Journal of Theoretical and Applied Mechanics, Sofia, 2005, vol. 35, No. 4, pp. 3–12

FLUID MECHANICS

ASYMPTOTIC SOLUTIONS OF THE QUASI-STATIC RELAXATION OF LIQUID DROPS TAKING INTO ACCOUNT THE DISSIPATION DURING THE CONTACT LINE MOTION

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[Received 13 October 2005. Accepted 21 November 2005]

Abstract. The spontaneous quasi-static relaxation dynamics of liquid drops on solid surfaces in the partial wetting regime is studied. We base our study on the phenomenological approach suggested in *de Ruijter et al.* (*Langmuir* **15** (1999) 2209-2216) which uses the standard mechanical description of dissipative system dynamics and which introduces a phenomenological dissipation term proportional to the contact line length. We derive here asymptotic solutions of the differential equations describing the base radius and the contact angle relaxation, for small initial deviations of the base radius from the final equilibrium value in the case of spherical cap approximation of the drop shape. We find that the time relaxation of the base radius and the contact angle are given by a sum of exponential functions up to a second order in the expansion of the small parameter. We compare the asymptotic solutions with the numerically obtained solutions and we find a very good agreement.
Key words: liquid drops, relaxation, dissipative system dynamics, dynamic contact angles.

1. Introduction

The spontaneous spreading of a liquid drop on a solid is a long studied problem. Numerous studies are devoted to it employing different approaches and techniques: macroscopic, molecular-kinetic and more recent microscopic approaches involving molecular dynamic simulations, and Monte Carlo simulations of lattice gas, Ising models, etc. The focus in the later years is on more accurate determination of the specific rates of spreading, how they depend on the physico-chemical properties of the contacting media etc. This information is crucial in many industrial applications where the rates of spreading play decisive role.

An important issue when studying the drop relaxation is the inclusion of the energy dissipation occurring when the drop spreads. Regarding the dissipation, several models have been proposed in the literature. In Refs [1–3] the dissipation due to the moving contact line is considered. In Refs [4–6] the emphasis is on the losses due to viscous flow in the core of the drop. The dissipative processes taking place in the precursor film are studied in Ref. [5]. The viscous dissipation due to the moving contact line was studied experimentally, e.g., in Refs [7–10]. Several combined models are also suggested [11–13]. Recently in de Ruijter *et al.* [13] a combined approach was proposed appropriate for the partial wetting regime, considering both types of dissipation, the hydrodynamic one and the friction dissipation due to the moving contact line.

The theoretical investigation of a relaxing drop is very difficult. Even in the simplest case when a spherical cap approximation can be used for the drop shape, there are incomplete numerical data and asymptotic studies, most of which are for small angles [13, 14], angles less than 90° and small initial deviations from the equilibrium state [3]. Basically two types of asymptotic behaviour of the spontaneously relaxing drop are found – exponential [8, 15] and power (see [16] and the references therein). Since in the experimental and numerical studies the data are analyzed with the type of functions found in the asymptotic studies it is important to find asymptotic solutions for the different models for all contact angles.

In this work we derive asymptotic solutions of the differential equations, describing the spontaneous quasi-static relaxation of the base radius and the contact angle of a liquid drop, obtained within the approach of de Ruijter *et al.* [13]. However, we consider only the dissipation due to the moving contact line (as in Blake and Haynes model [1]). The asymptotic solutions are derived using perturbation technique for small initial deviations of the base radius from the final equilibrium value in the case of spherical cap approximation of the drop shape. This derivation is valid for all contact angles.

2. Problem formulation

Consider a sessile liquid drop of volume V which is placed at time $t = 0$ on an ideal, horizontal solid substrate, both enclosed in an ambient gas phase. Initially the drop deposited on the substrate is out of equilibrium. Under the action of the surface tension the incompressible liquid drop relaxes spontaneously towards spherical cap shape dissipating energy. The drop is assumed to be small enough so that the influence of the gravitation on its shape can be neglected. It is assumed also that at any moment in time $t \geq 0$, the drop retains the form of an ideal spherical cap with base radius $R(t)$ and contact angle $\theta(t)$. This implies that the instantaneous shape of the drop can be totally described by one parameter only: either by the time-dependent base radius $R(t)$ or by the contact angle $\theta(t)$.

