

Predicting slip by measuring contact angles

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Introduction

In capillary flow, the potential importance of slip between the liquid and the solid becomes increasingly significant as the width of the channel decreases. For channels at the nanometer scale, it may become dominant. However, despite much research over at least 70 years, we lack the ability to predict the magnitude of slip for a given system. Here, we propose a method based on the molecular-kinetic theory of dynamic wetting (the MKT) that enables us to estimate molecular slip by the relatively simple expedient of measuring the dynamic contact angle of the liquid on the relevant solid surface as a function of contact-line velocity. This proposal is supported by the results of recent large-scale molecular-dynamics (MD) simulations [1].

Theory

The MKT [2,3] predicts that the dynamic contact angle θ_D is determined by the statistical behavior of the liquid molecules at the contact line, which, when viewed on a molecular scale, is not a line but a zone, the three-phase zone (TPZ), of small but finite thickness δ . As the contact line moves, the interaction of these molecules with the periodic energy landscape of the solid surface generates a frictional force hindering motion. This ‘contact-line friction’ is overcome by the deviation in the contact angle from its equilibrium value, which generates a balancing surface tension force $\gamma_L(\cos\theta^0 - \cos\theta_D)$, where θ^0 is the equilibrium contact angle and γ_L the surface tension. The resulting equation linking θ_D with contact-line velocity U is

$$U = 2\kappa^0\lambda \sinh\left[\gamma_L(\cos\theta^0 - \cos\theta_D)/2nk_B T\right]. \quad (1)$$

Here, λ is a molecular length scale that characterizes the periodicity of n energy wells per unit area of the solid surface. If these are uniformly distributed, $n = 1/\lambda^2$. The quantity κ^0 is the characteristic frequency at which liquid molecules jump from one energy well to the next at equilibrium, k_B is the Boltzmann constant and T the temperature. Provided the argument of \sinh is small, which is the case in our MD simulations, Eq. (1) reduces to the linear expression

$$U = \gamma_L(\cos\theta^0 - \cos\theta_D)/\zeta, \quad (2)$$

where, $\zeta = nk_B T/\kappa^0 \lambda \approx k_B T/\kappa^0 \lambda^3$ is the coefficient of contact-line friction. This has the same units as shear viscosity. Based on an analysis of results obtained in a previous MD study of dynamic wetting [4], we have argued [1] that the mechanism of contact-line friction is just a special case of the interaction of a liquid undergoing shear against a solid wall. Thus, it should be possible to generalize the MKT to describe molecular slip at this interface in terms of κ^0 and λ . But, whereas, the shear stress across the TPZ originating from surface tension forces and responsible for velocity U against contact-line friction ζ can be estimated as $\tau_{TPZ} = \gamma_L(\cos\theta^0 - \cos\theta_D)/\delta$, that due to a velocity gradient du_x/dz in the liquid near a solid wall is $\tau_{SL} = \eta_L(du_x/dz)$. If this generates slip and we invoke the Navier slip condition then $\tau_{SL} = \beta U_{Slip} = \eta_L U_{Slip}/l_{Slip}$, where β is the slip coefficient and U_{Slip} and l_{Slip} are, respectively, the slip velocity and slip length (*i.e.* the distance from the solid surface at which the velocity vanishes). If the underlying mechanisms are indeed the same then $\beta = \zeta/\delta$. Thus, if we can estimate δ we can predict the magnitude of slip by measuring the velocity dependence of the dynamic contact angle, using Eqs. (1) or (2) to calculate ζ . Specifically, we expect

$$U_{slip} = \eta_L \delta (du_x/dz)/\zeta \quad \text{and} \quad l_{slip} = \delta(\eta_L/\zeta). \quad (3)$$

MD simulations and results

In order to study both dynamic wetting and slip we have modeled a liquid bridge confined in a stationary position between two solid plates moving at an equal speed U_{plate} in opposite directions (Fig. 1). Our simulations follow well-rehearsed methods [1,4]. In brief, all the interactions are based on Lennard-Jones potentials:

$$V_{ij} = 4C\epsilon_{ij} \left[\left(\sigma_{ij}/r_{ij} \right)^{12} - \left(\sigma_{ij}/r_{ij} \right)^6 \right], \quad (4)$$

where r_{ij} is the distance between any pair of atoms i and j . For all the atoms, $\epsilon_{ij} = 33.33$ K (4.6×10^{-22} J) and $\sigma_{ij} = 0.35$ nm. We implement a cut-off at $r_{ij} = 2.5 \sigma_{ij}$ and periodic boundary conditions in the x and y directions. The temperature is maintained at 33.33 K by velocity scaling, applied to both liquid and solid during equilibration, but to only the solid during dynamic wetting simulations. The coupling parameter C enables us to tune the relative affinities between the different types of atoms. We set $C = 1$ for all the interactions except that between liquid and solid atoms, which we adjust from 0.4 to 0.8 to explore a range of equilibrium contact angles θ^0 (137° to 75° , respectively). The solid plates are constructed as rectangular, square-planar lattices having three atomic layers and bound by a strong harmonic potential. The lattice parameter is 0.393 nm. The distance between the plates is either $H = 8.85$ nm or 36.1 nm. The liquid is modeled as 8-atom chains to increase viscosity and minimize evaporation. It has a surface tension $\gamma_L = 2.49$ mN/m and viscosity $\eta_L = 2.48$ mPa.s, obtained by standard methods [4]. The density is 18.3 atoms/nm³. Contact angles are measured, as in a real experiment, by fitting a suitable curve to the interface and measuring its tangent at the solid. To measure the flow within the liquid we project all the atoms onto the x - z plane, subdivided into 0.5 nm square bins. By computing the positions of the atoms in each bin at successive time intervals we can determine velocity components u_x and u_z and so construct the required flow profiles and velocity gradients necessary to evaluate the magnitude of slip [1]. For a linear velocity gradient across the liquid bridge, l_{slip} is given by

