

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

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ABSTRACT. The quasi-static relaxation is considered of straight contact lines when a vertical homogeneous solid plate is withdrawn from a bath of liquid in the partial wetting regime. We apply the contact line dissipation approach to describe the relaxation of the contact line taking into account both the friction dissipation at the moving contact line and the viscous flow dissipation in the wedge. The asymptotic solutions are derived of the differential equations describing the capillary rise height 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 up to a second order in the expansion of the small parameter. We point out the implications which follow when only one dissipation channel is taken into account and compare them to the case when both dissipation channels are included.

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

1. Introduction.

The spreading of liquid on solid surface has numerous applications and that has provoked a great number of studies employing different experimental and theoretical approaches. An important theoretical problem is the description of the dynamics of the three-phase contact line and its relation to the dynamics of the so called inner part of the system in close vicinity of the contact line. A number of

**S.I. has received financial support from the NSF-Bulgaria under grant number DO-02-75/2008.

different approaches and techniques have been suggested in the literature. Testing of these approaches against the experimental data and determination of the range of validity of the approximations made is a necessary step. Here we obtain the asymptotic solution for the relaxation of the contact line in the Wilhelmy plate geometry (a vertical homogeneous solid plate is withdrawn from a liquid bath at constant speed) in the framework of the Contact Line Dissipation Approach (CLDA) for velocities below the entrainment transition and for arbitrary finite contact angles when both the friction dissipation at the moving contact line and the viscous flow dissipation in the wedge, are taken into account.

2. Problem formulation.

A theoretical approach which treats on equal footage all channels of dissipation occurring when a liquid spreads on a solid surface and which leads to a relation between the contact line velocity and the dynamic contact angle θ was put forward by de Gennes [3]. As suggested by de Gennes [3], the following equation holds for the macroscopic motion of the contact line with velocity v , relating the total dissipation function Σ in the vicinity of the contact line to the unbalanced Young force: $\partial\Sigma/\partial v = \gamma(\cos\theta_{eq} - \cos\theta)$, where γ is the liquid/vapour surface tension, and θ_{eq} and θ are the equilibrium and the dynamic contact angles. In the Molecular Kinetic Model (MKM) the focus is on the dissipation Σ_l in the immediate vicinity of the moving contact line which is due to the attachment and detachment of liquid molecules to the solid surface. At low velocities v of the contact line the expression for the dissipation function per unit length of the contact line can be written as [1, 7, 9] $\Sigma_l = \xi v^2/2$, where ξ is a friction dissipation coefficient. An expression for ξ was derived in the molecular-kinetic theory of Blake and Heynes [1]. In the Hydrodynamic Model (HDM) the emphasis is on the viscous flow dissipation Σ_w in the wedge. The expression for the viscous dissipation function for finite contact angles [4, 8] is (per unit length of the contact line): $\Sigma_w = 3\eta lv^2/tg\theta$; $l = \ln(x_{max}/x_{min})$, where x_{max} and x_{min} are some macroscopic and microscopic cut-off lengths, η is the liquid viscosity. Substituting for the total dissipation Σ the sum $\Sigma_w + \Sigma_l$ one obtains:

$$(2.1) \quad v = \gamma(\cos\theta_{eq} - \cos\theta)/(\xi + \psi ctg\theta),$$

where we have set $\psi = 6\eta l$.

Our goal here is to find asymptotic solution of Eq. (2.1) when a partially immersed homogeneous solid plate is moving vertically in a bath of liquid with constant speed u . The considered velocities are sufficiently small so that the motion of the meniscus can be considered quasi-static. Therefore, at any time moment the equilibrium relation is used which follows from the Laplace equation [10]