Following the suggestion made by de Gennes [5], in Ref. [13] the standard mechanical description of dissipative system dynamics was applied to obtain the time evolution of the drop in the case of a spherical cap approximation for the drop shape. Using the variational principle of Hamilton, and taking into account the dissipation due to the moving contact line occurring when the drop spreads (see also Ref. [17] where arbitrary drop shape was considered), in the quasi-static regime one arrives at the following equation, relating the rate of dissipation function T, the equilibrium contact angle θ_{eq} and the dynamic contact angle $\theta(t)$:

$$T = \sigma \left(\cos\theta_{eq} - \cos\theta\left(t\right) \right), \tag{1}$$

where σ is the liquid surface tension.

In this work we consider the Blake and Haynes's model where the energy dissipation function T is given by

$$T = \varsigma_0 \frac{dR\left(t\right)}{dt}, \tag{2}$$

where ς_0 is considered to be a friction coefficient per unit length of the contact line.

The problem is to find asymptotic solution $R(t)$ (or equivalently $\cos\theta\left(t\right)$) of the of differential equation

$$\varsigma_0 \frac{dR\left(t\right)}{dt} = \sigma \left(\cos\theta_{eq} - \cos\theta\left(t\right) \right) \tag{3}$$

taking into account that at any moment in time due to the volume conservation the following relation between the base radius $R(t)$ and the contact angle $\theta(t)$ holds:

$$\pi R^3\left(t\right) - 3V\Phi\left(\theta\left(t\right)\right) = 0. \tag{4}$$

The function $\Phi\left(\theta\left(t\right)\right)$ is given by the following expression:

$$\Phi\left(\theta\left(t\right)\right) = \frac{\left(1 - \cos^2\theta\left(t\right)\right)^{3/2}}{2 - 3\cos\theta\left(t\right) + \cos^3\theta\left(t\right)}. \tag{5}$$

3. Asymptotic solution

We are looking for asymptotic solution $R(t)$ in the case of small initial deviations $r_0 \equiv r(0)$ of the base radius from the final equilibrium value R_{eq} in the following form:

$$R(t) = R_{eq}(1 + r(t))\,; \text{ with } |r(t)| \ll 1. \tag{6}$$

First, from eq. (4) we shall obtain Taylor's expansion of $\cos\theta(t)$ in powers of the small parameter $r(t)$. Then by substituting $\cos\theta(t)$ into eq. (3) we shall obtain an ordinary differential equation for $r(t)$. The solution of this differential equation will be sought by the perturbation technique.

Considering $\cos\theta$ as an implicit function of the base radius R, from eq. (4) by substituting the expression (6) for R and grouping together the same powers of $r(t)$, we obtain

$$\cos\theta = \cos\theta_{eq} + A_1 R_{eq} r + \left(\frac{A_1}{R_{eq}} - \frac{A_2}{R_{eq}}\right) R_{eq}^2 r^2 + O\left(R_{eq}^3 r^3\right), \tag{7}$$

where $\cos\theta(R_{eq}) = \cos\theta_{eq}$ and the coefficients A_1 and A_2 are given by

$$A_1 = \frac{(2+\cos\theta_{eq})\left(1-\cos^2\theta_{eq}\right)}{R_{eq}}, \quad A_2 = \frac{3\cos^2\theta_{eq} + 4\cos\theta_{eq} + 2}{2}. \tag{8}$$

