we apply the obtained asymptotic solution to the specific system studied experimentally in Ref. [4] in order to see how well it can describe the experimental data. In Ref. [4] the Wilhelmy plate experiment is performed: a solid plate is withdrawn vertically with velocity u from a bath of liquid. The plate is cut from a silicon wafer (Siltronix) covered with a thin layer of fluorinated material. The liquid used in the experiment in Ref. [4] is PDMS with dynamic viscosity $\eta = 4.95$ [Pa·s], surface tension $\gamma = 20.3$ [mN/m], and density $\rho = 970$ [kg/m^3] (the capillary length is respectively $l_c = 1.46$ [mm]). It forms a static receding angle $\theta^r_{eq} = 51.5°$ and static advancing angle $\theta^a_{eq} = 57.1°$ with the solid plate. The experimental studies show that the relaxation of the height of the contact line is well described by exponential decay function for velocities below the capillary number $Ca = 9.1 * 10^{-3}$ ($Ca = u\eta/\gamma$). The asymptotic solution obtained in the framework of the CLDM agrees with this experimental result. The experimentally obtained dependence in Ref. [4] of the dimensionless relaxation rates $\sigma^* = \eta l_c/\tau\gamma$ on the dimensionless velocity Ca below the entrainment transition is reproduced here in Fig. 2 with solid squares with error bars indicating the variation in the experimental results.

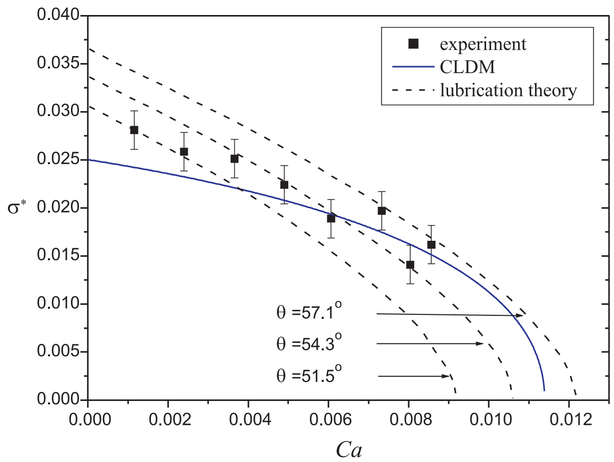

Fig. 2. Dimensionless relaxation rate σ^* as function of the velocity Ca: experimental results (Fig. 8(b) of [4]) – solid squares with error bars; CLDM results – solid line; results of a lubrication theory with a correction factor (Fig. 8(b) of [4]) – dashed lines

In Figure 2 with solid line is shown the result for the relaxation rate $\tilde{\sigma}(\tilde{u})$ which follows from the asymptotic solution of the CLDM converted to the dimensionless variables used in [4] (through $\tilde{\sigma}\eta/\xi \to \sigma^*$ and $\tilde{u}\eta/\xi \to Ca$ (see the definition of the dimensionless variables and the notation of Fig. 8(b) of [4])). It yields $\xi = 153.3$ [Pa·s]. Thus one has that the friction dissipation coefficient ξ is about 30 times bigger than the viscosity $\eta = 4.95$ [Pa·s]. In Figure 2 we have also reproduced the results of a lubrication theory with a correction factor for finite contact angles, which was applied to the experimental data in Ref. [4]. In this theory one has two fitting parameters which are adjusted by comparison with the experimental data - the microscopic contact angle θ_m and the slip length l_s. The results shown with the dashed lines in Fig. 2 are for l_s=$10^{-5}l_c$ and for three values of $\theta_m = \theta^r_{eq}; \quad \left(\theta^r_{eq} + \theta^a_{eq}\right)/2; \quad \theta^a_{eq}$. The dynamics of the contact line is obtained by combining asymptotic and numerical methods, and after that the obtained solution is fitted with exponential function. As it is seen the CLDM leads to a good agreement with the experimental results and with the results of a lubrication theory with a correction factor for finite contact angles.

5. Conclusion

The asymptotic solution is derived for the quasi-static relaxation of the contact line in the Wilhelmy plate geometry in the framework of the CLDM. The obtained asymptotic solutions for the relaxation of the height of the contact line and for the cosine of the contact angle are sums of exponential functions. The solution found is valid and stable for arbitrary finite contact angles for velocities below the entrainment transition. The existence of experimental data [4, 10] where a loss of stability occurs for a non-zero stationary contact angle shows that perhaps other types of perturbation of the contact lines should be considered also when analizing the model. It is also possible that one should take into account other channels of dissipation in the model as well.

These asymptotic solutions are very similar to the asymptotic solutions found for the quasi-static relaxation of the radius and the cosine of the contact angle of a sessile drop in the CLDM in Ref [9].

The obtained asymptotic solution is applied to the specific system studied experimentally in Ref. [4]. The asymptotic solution agrees with the exponential relaxation of the height found there. Fits of the experimental data on the relaxation rates as function of the velocity are made, allowing the only adjustable parameter of the model, the dissipation coefficient ξ to be determined. The relaxation rates which follow from the asymptotic solution of the CLDM are in a good agreement with the experimental results.

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