Modeling of Drop Motion on Solid Surfaces with Wettability Gradients
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Extended Abstract :

Background. A liquid drop can move on a solid surface because of a gradient in wettability along the surface. Such a gradient can be chemically induced (Elwing et al., 1987, Chaudhury & Whitesides, 1992) or can arise from a temperature gradient (Brochard, 1989). The drop will move in the direction of increasing wettability. Available theoretical models are sparse (Greenspan, 1978, Brochard, 1989, Ford & Nadim, 1994) and make several approximations. The approximations include the assumption that the drop wets the surface very well so that the contact angles are small and that the lubrication approximation can be made in simplifying the Navier-Stokes equation. In fact, contact angles in the study of Daniel et al. (2001), as well as in experiments conducted in our own laboratory, are as large as 100°.

de Gennes (1985) argued that the rate of spreading is predominantly determined by viscous dissipation near the contact line. This region is typically approximated as a wedge, terminating in a foot, known as a precursor film, in some instances. The wedge is of macroscopic dimensions, whereas it is suggested that the precursor film can be as thin as 10 nm with a length that is of macroscopic dimensions. The use of the lubrication approximation is justified in a precursor film (when it exists) in which variations with distance are small, but is questionable in the wedge if the contact angle is not small.

Blake & Haynes (1969) developed a kinetic theory model of contact line motion. Their model indicates that a non-hydrodynamic frictional resistance to contact line motion exists. The origin of the frictional resistance is an energy barrier that molecules must cross to move from the liquid drop to available sites on the solid substrate. We will

present MD simulation results that suggest that this idea is correct. Indeed, the Blake-Haynes model predicts migration velocities for drops on wettability gradients that are in reasonable agreement with our MD results. Our results for drops on uniform surfaces suggest, however, that the energy barrier for receding contact lines is significantly larger than for advancing contact lines, which implies that a generalization of the model is needed.

Hydrodynamic theory. A driving force for motion on a wettability gradient exists because the free energy of the system decreases when the drop migrates to more hydrophilic portions of the surface. Let us assume that the cosine of the equilibrium contact angle is a linear function of position, *x*, along a surface with a wettability gradient

$$\cos\theta_0(x) = \cos\theta_0(0) + \alpha x \qquad (1)$$

If the planform of a small drop is approximately circular with a radius *R*, one can show that the driving force on the drop is $\pi R^2 \gamma \alpha$, where γ denotes the surface tension. If the Reynolds number for the motion is small compared with unity, one may use the results of Cox (1986) for the flow in the wedge region to obtain the migration velocity:

$$U = \frac{\gamma R \alpha}{\mu(B + AR/h)} \qquad (2)$$

where *h* is the height of the drop at its apex, *A* is a constant of order unity that depends on R/h , and B is given by

$$B = \frac{2\sin^2\theta}{\theta - \cos\theta\sin\theta}\ln(\frac{x_{max}}{x_{min}}) \qquad (3)$$

In Eq. (3), x_{max} is the macrosopic scale on which the wedge solution is valid and x_{min} is the cutoff length for no-slip. We tested Eq. (2) by comparing its predictions with experimental measurements of drop migration conducted in our laboratory. The experiments were conducted with ethylene glycol drops having planform radii between 0.20 mm and 1.20 mm on carefully cleaned silicon strips that were exposed to an alkylchlorosilane. We found that Eq. (2) over-predicted the experimentally observed velocities by an order of magnitude.

Blake-Haynes kinetic theory.

While factors such as surface roughness may account for part of the discrepancy between the prediction of Eq. (2) and our experimental observations, the kinetic theory model of Blake & Haynes (1969) offers another possible explanation: molecular scale frictional resistance at the contact line. The result for the velocity of the contact line obtained by Blake & Haynes is:

$$v = 2K_0 \lambda \sinh\left(\frac{w}{2nk_BT}\right) \qquad (4)$$

where K_0 is the molecular jumping frequency when equilibrium conditions prevail, λ is the characteristic displacement distance, n is the density of surface adsorption sites for the fluid molecules, and w is the work per unit area done by the driving force. Blake & Haynes argued that w could be related to the surface tension and the dynamic and equilibrium contact angles: $w = \gamma(\cos\theta_e - \cos\theta)$. Assuming that $w << 2nk_BT$ one obtains the following simplification for the velocity of the contact line.

$$v = \frac{\gamma}{\varsigma_0}(\cos\theta_e - \cos\theta) \qquad (5)$$

where the friction coefficient, ς_0, is given by $\varsigma_0 = \frac{nk_BT}{K_0\lambda}$.

de Ruijter et al. (1999) used MD simulations of spreading fluid drops to test the model of Blake & Haynes (1969). They computed the relaxation of the contact angle of a spreading drop from its initial value to its final equilibrium value by integrating the Blake-Haynes model and found good agreement with the results obtained directly from their MD simulation.