Next, we substitute the expansion (7) for $\cos\theta$ into eq. (3). From the volume conservation condition, eq. (4), one can derive the following presentation for the function $\Phi(\theta)$:

$$\Phi(\theta) \equiv (1+r)^3 \Phi_{eq}; \quad \Phi_{eq} \equiv \Phi(\cos\theta_{eq}), \tag{9}$$

and substitute it into eq. (3) to obtain the following equation for the deviation $r(t)$:

$$A_1 r + (A_1 - A_2) r^2 + O\left(r^3\right) = -B_1 \frac{dr}{dt}. \tag{10}$$

B_1 is constant depending on the physico-chemical parameters (ς_0, σ) of the system

$$B_1 = \frac{\varsigma_0}{\sigma}. \tag{11}$$

We shall find a solution of eq. (10) by the perturbation technique. Considering the initial deviation r_0 to be a small parameter, we now seek a solution of eq. (10) in the following form:

$$r(t) = r_0 X_1(t) + r_0^2 X_2(t) + \cdots \tag{12}$$

In this work we shall obtain only the first two terms $X_1(t)$, $X_2(t)$ in this expansion. It is clear that in the same way one can proceed to obtain the higher order corrections.

Inserting the expansion (12) for $r(t)$ into eq. (10), we obtain to a first order the equation for $X_1(t)$:

$$-A_1 X_1(t) = B_1 \frac{dX_1(t)}{dt}, \tag{13}$$

and to a second order the equation for $X_1(t)$ and $X_2(t)$:

$$-A_1 X_2(t) = (A_1 - A_2) X_1(t)^2 + B_1 \frac{dX_2(t)}{dt}. \tag{14}$$

The appropriate boundary conditions are

$$X_1(0) = 1,\ X_2(0) = 0. \tag{15}$$

The integration of eq. (13) follows trivially. By applying the boundary condition (15) we obtain

$$X_1 = \exp(-t/\tau), \tag{16}$$

where we have set

$$\tau = B_1/A_1. \tag{17}$$

Note that by substituting back into eq. (17) the expressions for B_1 and A_1 one arrives at the following expression for the relaxation time τ, showing its explicit dependence on the base radius R_{eq} and the parameters of the model - the contact angle θ_{eq}, the friction coefficient per unit length of the contact line ς_0 and the surface tension σ:

$$\tau(R_{eq}) = \frac{\varsigma_0 R_{eq}}{(2 + \cos\theta_{eq})(1 - \cos^2\theta_{eq})\sigma}. \tag{18}$$

This result is in agreement with the experimental observation in Ref. [11] that the relaxation time is proportional to the equilibrium base radius. The solution, given by eq. (16) with a relaxation time, given by eq. (18), was previously obtained for contact angles $\theta_{eq} < \pi/2$ in Ref. [3].

Next, by substituting the obtained solution (16) for X_1 into eq. (14) we obtain an equation only for X_2. The integration of the obtained equation also follows trivially. With the help of the boundary condition (15) we get

$$X_2(t) = C_1 \exp(-2t/\tau) - C_1 \exp(-t/\tau), \tag{19}$$

where we have set

$$C_1 = (1 - A_2/A_1)\,. \tag{20}$$

Now, by substituting back into eq. (12) the solutions found for X_1 (eq. (16)) and X_2 (eq. (19)) we finally obtain for $r\,(t)$ (up to a second order of the small parameter r_0)

$$r\,(t) = r_0\,(1 - r_0 C_1)\exp(-t/\tau) + r_0^2 C_1 \exp(-2t/\tau) + O\left(r_0^3\right). \tag{21}$$

By inserting the expression (21) for $r\,(t)$ into eq. (7) exponential time dependence follows also for the cosine of the contact angle $\cos\theta$ with the same relaxation times.

$$\begin{aligned}\cos\theta\,(t) = \cos\theta_{eq} + r_0 A_1 R_{eq}\,(1 - r_0 C_1)\exp(-t/\tau) +\\ + r_0^2 R_{eq}\left[(1 + C_1)\,A_1 - A_2\right]\exp(-2t/\tau) + O\left(r_0^3\right).\end{aligned} \tag{22}$$

Having in mind that the equilibrium contact angle, the equilibrium base radius and the surface tension can be measured then we are left with ς_0 as unknown parameter characterizing the model. One can try to determine this parameter by fitting experimental data for drop relaxation for a given value of the base radius R_{eq} with an exponential decay function of first order.

