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DETERMINATION OF THE DYNAMIC CONTACT ANGLE TROUGH THE MENISCUS PROFILE*

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We present here a real time hybrid experimental/numerical method for determination of the macroscopic dynamic contact angle which the liquid meniscus forms with a withdrawing/immersing at constant speed vertical solid plate partially immersed in a thank of liquid when the system is in a stationary state. This method is based on the full hydrodynamic model of Voinov. It allows one to obtain numerically with high precision the stationary shape of the dynamic meniscus profile (and from there the angle of the meniscus slope) using as boundary condition the experimentally determined meniscus height.

1. Introduction. There are many studies in the literature devoted to the definition and measurement of the dynamic contact angle (DCA). This is important for many natural processes and industrial applications. The capillary rise on a vertical plate (capillary rise method (CRM)) is a nice means to obtain the dynamic contact angles [1] for small capillary numbers by measurement of the height, h, of the meniscus on a partially immersed plate. It uses the relation between h and the contact angle known from the static case, i.e. it is a static approximation method. In previous studies for the determination of the DCA in the macroscopic region, also the method of matching [2, 3] was used for obtaining the asymptotic solutions in the viscous region – in close proximity of the contact line, and for the static-like region – sufficiently away from the contact line. This method does not take into account the characteristic for the moving vertical plate presence of a intermediate region (or else viscous/gravitation region) between the viscous and the static-like regions in which both, the viscous pressure and the gravitation pressure, are of comparable magnitude [4]. Unfortunately, asymptotic solutions are not available for this intermediate region. However, one can obtain numerically with high precision a solution for the dynamic meniscus profile using the full Voinov's equation [5] and this can help to improve significantly the accuracy of the determination of DCA.

2. Problem formulation. We consider a liquid of density ρ and dynamic viscosity η in an open vessel. The linear sizes of the container are considered sufficiently big as compared to the capillary length l_c ($l_c = (\gamma/\rho g)^{1/2}$, g is the gravity acceleration, γ is the liquid/air surface tension). A partially immersed in the liquid bath vertical homogeneous

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solid plate is moving vertically with constant speed U as shown in Fig. 1. We assume that a stationary state of the system is established at fixed constant speed U of the moving plate. Due to the homogeneity of the plate, the problem of studying the liquid meniscus S reduces to the study in Cartesian coordinate system shown in Fig.1 of the 2D projection $\partial S = \{X, Z(X)\}$ of the meniscus in the (X, Z)-plane, where $Z(\infty) = 0$. We denote by $H = Z(X)$ the height of the meniscus at distance X to the vertical plate.

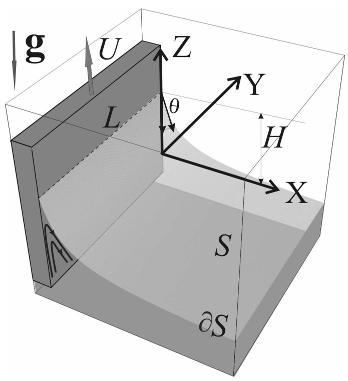

Fig. 1. Schematic drawing of the considered system and a typical flow field

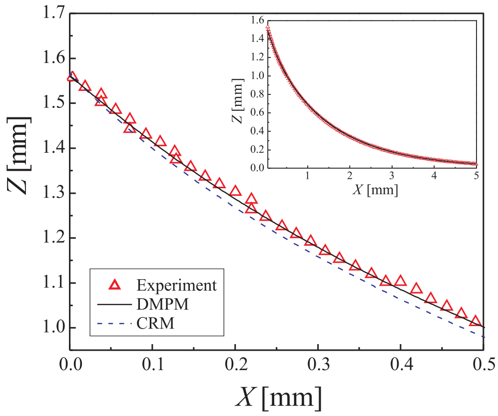

Fig. 2. Height Z of the meniscus as function of the distance X to the withdrawing plate

