

Boundary slip as a result of a prewetting transition

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Abstract

Some fluids exhibit anomalously low friction when flowing against a certain solid wall. To recover the viscosity of a bulk fluid, slip at the wall is usually postulated. On a macroscopic level, a large slip length can be explained as a formation of a film of gas or phase-separated 'lubricant' with lower viscosity between the fluid and the solid wall. Here we justify such an assumption in terms of a prewetting transition. In our model the thick-film transition together with the viscosity contrast gives rise to large boundary slip. The calculated value of the slip length has a jump at the prewetting transition temperature which depends on the strength of the fluid-surface interaction (contact angle).

What is "slip length"? When is it important?

It is accepted in hydrodynamics that the velocity of the liquid immediately adjacent to a solid is equal to that of the solid [1]. Such an absence of a jump in the velocity of a simple liquid at a surface seems to be a confirmed fact in *macroscopic* experiments. However, it is difficult to obtain the same conclusion using *microscopic* models. It has been noticed that, even in case of simple liquids, the no-slip boundary condition is not justified on a microscopic level.

Instead of imposing a zero tangential component of the liquid velocity at the solid, it is possible to allow for an amount of slippage, described by a slip length b . The slip length for a simple shear flow is the distance behind the interface at which the liquid velocity extrapolates to zero

$$v_s = b(\partial_z v)_{\text{wall}}, \quad (1)$$

where v_s is the tangential velocity at the wall, and the z axis is perpendicular to the surface. The definition of b is explained in Fig. 1.

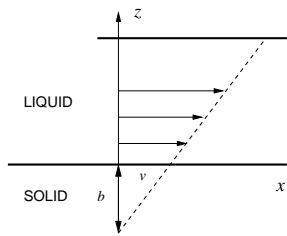


Figure 1 Definition of the slip length b for a simple shear flow.

It is clear that the boundary slip is important only when the length-scale over which the liquid velocity changes approaches the slip length. Therefore, it is not surprising that the slippage effect has not been detected in macroscopic experiments. In microfluidic devices, however, where the liquid is highly confined, the boundary slip is important.

One of the explanations of a large boundary slip relies on the formation of a new phase at the wall. The possible source of the surface layer could be a gas (lubricant) dissolved in the liquid at a metastable concentration. Because of the pressure drop in the slab this new phase can form bubbles nucleating at the liquid/solid interface.

In a sharp interface limit, when the width of the interface is much smaller than the width of the gap and thickness of the boundary layer, we can neglect the structure of the interface and use the condition of zero divergence of the stress tensor.

This allows for a slip length (see Fig. 2)

$$b = \delta \left(\frac{\eta_b}{\eta_s} - 1 \right), \quad (2)$$

where δ is the thickness of the boundary layer.

According to eq. (2) the boundary slip can be observed if the viscosity depends on the composition ($\eta_b \neq \eta_s$) and the less viscous fraction of the liquid wets the walls better than the more viscous one ($\eta_b > \eta_s$). It is also clear that there are two ways to obtain large slip length. First, by having macroscopically thick boundary layer, since the slip length has the same order of magnitude as the thickness of this layer. Second, by providing large values of the viscosity contrast η_b/η_s .

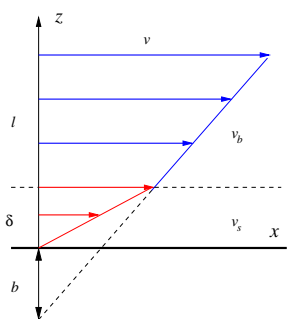


Figure 2 Slip length b for a binary mixture.

A more realistic description should allow for a prewetting transition [2, 3] for the liquid/gas or liquid/lubricant mixture and take into account the structure and the finite width of the interface region. The aim of this paper is to include these effects and relate the slip length to the wettability of the walls, composition of the mixture, and thermodynamic parameters of the system. We show that the prewetting transition can give rise to a large boundary slip of the fluid by generating a thick film of a phase-separated 'lubricant' at the wall which has a lower than the bulk fluid viscosity.