$$l_{slip} = (U_{plate} / (du_x/dz) - H/2). \quad (5)$$

Fig. 2 compares the results obtained in this way for each solid-liquid coupling with those given by Eq. (3) using the measured values of ζ and an estimate of $\delta = 3.52$ nm determined from an analysis of the density and velocity components across the TPZ, as shown in Fig. 3 [1]. Evidently, there is good agreement between the predicted slip lengths and those found from the simulations. Both vary systematically with the affinity between the liquid and the solid, ranging from ~ 2 nm for $\theta^0 = 75^\circ$ to ~ 6 nm for $\theta^0 = 137^\circ$. This dependence can also be modeled using the MKT [1]. The values revealed in Fig. 2, though smaller than some reported in the literature, are consistent with the latest figures obtained from simulation and

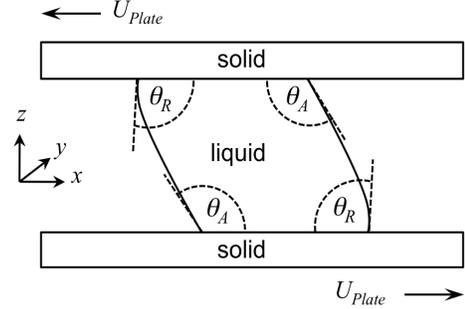


Figure 1: Liquid bridge used in simulation

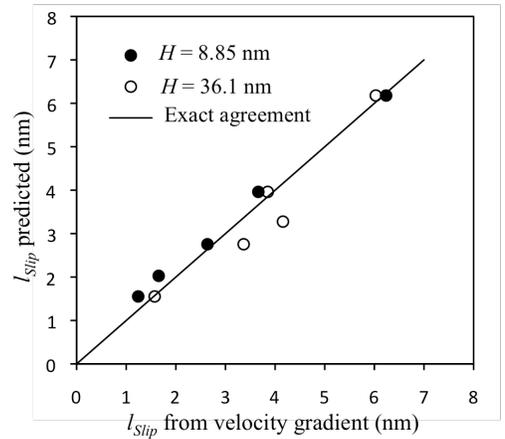


Figure 2: Measured slip length compared with that predicted by the MKT

experiment [5]. Their small value may reflect the fact that the liquid atoms and the solid lattice in our simulations are effectively commensurate, which increases the energy barriers to molecular slip.

References

- [1] T. D. Blake, J-C. Fernandez-Tolendano, G. Doyen and J. De Coninck, ‘Forced wetting and hydro-dynamic assist,’ *Phys. Fluids* **27** (2015) 112101.
- [2] T. D. Blake and J. M. Haynes, ‘Kinetics of liquid-liquid displacement,’ *J. Colloid Interface Sci.* **30** (1969) 421-423.
- [3] T. D. Blake, ‘Dynamic contact angles and wetting kinetics,’ in *Wettability*, J. C. Berg, ed.: Dekker, New York, 1993, pp. 251–309.
- [4] E. Bertrand, T. D. Blake and J. De Coninck, ‘Influence of solid-liquid interactions on dynamic wetting: a molecular dynamics study,’ *J. Phys. Condens. Matter* **21** (2009) 46124.
- [5] E. Lauga, M. P. Brenner and H. Stone, ‘Microfluidics: The no-slip boundary condition,’ in *Springer Handbook of Experimental Fluid Mechanics*, J. Foss, C. Tropea and A. Yarin, eds.: Springer, Berlin, 2007, pp. 1219-1240.

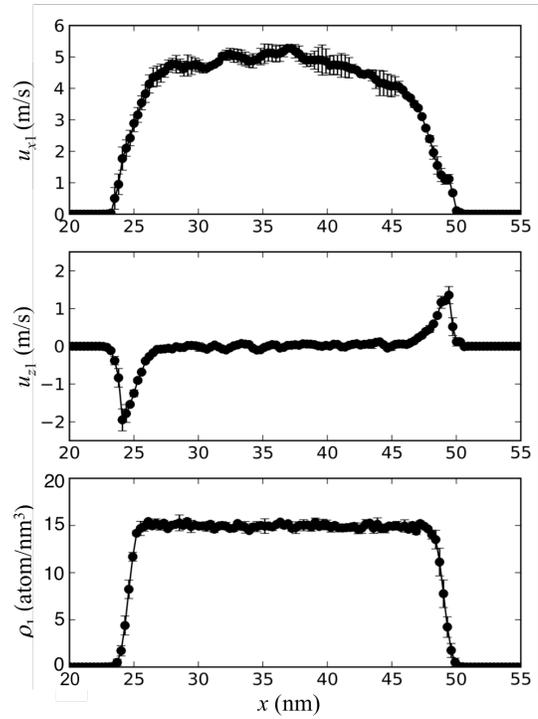


Figure 3: Velocity (u_{x1} and u_{z1}) and density (ρ_1) profiles for the first layer of liquid in contact with the solid with $C_{S-L} = 0.6$ at $U_{plate} = 8$ m/s.