The Blake-Haynes model suggests that the friction coefficient is the same for advancing and receding contact lines. de Ruijter et al. (1999) did not test this idea because they considered only advancing contact lines. Our results indicate that the value of the friction coefficient is significantly different for advancing and receding contact lines.

MD simulations. Following a procedure described by Yang et al. (1992) the MD simulations were performed for diatomic liquid drops in contact with an FCC crystal lattice. The atoms interacted through modified Lennard-Jones (LJ) potentials with

characteristic energies ε_{ff}, ε_{wf}, and ε_{ww} for the interactions between fluid atoms and other fluid atoms, fluid and wall atoms, and wall atoms and other wall atoms, respectively. The wettability of the surface was varied by choosing different values for ε_{wf}. The LJ potential energy of interaction V between atoms of type i and type j located a distance r apart is given by

$$V(r) = 4\varepsilon_{ij}\left\{\left(\frac{\sigma}{r}\right)^{12} - \delta_{ij}\left(\frac{\sigma}{r}\right)^{6}\right\} \qquad (6)$$

where $2^{1/6}\sigma$ can be interpreted as a molecular diameter, and δ_{ij} is an adjustable parameter. In the following discussion dimensionless quantities are used. The reference mass is that of a fluid atom, the reference length is σ, and the reference time is $\sqrt{m\sigma^2/\varepsilon}$. To reduce computation time, periodic boundary conditions were imposed in the direction normal to the wall, which was 5 atomic layers thick (Yang et al., 1992). Periodic boundary conditions were also imposed in the transverse (x and y) directions.

Figure 1 shows a side view of an equilibrium drop containing 51,622 diatomic molecules in contact with a partially wetting wall containing 50,000 atoms. In units based on the length parameter in the fluid-fluid LJ potential, the periods are 200 in x, 100 in y, and 85 in z, where x and y are measured parallel to the solid surface and z is in the normal direction. The equilibrium contact angle was determined to be 44° by fitting the drop to a spherical cap shape and excluding the 10 fluid layers closest to the wall (de Ruijter et al., 1999.)
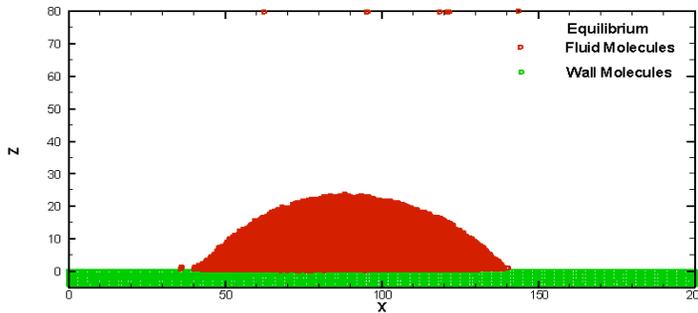

Figure 1. An equilibrium drop on a uniform surface with $\varepsilon_{wf} = 1.3$.