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Phase-field approach

To describe the bulk phase as well as the interface structure, the 'phase-field' models are often used. In this approach the order parameter ϕ (for a binary mixture it is the density difference of the two phases) is introduced. This order parameter varies slowly in the bulk regions and rapidly on length scales of the interfacial width. The free energy functional $\mathcal{F}(\phi)$ determines the *bulk* phase behavior. Since the material is confined in a container in any experiment, phase separation is always affected by surface effects [4, 5]. To include them, appropriate surface terms responsible for the interaction of the liquid with the container walls shall be added to the free energy [6, 2, 7, 8, 3, 9]. In the phase-field approach the grand potential of a binary mixture can be written as [3]

$$\Omega\{\phi\} = \int dV \left[\frac{k}{2} (\nabla\phi)^2 + f(\phi) - \Delta\mu\phi \right] + \Psi_s, \quad (3)$$

where $f(\phi)$ is the Helmholtz free energy density of the mixture, $\phi = \phi_1 - \phi_2$ is the order parameter, $\phi_i = n_i/(n_1 + n_2)$ are the mole fractions of particles of type 1 and 2, $\Delta\mu = \mu_1 - \mu_2$ is the difference of chemical potentials which allows one to tune the bulk value of the order parameter ϕ , and Ψ_s is the surface energy. For a *regular mixture* the free energy $f(\phi)$ is given by [10, 11]

$$f(\phi) = \frac{\chi}{4} (1 - \phi^2) + k_B T \left[\frac{1 + \phi}{2} \ln \frac{1 + \phi}{2} + \frac{1 - \phi}{2} \ln \frac{1 - \phi}{2} \right], \quad (4)$$

where the first term on the right-hand side corresponds to the excess energy of mixing.

To describe the interaction with the walls we used the quadratic approximation for the surface energy [3, 12]

$$\Psi_s = \int \left[-h\phi_s - \frac{1}{2}\gamma\phi_s^2 \right] dS, \quad (5)$$

where ϕ_s is the surface value of the order parameter and the parameters h and γ are referred to as the short-range surface field and the surface enhancement, respectively. The short-range surface field, h , is a measure of the attractiveness (or repulsiveness, if negative) of the surface by the component 1, due to the choice of the order parameter in the form $\phi = \phi_1 - \phi_2$. In real systems it can be of either sign and of any magnitude. The surface coupling enhancement, γ , represents the effect that a molecule close to the substrate has fewer neighbors than a molecule in the bulk; γ is estimated to be small and negative.

In thermal equilibrium the grand potential (3) must be minimal. Variation of this functional yields an Euler-Lagrange equation together with two boundary conditions. In the geometry with two symmetric walls it is convenient to choose the origin of the coordinates at the center of the film. Then the Euler-Lagrange equations and boundary conditions read

$$\frac{\partial^2 \phi}{\partial z^2} + \frac{1}{2}\phi - \frac{1}{2}T \ln \frac{1 + \phi}{1 - \phi} + \Delta\mu = 0, \quad (6)$$

$$\pm \frac{\partial \phi}{\partial z} + h + \gamma\phi \Big|_{z = -L/2, L/2} = 0, \quad (7)$$

where we introduced the dimensionless units by putting $k_B = 1$, $k = 1$, $\chi = 1$.

To obtain the order parameter profiles the boundary-value problem of Eqs. (6,7) was solved using the relaxation method [13].

To select stable solutions, we calculated the grand potential of the mixture, Ω , for both stable and metastable solutions and picked up the solution with the lowest grand potential. This allows the accurate determination of the phase diagram.

To calculate the velocity profiles, we assumed that the viscosity of the system is a linear combination of that of the individual components

$$\eta(z) = \eta_\alpha \phi(z) + \eta_\beta [1 - \phi(z)], \quad (8)$$

where the viscosity contrast between the two components has been chosen as $\eta_\alpha : \eta_\beta = 1 : 3$. The stationary velocity profile then reads

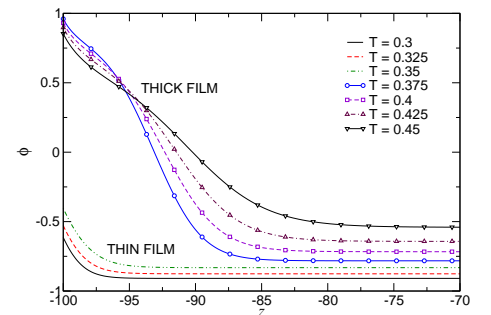
$$v = v_0 c^{-1} \int_{-L/2}^z \frac{dz}{\eta(z)}, \quad (9)$$

where $c = \int_{-L/2}^{L/2} \frac{dz}{\eta(z)}$. The value of the slip length was calculated from eq. (1) where $v(z)$ was obtained by fitting the *bulk* region of the velocity profile (9) with a linear regression.

