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Historical perspective

Capillary dynamics driven by molecular self-layering

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ABSTRACT

Capillary dynamics is a ubiquitous everyday phenomenon. It has practical applications in diverse fields, including ink-jet printing, lab-on-a-chip, biotechnology, and coating. Understanding capillary dynamics requires essential knowledge on the molecular level of how fluid molecules interact with a solid substrate (the wall). Recent studies conducted with the surface force apparatus (SFA), atomic force microscope (AFM), and statistical mechanics simulation revealed that molecules/nanoparticles confined into the film/wall surfaces tend to self-layer into 2D layer/s and even 2D in-layer with increased confinement and fluid volume fraction. Here, the capillary rise dynamics of simple molecular fluids in cylindrical capillary is explained by the molecular self-layering model. The proposed model considers the role of the molecular shape on self-layering and its effect on the molecularly thin film viscosity in regards to the advancing (dynamic) contact angle. The model was tested to explain the capillary rise dynamics of fluids of spherical, cylindrical, and disk shape molecules in borosilicate glass capillaries. The good agreement between the capillary rise data and SFA data from the literature for simple fluid self-layering shows the validity of the present model. The present model provides new insights into the design of many applications where dynamic wetting is important because it reveals the significant impact of molecular self-layering close to the wall on dynamic wetting.

1. Introduction

In motion driven by the capillarity, for instance, a small water droplet spreading on a glass surface, it takes time to reach equilibrium. The dynamic evolution of droplet shape toward its equilibrium is a typical capillary dynamic process. The main feature characterizing the capillary dynamics is the three-phase (usually liquid/air/solid or liquid/liquid/solid) dynamic contact angle, which deviates from the equilibrium value because of the energy dissipation in the moving three-phase contact line (TPCL). Theoretical models for dynamic contact angle can be classified into two categories: (1) hydrodynamic model considering energy dissipation in the macroscopic bulk liquid and (2) molecular kinetic theory considering energy dissipation at the vicinity of the TPCL. Some empirical equations are also reported.

1.1. Hydrodynamic model

Hydrodynamic model was developed by Cox [1], Voinov [2] and Dussan [3]. In the hydrodynamic model, liquid is allowed to slip on the solid surface at molecular scale to remove the conflict between the moving TPCL and the conventional no-slip boundary condition. Dynamic contact angle results from the viscous bending of the liquid-gas interface on the mesoscale. The dependence of dynamic contact angle on capillary number is shown as below:

$$G(\theta_d) = G(\theta_e) + \ln\left(\frac{L}{L_m}\right)Ca \qquad (1)$$

where $G(\theta) = \int_0^\theta \frac{x - \sin x \cos x}{2\sin x}dx$, L and L_m are the appropriately macroscopic and microscopic length scale, respectively. $Ca = \frac{\mu v}{\gamma}$ is the capillary number, with μ being the liquid viscosity; v being the contact line velocity; and γbeing liquid surface tension. When $\theta < 3\pi/4$, $G(\theta) = \int_0^\theta \frac{x - \sin x \cos x}{2\sin x}dx \approx \theta^3/9$, and Eq. (1) reduces to:

$$\theta_d^3 - \theta_e^3 = 9\chi Ca \qquad (2)$$

where $\chi = \ln\left(\frac{L}{L_m}\right)$.

Brochard-Wyart and de Gennes [4] also derived an equivalent equation using the lubrication approximation for small contact angle.

$$\theta_d\left(\theta_d^2 - \theta_e^2\right) = 6\ln\left(\frac{x_{\max}}{x_{\min}}\right)Ca \qquad (3)$$

Here $x_{\min}$ is the molecular cut off below which the continuum theory breaks down and $x_{\max}$ is macroscopic cut off proportional to the radius of curvature of the meniscus.

The hydrodynamic model requires a small equilibrium contact angle due to the lubrication approximation in the model. Besides, the

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hydrodynamic model only considers the viscous energy dissipation in the bulk liquid and neglects the liquid-solid interaction at the molecular level, which is very important in capillary dynamics.

1.2. Molecular kinetic theory

Cherry and Holmes [5] considered the wetting process to be an activated rate process since Eyring [6] showed that the theory of the absolute reaction rate could be applied to the mechanism of flow. They assumed the TPCL moves between the successive positions of equilibrium across the intervening activation energy barriers when a wetting liquid spreads on a solid surface. The resulting differential equation for the time-dependent dynamic contact angle is

$$\frac{d(\cos\theta_t)}{dt} = \frac{\gamma xy}{\mu V}(\cos\theta_e - \cos\theta_t) \tag{4}$$

where θ_t is the time-dependent dynamic contact angle, x is the distance between the positions of equilibrium, y is the dimensions of the jumping unit in the direction parallel to the three-phase boundary, and V is the displacement volume of the unit of flow. Though there are three unknown parameters and the fitted $\frac{V}{xy}$ value from the spreading of the polymer melt seems unreasonably large, this is the first attempt to theoretically model the spreading dynamics (to the best of our knowledge).