The obtained asymptotic solutions, given by eqs (21), (22) are in a very good agreement with the fits of the numerical solutions of eqs (3) and (4) obtained in Ref. [17]. There we found that the fit with a sum of two exponential functions with different relaxation times approximates best the numerical solution for initial deviations $|r_0| = 0{,}03; 0{,}2$. We have used as criterion for the fit the maximum of the relative difference between the numerical solution and the fitting function on a time interval $[0, t^*]$, where t^* is the time for which $r\,(t^*)$ decreases hundred times from the its initial value r_0.

Here, we present results when $B_1 = 1$, $R_{eq} = 1$ for advancing contact line. By fitting the obtained numerical solutions with exponential decay function of second order, i.e., with

$$\overline{R\,(t)} = R_{eq} + a_1 \exp\left(-t/\tau_1\right) + a_2 \exp\left(-t/\tau_2\right); |a_1| \geq |a_2|\,, \tag{23}$$

where a_1, a_2, τ_1, τ_2 are fitting parameters, we determined the corresponding relaxation times τ_1, τ_2. We also considered fits by a single exponential decay function and a power function.

The relaxation of the base radius and the contact angle are shown in Fig. 1 for $\theta_{eq} = 60°$, $\theta\,(0) = 64°$, i.e., for $r_0 \approx 0{,}03$.

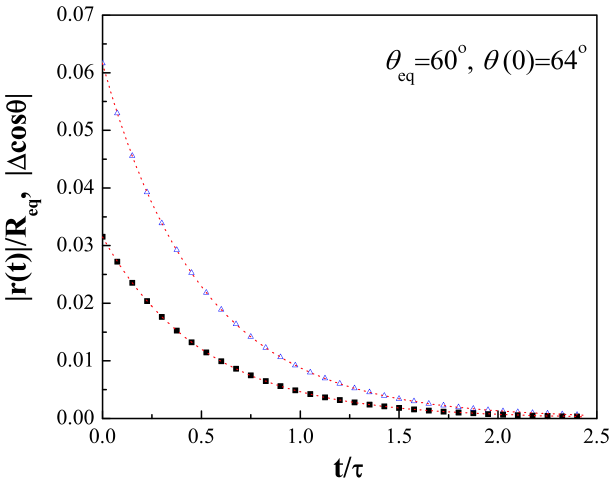

Fig. 1. Time relaxation in τ units of the base radius and the contact angle are shown for $\theta_{eq} = 60°$, $\theta(0) = 64°$ ($r_0 \approx 0{,}03$). The squares represent the numerical result for the absolute value of the deviation of the base radius from its equilibrium value, $|r(t)| = |R(t) - R_{eq}|$ in R_{eq} units, the triangles represent the numerical result for the absolute value of the deviation of the cosine of the contact angle from its equilibrium value, i.e., $\Delta\cos\theta = |\cos\theta(t) - \cos\theta_{eq}|$, the corresponding dotted lines are the fits with exponential decay functions of second order. (Note that not all the numerical data are displayed)

The squares represent the numerical result for the absolute value of the deviation of the base radius from its equilibrium value $|r(t)| = |R(t) - R_{eq}|$, the triangles are the numerical result for the absolute value of the deviation of the cosine of the contact angle from its equilibrium value, i.e., $\Delta\cos\theta = |\cos\theta(t) - \cos\theta_{eq}|$, the corresponding dotted lines are the fits with exponential decay functions of second order. In this case for the approximating functions we found:

$$\overline{\Delta\cos\theta} = 0{,}05684\exp(-t/0{,}53292) + 0{,}00479\exp(-t/0{,}25697), \tag{24}$$

$$\overline{|r(t)|} = 0{,}03025\exp(-t/0{,}53319) + 0{,}00127\exp(-t/0{,}25995). \tag{25}$$

The values found for τ from the two fits are very close to which other and also to the theoretical value, which in this case is $\tau = 0{,}5333$.