Relaxation of the Contact Line - Asymptotic Solutions

$$(2.2) \quad h(t) = l_c \sqrt{2(1 - \sin \theta(t))},$$

where h is the contact line height relative to the equilibrium level of the liquid bath and l_c is the capillary length ($l_c = \sqrt{\gamma / \rho g}$, ρ is the liquid density, g is the gravity acceleration). Without a loss of generality one can study the case $0 \leq h < l_c \sqrt{2}$. The contact line velocity with respect to the solid reads: $v = \dot{h}(t) - u$. Eq. (2.1) can be made dimensionless by the help of l_c and $\tau_0 = l_c (\xi + b\psi) / \gamma$, where $b \equiv \text{const}$, i.e., $\tilde{h} = h / l_c$, $\tilde{t} = t / \tau_0$ and therefore the dimensionless velocity is $\tilde{u} = (\xi + b\psi) u / \gamma$:

$$(2.3) \quad \dot{\tilde{h}} = \tilde{u} + (a\xi + b\psi) \left(\cos \theta_{eq} - 0.5\tilde{h}\sqrt{4 - \tilde{h}^2} \right) / \left(\xi + \psi \tilde{h}\sqrt{4 - \tilde{h}^2} / (2 - \tilde{h}^2) \right).$$

After a solution is found for the contact line height $\tilde{h}(t)$, one can obtain the time evolution of the cosine of the contact angle by the help of Eq. (2.2).

3. Asymptotic solution.

We proceed in the usual way to obtain first the stationary solution \tilde{h}_{st} of Eq. (2.3) and then we look for the asymptotic solution $\tilde{h}(\tilde{t})$ in the neighborhood of \tilde{h}_{st} . In the CLDM-lubrication approximation though \tilde{h}_{st} is a solution of an algebraic equation of fourth order in \tilde{h}_{st}^2 . The expression of the stationary height \tilde{h}_{st} in terms of the four parameters ($u, \theta_{eq}, \xi, \psi$) is very long and cumbersome and is difficult to analyze. That is why we use here another approach for practical applications which allows a compact expression of the asymptotic solution. For given values of the parameters (θ_{eq}, ξ, ψ) and \tilde{h}_{st} one gets the corresponding dimensionless velocity \tilde{u} and then finds the dimensional velocity u , i.e., one has $\tilde{h}_{st} \Rightarrow \tilde{u} \Rightarrow u$; then one obtains the asymptotic solution $\tilde{h}(\tilde{t})$; $\tilde{h}_{st} \Rightarrow \tilde{h}(\tilde{t})$; i.e., $\tilde{h}_{st} \Rightarrow u(\tilde{h}_{st}) \Rightarrow \tilde{h}(\tilde{t}, \tilde{h}_{st})$. In this case we set $b = ctg\theta_{st}$ and \tilde{h}_{st} is given by the following expression:

$$(3.1) \quad \tilde{h}_{st} = \sqrt{2 \left(1 - \sqrt{1 - (\cos \theta_{eq} + \tilde{u})^2} \right)},$$

From here for the dimensionless velocity in the stationary state one has:

$$(3.2) \quad \tilde{u} = \frac{1}{2} \tilde{h}_{st} \sqrt{4 - \tilde{h}_{st}^2} - \cos \theta_{eq};$$

The dimensional velocity u ($\tilde{h}_{st} \Rightarrow \tilde{u} \Rightarrow u$) is

$$(3.3) \quad u = \left(\frac{1}{2} \tilde{h}_{st} \sqrt{4 - \tilde{h}_{st}^2} - \cos \theta_{eq} \right) \gamma / \left(\xi + \psi \tilde{h}_{st} \sqrt{4 - \tilde{h}_{st}^2} / (2 - \tilde{h}_{st}^2) \right).$$

That is instead of the explicit dependence $h(t; u)$ of the asymptotic solution on u , here we obtain an implicit relation between the asymptotic solution and the dimensional velocity of the plate $h(t; h_{st}), u = u(h_{st})$.