The DCA is defined as the angle of the slope of the meniscus profile ∂S at the top of the meniscus next to the solid wall. The so defined contact angle is not unique and depends on the distance X to the moving plate at which it is determined: $\theta = \theta(X)$. In stationary regime at distances to the plate $X > X_{\min}$, $Z(X)$ is described by the following equation [5]:

$$(1) \quad \gamma \frac{d^2Z/dX^2}{(1 + dZ/dX)^{3/2}} = p_h + p_v; \quad p_h = \rho g Z; \quad p_v = \frac{-2\eta U \sin^2\theta(X)}{X(\theta(X) - \sin\theta(X)\cos\theta(X))},$$

where $\theta(X) = \operatorname{arcctg}(-dZ/dX)$, p_h is the gravitational pressure, p_v is the viscous pressure term. $X_{\min}$ is determined by the assumptions for the applicability of the equation (1). We present here solutions for distances to the plate down to $X_{\min} = 10^{-6}$ mm [5]. When $X \ll 1$, from Eq. 1 one can obtain Cox-Voinov's law (CVL)

$$(2) \quad \theta^3(X) = \theta^3(X_i) - 9U\eta/\gamma \ln(X/X_i),$$

where $\theta(X_i)$ is the angle at some other distance X_i. When p_v can be neglected (static case) Eq. (1) has analytic solution, and the following relations hold:

$$(3) \quad Z(X) = (2 - 2\sin\theta(X))^{1/2}, \quad \theta(X) = \arcsin\left(1 - Z^2(V)/2\right).$$

Until now, the relations (3) (the static approximation – CRM) were used for the determination of the dynamic contact angle.

Let the height H_0 of the meniscus at distance to the plate X_0 is measured experimentally $Z(X_0) = H_0$. Our goal here is to obtain a numerical solution for the meniscus profile $Z(X)$ of Eq. (1) in the interval $[X_{\min}, 30l_c]$, such that:

$$Z(X_0) = H_0, \quad |Z(30l_c)| < 10^{-6} l_c. \tag{4}$$

First, we find numerically a solution $Z(X)$ in the interval $[X_0, 30l_c]$ of Eq. (1) subject to the boundary conditions (4). Using this solution we obtain the angle $\theta_0 = \theta(X_0)$ This condition allows one to obtain the solution of Eq. (1) at distances to the plate $[X_{\min}, X_0)$ smaller than X_0. For the numerical determination of the meniscus profile we apply the Runge-Kutta algorithm. For solving Eq. (1) for distances to the plate $X \geq X_0$ this method is modified for solving ordinary differential equations with Dirichlet boundary conditions. For the realization of the Runge-Kutta algorithm we use the subroutine RKF45 given in Ref. [6].

3. Results. We will demonstrate the effectiveness of the suggested procedure for the system studied experimentally in [3] – a withdrawing plate and meniscus in rise. For the example we use the experimentally obtained profiles of the dynamic meniscus shown in Fig. 8d in Ref. [3] for the silicon oil with viscosity $\eta = 50$ mPa·s and density $\rho = 970$ kg/m^3 and the highest plate speed 1.2 mm/s. For convenience the same data are reproduced here in the interval [10 μm, 0.5 mm] in Fig. 2 with empty triangles.

A. Dynamic meniscus profile. Taking into account that in the experiment in Ref. [3] the resolution of the images is 20 μm, we take first as X_0 the center of the first pixel, i.e., $X_0 = 10$ μm. The numerically obtained solution of the full Eq. (1) with boundary condition $Z(X_0) = 1.548$ mm at $X_0 = 10$ μm is shown with a solid line in Fig. 2. The numerical analysis shows that all the solutions of the full Eq. (1) using as boundary conditions $Z(X_0)$ where X_0 varies in the whole interval [10 μm, 0.5 mm] shown in Fig. 2 agree very well with the experimental results. For comparison, also the static approximation solution (CRM) for the meniscus profile is shown in Fig. 2 with a dashed line. We obtain here this solution numerically using the same numerical algorithm as for the dynamic meniscus profile, but we set $p_v = 0$ in Eq. (1). One can see that the dynamic numerical solution of Eq. (1) (when the viscous pressure term is taken into account) agrees much better with the experimental data as compared to the numerical static approximation solution (CRM). This good agreement is the basis for the more accurate determination of the dynamic contact angle.

As explained in Section 2, one can find the dynamic meniscus profile and the angle of the meniscus slope at distances to the plate smaller than the experimentally observed. For the analysis and the matching of the solution of Eq. (1) with solutions of the inner region, it is of interest to find the solution of Eq. (1) up to the distance $X_{\min}$. The numerical solutions for the DMPM and CRM are shown in Fig. 3a in the interval [10^{-6} mm, 0.01 mm] with solid line and dashed line respectively. Though these solutions look close to each other in Fig. 2, one can see that the solutions for the dynamic meniscus (DMPM) and the static approximation (CRM) of the meniscus have a fairly different behavior in the region closer to the solid plate shown in Fig. 3a and this is reflected in the quite different values of the DCA they produce – Fig. 3b.