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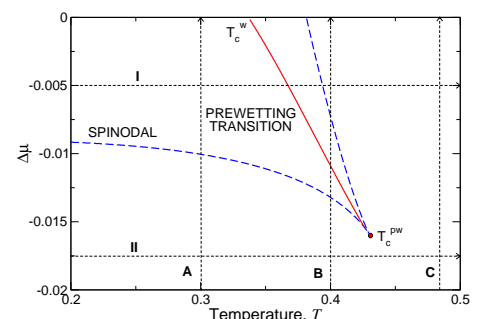
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Order parameter profiles



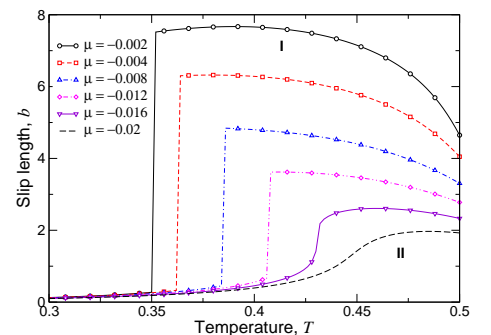
Typical order parameter profiles. Only the part next to the wall is shown. Thickness of the slab $L = 200$, $\Delta\mu = -0.002$, $\gamma = -0.01$, $h = 0.2$. For this chemical potential difference the thin-thick film transition occurs at $T \approx 0.35$.

Prewetting phase diagram

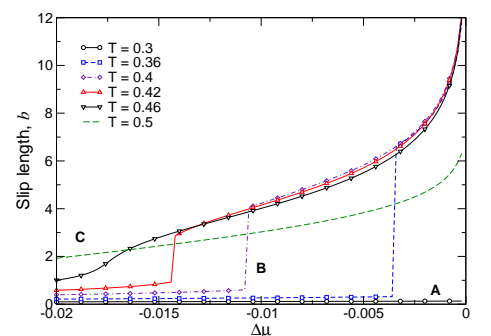


Prewetting phase diagram calculated for $h = 0.2$, $\gamma = -0.01$, $L = 200$. The solid line is the prewetting transition line ending at the prewetting critical point. Metastability limits of thick and thin films (spinodals) are shown with dashed lines. A, B, C, I, and II are thermodynamic paths used in the text.

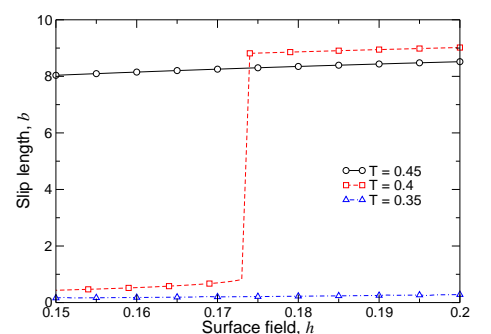
Slip length



Slip length vs. temperature calculated for several values of the chemical potential. $h = 0.2$, $\gamma = -0.01$, $L = 200$.



Slip length vs. chemical potential difference. $h = 0.2$, $\gamma = -0.01$, $L = 200$.



Slip length vs. short-range surface field.

Conclusions

When the prewetting transition occurs in a flow experiment, it may indeed generate a strong slippage. Prewetting provides a mechanism of generating a macroscopically thick film at the wall. If this film has lower than in the bulk viscosity, a strong slippage can be observed above the prewetting transition temperature. The value of the slip length has a jump-like dependence on temperature, concentration of the phase-separated liquid, and surface field (contact angle).