Later, Blake et al. [7,8] proposed the molecular kinetic theory based on Eyring's activated-rate theory considering the adsorption and desorption dynamics of liquid molecules on solid surface near the TPCL. Yarnold's idea [9] that the velocity dependent contact angle is from the disturbed adsorption equilibria is also applied. For the moving contact line, the adsorption equilibrium is disturbed. As a consequence, the local curvature is changed, resulting in a dynamic contact angle θ_d larger the equilibrium one θ_e and an unbalanced surface tension force $\gamma(\cos\theta_e - \cos\theta_d)$, which is the driving force of contact line movement. According to their theory, the equation for the velocity v of moving TPCL is given by

$$v = 2\kappa^0\lambda \sinh\left[\gamma(\cos\theta_e - \cos\theta_d)\lambda^2/2k_BT\right] \tag{5}$$

where $\lambda$is the distance between adsorption sites on the solid surface; k_B is the Boltzmann constant; T is the absolute temperature; and κ^0 is the characteristic frequency and is determined by the activation free energy of wetting ΔG_w^*.

$$\kappa^0 = \left(\frac{k_B}{\hbar}\right)\exp\left(\frac{-\Delta G_w^*}{n'k_BT}\right) \tag{6}$$

where $\hbar$ is the Planck constant and n' is the number of adsorption sites per unit area. For small argument in the sinh function, Eq. (6) can be linearized as:

$$v = \kappa^0\gamma(\cos\theta_e - \cos\theta_d)\lambda^3/k_BT \tag{7}$$

Eq. (7) can be reorganized into Eq. (8):

$$\gamma(\cos\theta_e - \cos\theta_d) = \beta v \tag{8}$$

with $\beta = \frac{k_BT}{\kappa^0\lambda^3}$ being the frictional coefficient between liquid and solid surface at the TPCL.

The molecular kinetic theory can be applied to a wide range of equilibrium contact angles. However, for a small equilibrium contact angle, the prediction is not as good as that from the hydrodynamic model [10]. While the molecular kinetic theory shows the significance of the solid surface properties in dynamic wetting, it overlooks the effect of the shape of the liquid molecules, which is also important, as shown in this work and in the literature [11].

Hoffman [12,13] proposed a similar model to the molecular kinetic theory by assuming the jumping of liquid molecules forward and backward on the solid surface control the movement of the three phase contact line. Resulted equation from Hoffman's model is:

$$Ca = 2\frac{1}{\kappa}\exp\left(\frac{-\Delta G_0{}'}{RT}\right)\sinh[\kappa(\cos\theta_e - \cos\theta_d)] \tag{9}$$

where $\kappa = \frac{\gamma N}{nRT}$, $\Delta G_0{}'$ is the potential energy barrier difference between molecule in bulk and at the contact line, N is Avogadro number, R is gas constant, and n is number of molecules per unit area at the surface. For $\kappa(\cos\theta_e - \cos\theta_d) << 1$, Eq. (9) can be reduced to Eq. (10):

$$\cos\theta_e - \cos\theta_d = \frac{1}{2}\exp\left(\frac{\Delta G_0{}'}{RT}\right)Ca \tag{10}$$

which has the same form as Eq. (8).

Ruckenstein and Dunn [14] also made a contribution using a similar scenario that involved liquid molecules jumping from one potential well to the next on a solid surface. In their model, the driving force for the spreading is the chemical potential gradient in the liquid along the solid-liquid interface. The relationship between the velocity of the TPCL v and the dynamic contact angle θ_d given by their model is

$$v = \frac{D}{n_L}\frac{A_{SL}\cos^3\theta_d}{4\pi x^4}\left[\frac{A_{LL} - A_{SL}}{A_{SL}}G(\theta_d) - G(\pi - \theta_d)\right] \tag{11}$$

where $G(\theta_d) = \csc^3\theta_d + \cot^3\theta_d + 1.5\cot\theta_d$, D is the surface diffusion coefficient, n_L is the liquid molecular density, and A_{SL} and A_{LL} are the Hamaker constants for the solid-liquid and liquid-liquid molecular interactions, respectively.

1.3. Combined model

The combined model is the combination of Eq. (2) from hydrodynamic model and Eq. (8) from molecular theory. The model was proposed by Petrov [15] taking into account both the viscous energy dissipation in the bulk and energy dissipation in the immediate proximity to the TPCL.

1.4. Shikhmurzaev's model

Shikhmurzaev's [16,17] proposed a model considering the viscous dissipation in the hydrodynamic model and also the energy dissipation during the interfacial creation and destruction process. At low capillary number and Reynolds number, the proposed velocity dependent contact angle is:

$$\cos\theta_e - \cos\theta_d = \frac{2V(\rho_{2e} + \rho_{1e}u_0)}{(1 - \rho_{1e})\left[(\rho_{2e} + u^2)^{1/2} + u\right]} \tag{12}$$

where $u = Sc \times Ca$, $u_0 = \frac{\sin\theta_d - \theta_d\cos\theta_d}{\sin\theta_d\cos\theta_d - \theta_d}$, $\rho_{2e} = 1 + (1 - \rho_{1e})(\cos\theta_e - \sigma_{SG})$, Sc is a scaling factor depending on material properties and, ρ_{1e} and ρ_{2e} are phenomenological coefficients [17]. The complicated mathematical expression and three unknown parameters limit the application of Shikhmurzaev's model.

Detail discussion of the above-mentioned theoretical models can be found elsewhere [18]. All the theoretical models contain unknown parameters, which hide the physics of the TPCL.

1.5. Empirical equations

Besides the theoretical models, there are also some empirical equations relating the dynamic contact angle and capillary number. Newman [19] analyzed the rate of the penetration of the polymer melt into the capillaries and proposed Eq. (13) to correct the effect of the time-