When $\dot{\tilde{h}} \neq 0$ we look for the asymptotic solution $\tilde{h}(\tilde{t})$ of Eq. (2.3) in the case of small initial deviations $\tilde{h}_0 \equiv \tilde{h}(0)$ from the final value \tilde{h}_{st} (Eq. 3.1) in the following form:

$$(3.4) \quad \tilde{h}(\tilde{t}) = \tilde{h}_{st} + \tilde{H}(\tilde{t}), \text{ where } |\tilde{H}(\tilde{t})| \ll 1.$$

Substituting (3.4) in (2.3) and presenting the right-hand side of Eq. (2.3) as a Taylor series (in terms of the small parameter \tilde{H}) one has

$$(3.5) \quad \dot{\tilde{H}}(\tilde{t}) = -A\tilde{H} + B\tilde{H}^2 + O(\tilde{H}^3),$$

where

$$(3.6) \quad A = h_{st} \left[\text{tg}\theta_{st} - (\cos\theta_{eq} - \cos\theta_{st}) / ((\xi/\psi + \text{ctg}\theta_{st}) \sin^2\theta_{st} \cos\theta_{st}) \right],$$

$$(3.7) \quad B = \frac{h_{st}^4 (6 - \tilde{h}_{st}^2)}{16 \cos^3\theta_{st}} + \frac{h_{st} (\cos\theta_{eq} - \cos\theta_{st}) (5\tilde{h}_{st}^2 - 18)}{2 (\xi/\psi + \text{ctg}\theta_{st}) (4 - \tilde{h}_{st}^2)^{3/2} \sin^3\theta_{st}} + \\ (4 \sin\theta_{st}^3 - \tilde{h}_{st}^2 (4 - \tilde{h}_{st}^2) \cos\theta_{st} + 4 \cos\theta_{eq}) / ((\xi/\psi + \text{ctg}\theta_{st})^2 \sin^4\theta_{st} (4 - \tilde{h}_{st}^2)).$$

We will find a solution of Eq. (3.5) 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 Eq. (3.5) in the following form:

$$(3.8) \quad \tilde{H}(\tilde{t}) = H_0 X_1(\tilde{t}) + H_0^2 X_2(\tilde{t}) + \dots$$

In this work we will obtain only the first two terms $X_1(\tilde{t}), X_2(\tilde{t})$ in this expansion. It is clear that in the same way one can proceed to obtain the higher order corrections. Inserting (3.8) for $\tilde{H}(\tilde{t})$ into Eq. (3.5), we obtain $\dot{X}_1(\tilde{t}) = -AX_1(\tilde{t}), \dot{X}_2(\tilde{t}) = -AX_2(\tilde{t}) + BX_1^2(\tilde{t})$. The appropriate boundary conditions are: $X_1(0) = 1, X_2(0) = 0$. The integration of these equations is trivial.

$$X_1 = \exp(-A\tilde{t}), X_2(\tilde{t}) = -\exp(-A\tilde{t})(\exp(-A\tilde{t}) - 1)B/A.$$

Now, by substituting X_1 and X_2 in Eq. (3.8) we finally obtain for $\tilde{h}(\tilde{t})$

$$(3.9) \quad \tilde{h}(\tilde{t}) = \tilde{h}_{st} + H_0 \exp(-A\tilde{t}) - H_0^2 \exp(-A\tilde{t})(\exp(-A\tilde{t}) - 1)B/A + O(H_0^3).$$

By inserting \tilde{h} in the dimensionless Eq. (2.2) an exponential time dependence follows also for the cosine of the contact angle, $\cos\theta$, with the same relaxation times

$$(3.10) \quad \cos\theta(\tilde{t}) = \cos\theta_{eq} + \tilde{u} + H_0 A \exp(-A\tilde{t}) - \\ - H_0^2 B \exp(-A\tilde{t})(2 \exp(-A\tilde{t}) - 1) + O(H_0^3).$$

4. Analysis and discussion.

The asymptotic solutions found for the relaxation of the height of the contact line (3.9) and the cosine of the contact angle (3.10) in the Wilhelmy plate geometry are sums of exponential functions. The obtained expressions for $\tilde{h}(\tilde{t})$ and $\cos\theta(\tilde{t})$ describe a relaxation towards a stable stationary state only for $A > 0$. By the help of the obtained expressions for A we can determine the maximal value of the velocity \tilde{u} for which a relaxation towards stationary state exists and respectively we can determine the maximal attainable stationary height of the meniscus. In the case when $\psi = 0$ (MKM), A is always positive. A reaches zero at critical height $\tilde{h}_{st}^* = \sqrt{2}$ and zero critical stationary angle. In the general case ($\psi \neq 0, \xi \neq 0$) the situation is quite different. It is convenient to represent Eq. (3.6) in the following form:

$$(4.1) \quad A = \tilde{h}_{st} \left(\left(\frac{\xi}{\psi} \right) \sin^3 \theta_{st} + \cos \theta_{st} \sin^2 \theta_{st} - \tilde{u} \right) / \left(\left(\frac{\xi}{\psi} + ctg \theta_{st} \right) \sin^2 \theta_{st} \cos \theta_{st} \right).$$

The sign of A is determined by the sign of the term in the braces:

$$(4.2) \quad A_0 = \left(\frac{\xi}{\psi} \right) \sin^3 \theta_{st} + \cos \theta_{st} \sin^2 \theta_{st} - \tilde{u}.$$

If $\tilde{u} > 0$ the sign of A_0 (Eq. (4.2)) is always negative for $\theta_{st} = 0^\circ$. Thus it follows that (when increasing the velocity of the plate \tilde{u}) the solution loses stability before the stationary angle becomes 0° and respectively before the stationary height could reach the value $\sqrt{2}$. In the approximation of small contact angles Eq. (4.2) is approximately written as:

$$(4.3) \quad A_0 = \left(\frac{\xi}{\psi} \right) \theta_{st}^3 + \theta_{st}^2 - \left(\theta_{eq}^2 - \theta_{st}^2 \right) / 2 + O(\theta_{st}^4).$$

From here it follows that (up to terms of the order of $O(\theta^3)$) A_0 and therefore A becomes zero at the critical stationary contact angle: $\theta_{st}^* = \theta_{eq} / \sqrt{3}$. This is in agreement with the result of De Gennes [4] for the relaxation of the contact line in the Wilhelmy plate geometry for the HDM ($\xi = 0$) and also with the result of Golestanian and Rafaël [6]. Without the assumption of small contact angles one cannot find simple relation from Eq. (4.2) only between θ_{st}^* and θ_{eq} , it depends also on the parameter ψ . Eq. (4.3) shows that for the pure HDM ($\xi = 0$) the dependence $\theta_{st}^{*\psi} = \theta_{st}^{*\psi}(\theta_{eq})$ is not linear. For small contact angles θ_{eq} ($\theta_{eq} \leq 4^\circ$) the linear fitting $\theta_{st}^{*\psi} = b\theta_{eq} + d$ gives $b^{(1)} \approx 0.578$ which is very close to the value of $\theta_{st}^* / \theta_{eq}$ obtained by de Gennes, i.e., $1/\sqrt{3} \approx 0.57735$. When θ_{eq} is increased this coefficient changes and for example a linear fitting in the interval $20^\circ \leq \theta_{eq} \leq 60^\circ$ gives $b^{(2)} \approx 0.645$. For bigger contact angles this coefficient changes even faster.

In the case when $\xi \neq 0, \psi \neq 0$ (the combined CLDM), depending on the value of the ratio ξ/ψ the critical stationary contact angle θ_{st}^* lies in the interval $\theta_{st}^* \in (0, \theta_{st}^{*\psi})$. For a nonzero critical stationary contact angle the critical stationary height is strictly less than $\sqrt{2}$ (see eq. (4.2)). In other words in the case when one considers only the friction dissipation of the moving contact line one obtains that the contact angle goes continuously to zero at maximal height $\sqrt{2}$ (second order phase transition as noted by Golestanian and Raphaël [6]), while in the case when one considers only the viscous dissipation in the wedge one gets that the contact angle changes with a jump. The same holds true also for the combined CLDM.

5. Conclusion.

The asymptotic solutions are derived of the differential equations in the combined CLDM describing the capillary rise height and the contact angle relaxation in the Wilhelmy plate geometry valid for arbitrary equilibrium contact angles. They are sums of exponential functions. Critical velocities above which a relaxation towards stationary state is no longer possible (and respectively critical heights and critical contact angles) are obtained for the MKM, the HDM and the combined CLDM.

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