B. Dynamic contact angle. Since the solutions of the full Eq. (1) give a good approximation of the experimental data on the meniscus profile, one can expect that the angle of the meniscus slope, obtained from these solutions also approximates well the slope of the experimental meniscus profile. The angles of the meniscus slope in the interval [10^{-6} mm, 0.055 mm] are shown in Fig. 3b with a solid line for the dynamic meniscus

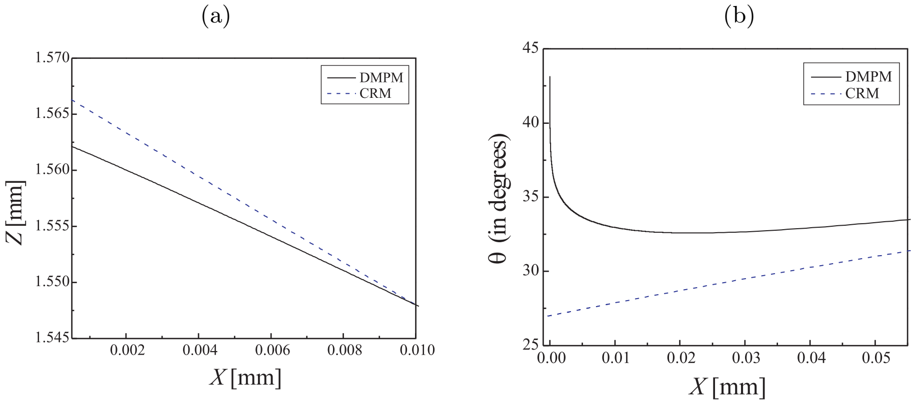

Fig. 3. (a) The height Z of the meniscus and (b) the angle θ of the meniscus slope as functions of the distance to the plate in the interval (a) [10^{-6} mm, 0.01 mm] and (b) [10^{-6} mm, 0.055 mm]: solid line – the numerical solution of the full Eq. (1) (DMPM); dashed line – the static approximation solution (CRM)

solution (DMPM) and with a dashed line for the static approximation solution (CRM). One can see that close to the plate ($X < 0.01$ mm) the angle which arises from the dynamic solution increases fast. However, there is an interval ([0.01 mm, 0.055 mm]) where the angle changes slowly and all the angles corresponding to this interval differ with less than 1°. The slow variation of the meniscus slope in this relatively big interval allows one to define unique observable macroscopic dynamic contact angle. We find that the angle of inclination at a distance $X_0 = 10$ μm to the plate is 33° (the averaged angle in the interval [10 μm, 40 μm] is 32.8°). These angles are very close to the angle of 32.6° obtained from the fitting of the first few points of the experimental profile with a line, which is an analog of the Tangent line method [3]. The values of the DCA, which follow from the DMPM differ significantly from the value obtained by the static approximation solution (CRM) for the meniscus profile leading to a difference of 5°. The CRM gives an angle of 27.87° at $X_0 = 10$ μm, known in the literature as apparent [7] DCA. That is, in close proximity of the plate, the static approximation (CRM) underestimates the angle of the slope as compared to the value which follows from the dynamic meniscus solution obtained by taking into account the viscous pressure term.

We have shown above why it is preferable to use the DMPM over the static approximation method (CRM) for determining the DCA. Now we show also that it is better to use the DMPM instead of the method of matching [3] of the viscous asymptotic solution (2) (CVL) with the static approximation solution (3) (derived for the "gravitation" region far away from the contact line) especially when one wants to obtain the DCA in the intermediate region which is usually used to define the DCA. Note, the static approximation solution in the gravitation region is another *variant* of the static approximation for the meniscus profile different from the CRM. It is obtained again from Eq. (1) (neglecting the viscous pressure term p_v) and assuming that at distance far away from the plate (e.g., at l_c) the height of the static solution coincides with the height of the solution of the full Eq. (1) (DMPM). This static approximation solution is termed in Ref. [3] as

"Fitting the whole profile"(FWP).

One can determine the regions of applicability (for determination of the meniscus slope) of the viscous approximation solution and the static approximation solution (FWP) by comparing them with the solution of the full Eq. (1) (DMPM). It is very informative to compare the magnitudes of the gravitational pressure p_h and the viscous pressure term p_v which are obtained when solving the full Eq. (1).