A wettability gradient was created by setting $\varepsilon_{wf} = 0.4 + 0.006x$. A spherical drop was created and then a body force was applied to put it into contact with the solid surface. Once the drop had begun to wet the surface, the body force was removed. Figure 2 shows the center of mass x-coordinate of the drop as a function of dimensionless time. It may be seen that the velocity gradually decreases with time.
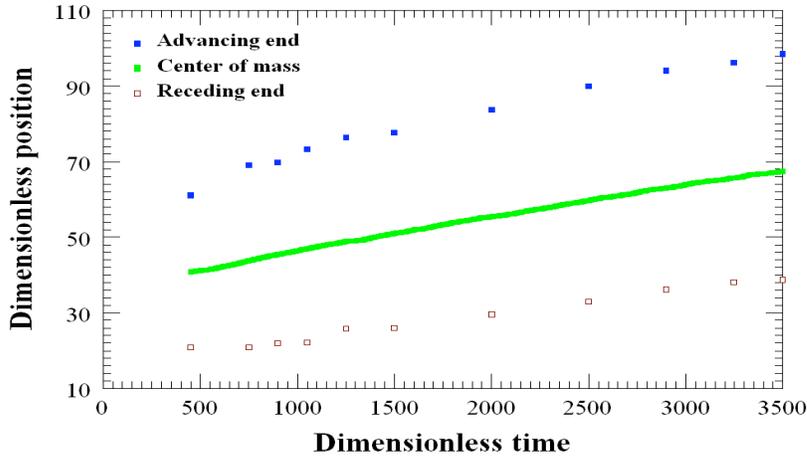

Figure 2. The x-coordinate of the center of mass and the advancing and receding ends of a drop on a wettability gradient are shown as a function of dimensionless time.

The Blake-Haynes theory was used to derive an expression for the migration velocity by assuming that the friction coefficient was relatively constant around the perimeter of the drop and that viscous drag could be neglected. If the cosine of the equilibrium contact angle is given by Eq. (1), the velocity of the drop is $v = \dfrac{\alpha \gamma R}{\varsigma}$. To determine a value for ς_0 one can consider the spreading of drops on uniform surfaces. At regular time intervals, the dynamic contact angle was determined by fitting a spherical cap to the instantaneous drop. The results are shown in Figure 3.
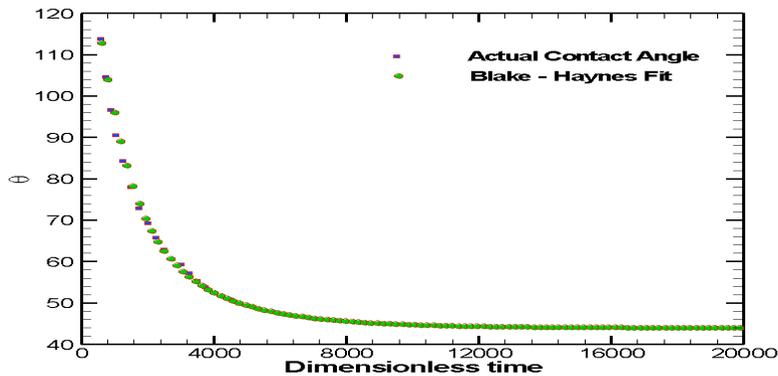
Figure 3. The dynamic contact angle determined from an MD simulation and the value predicted by the Blake-Haynes theory are plotted versus dimensionless time.

Also shown in Figure 3 is the dynamic contact angle versus time predicted by the Blake-Haynes kinetic theory model. To obtain this result, the friction coefficient was varied to obtain the best agreement with the results from the MD simulation. The value obtained by this method was $\varsigma_0 = 105$. Using the same procedure at other wettabilities, we found that ζ_0 varied monotonically from 31 at $\varepsilon_{wf} = 0.4$ to 165 at $\varepsilon_{wf} = 1.3$. At the dimensionless time 5500, the friction constant at the value of ε_{wf} corresponding to the location of the center of mass was 81. Using this value, the predicted migration velocity is 0.0090. The actual velocity was 0.0058. The discrepancy between the theoretical and observed values is probably due in part to the fact that the friction coefficient varies significantly over the perimeter of the drop (see below).

To predict the translation velocity of a drop on a surface, one should also consider the friction coefficient for a receding contact line. This was done by starting with an equilibrium drop on a surface and abruptly reducing the value of the wettability (i.e., the value of ε_{wf}). For the equilibrium drop in Figure 1, the value of ε_{wf} was changed from 1.3 to 0.7. The value of ς_0 for a receding contact line on a surface with $\varepsilon_{wf} = 0.7$ was thereby found to be 90. For an advancing contact line on the same surface, the friction coefficient is 60. For $\varepsilon_{wf} = 0.4$, the values of ς_0 for advancing and receding contact lines were 31 and 38, respectively. The discrepancy between the two cases increases

as ε_{wf} increases. Therefore, it appears that, while the friction coefficient model is useful, it requires modification.

References
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