A power function, $a\,t^n$, does not approximate well the numerical solutions on the interval $[0, t^*]$, defined above, for all studied values of r_0 and θ_{eq}. We show typical results of fitting the numerical solution on the interval $[0, t_*]$

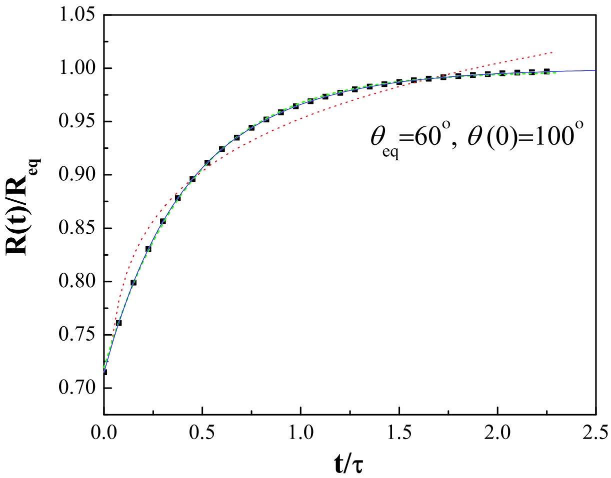

Fig. 2. Time relaxation in τ units of the base radius $R(t)$ in R_{eq} units: for $\theta_{eq} = 60°$, $\theta(0) = 100°$. The squares represent the numerical result for the base radius (not all the data are shown), the dotted line is the power fit, the dashed line is the fit with a single exponential decay function, and the thin solid line is the fit with exponential decay function of second order

with a power function in Fig. 2 for $\theta_{eq} = 60°$, $\theta(0) = 100°$ ($r_0 \approx 0{,}3$). We found that the best power fit is given by

$$\overline{R(t)} = 0{,}95276\ t^{0{,}07647}, \tag{26}$$

shown with the dotted line in Fig. 2. The numerical solution is represented by solid squares, the dashed line is the fit with a single exponential decay function:

$$\overline{R\,(t)} = 0{,}997 - 0{,}278 \exp(-t/0{,}449). \tag{27}$$

One can clearly see that the fit with the exponential decay function is much better on $[0, t^*]$ interval than the fit with the power function. The fit with the exponential decay function of second order

$$\overline{R\,(t)} = 1{,}0 - 0{,}0833 \exp(-t/0{,}268) - 0{,}202 \exp(-t/0{,}543), \tag{28}$$

is best and practically can not be distinguished from the numerical solution and from the fit with a single exponential decay function: it is shown with thin solid line.

4. Conclusion

We derived asymptotic solutions of the differential equations, describing the spontaneous quasi-static relaxation of the base radius and the contact angle of a liquid drop, obtained within the approach of de Ruijter *et al.* [13]. However, we considered here only the dissipation due to the moving contact line. The asymptotic solutions are derived for small initial deviations of the base radius from the final equilibrium value in the case of spherical cap approximation of the drop shape. This derivation is valid for all contact angles. Instead of the commonly used in previous studies approximation for the cosine of the contact angle, i.e., $\cos\theta \approx 1 - \theta^2/2$, which is valid only for small contact angles ($\theta \to 0$), we used the existing relation between the contact angle and the base radius which is due to the volume conservation condition. We find that the time relaxation of the base radius and the cosine of the contact angle are exponential. We find also in agreement with the experimental observations in Ref. [3] that the relaxation time is proportional to the equilibrium base radius.

The obtained asymptotic solutions, given by eqs (21), (22) are in a very good agreement with the fits of the numerical solutions of eqs (3) and (4) obtained in Ref. [17]. We found that the fit with a sum of two exponential functions with different relaxation times approximates best the numerical solution. A power function does not approximate well the numerical solution for all studied values of r_0 and θ_{eq}.

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