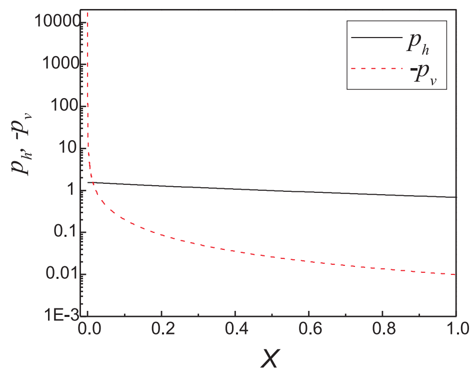

Fig. 4a. Magnitudes of the gravitational pressure $|p_h|$ – solid line; and the viscous pressure $|p_v|$ – dashed line as functions of the distance to the plate x in the interval [10^{-6} mm, 1 mm]

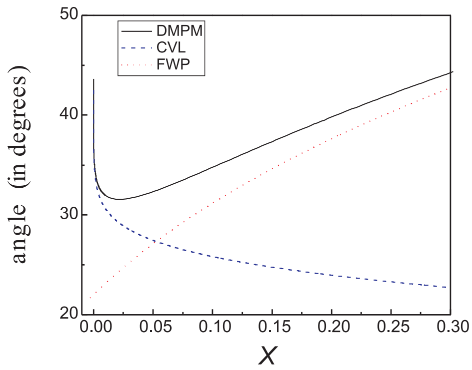

Fig. 4b. Angle of the meniscus slope as function of the distance to the plate in the interval [10^{-6} mm, 0.3 mm], solid line – DMPM; dashed line – viscous approximation – Eq. (2) (CVL), dotted line – static approximation solution (FWP)

The behavior of the two terms, p_h and $-p_v$, are shown in Fig. 4a as functions of the distance to the plate in the interval [10^{-6} mm, 1 mm]. At distance $X = 0.002$ mm, $-p_v$ is 10 times bigger than p_h. For smaller distances to the plate the ratio $-p_v/p_h$ increases very fast. At the other end of the interval shown, i.e., at $X = 1$ mm, p_h dominates and it is approximately 46 times bigger than $-p_v$. This shows that indeed very close to the plate one can use CVL and far away from the plate one can use the static approximation for the meniscus profile (FWP). The angle of the meniscus slope as function of the distance to the plate is shown in Fig. 4b in the interval [10^{-6} mm, 0.3 mm], DMPM is shown with solid line, CVL with dashed line and FWP with dotted line. The CVL is obtained from Eq. (2) by assuming that at $X = 10^{-6}$ mm the angle of the meniscus slope coincides with the angle of the meniscus slope of the solution of the full Eq. (1) at the same distance. The static approximation solution (FWP) is obtained assuming that at distance l_c to the plate the height of the static solution coincides with the height of the dynamic solution of the full Eq. (1). However, as one can see from Fig. 4b, the angle of this solution at $X_0 = 10$ μm is 23.2° (extrapolated DCA) while the solution of the DMPM at the same distance has an angle of 33°. The CVL differs from the solution of the DMPM with no more than 0.5° up to $X = 1$ μm and the FWP differs from the solution of the full Eq. (1) with no more than 0.5° down to $X = 0.69$ mm. This means that the viscous approximation is a good approximation while in Eq. (1) the magnitude of the gravitation term is less than 5% from the viscous pressure term. The static approximation (FWP) of the meniscus profile and of the meniscus slope is a good approximation while the magnitude of the viscous pressure term is less than 2% of the magnitude of the gravitation term. Therefore, it remains an interval, i.e., [1 μm,0.69 mm] where the asymptotic solutions do not approximate so well the solution of the full Eq. (1). Thus in this case one has three distinct regions: *a viscous region*, *a viscous/gravitation region* and *a gravitational region*. The above analysis shows why it is preferable to use the DMPM over the method of matching of the approximate solutions.

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ОПРЕДЕЛЯНЕ НА ДИНАМИЧНИЯ КОНТАКТЕН ЪГЪЛ ЧРЕЗ ПРОФИЛА НА МЕНИСКУСА

Станимир Д. Илиев, Нина Хр. Пешева

Представен е хибриден експериментално-числен метод, работещ в реално време, за определяне на макроскопичния динамичен контактен ъгъл, който менискусът на течност в съд формира с вертикална пластина, която се потапя или издърпва с постоянна скорост от съда с течността. Този метод е приложим, когато системата е в стационарно състояние. Методът се базира на пълния хидродинамичен модел на Войнов. Той позволява да се получи числено с висока точност стационарната форма на профила на динамичния менискус (и от там ъгълът на наклон на менискуса) като се използва като гранично условие експериментално определената височина на менискуса на пластината.