

Boundary slip of binary mixtures

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Abstract

We propose an explanation of possible anomalously low friction of a binary fluid flowing against a solid wall by postulating that the fluid with the lower viscosity forms a film between the other fluid and the wall (wetting transition). We are able to calculate the slip length which can be very large and depends on the value of the contact angle.

Introduction

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 simple liquids at a surface seems to be 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 conditions are not justified on a microscopic level.

Therefore, the conventional condition of continuity of the velocity, or the *no-slip* boundary condition, is not an exact law but a statement of what may be expected to happen, approximately, in normal circumstances. In other words, instead of imposing zero of the 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. The definition of b is explained in Fig. 1.

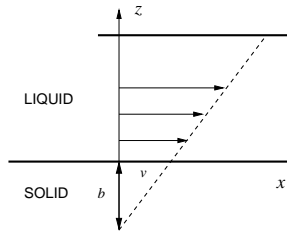


Figure 1 Definition of the slip length b for a simple shear flow.

Here we consider the origin of the slip effect in a strongly confined binary mixture. In this situation, depending on the fraction of the more wettable phase, two equilibrium configurations are possible [9]. When the more wettable phase is a majority phase, a disc-like droplet structure is formed, with non-wettable droplets of size comparable to the wall separation (see Fig. 2.a, partial wetting). When the minority phase is more able to wet the surface, the layered structure is formed (Fig. 2.b, complete wetting). These arguments, together with the assumption that the composition of the mixture is strongly asymmetric and the minority phase is more able to wet the wall justifies the idea that the slippage effect can be a consequence of a formation of a boundary layer with lower than in the bulk viscosity. Our aim will be to relate the slip length to the wettability of the walls, composition of the mixture, and thermodynamic parameters of the system.

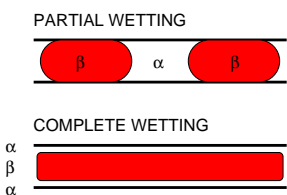


Figure 2 Possible equilibrium structures of partial and complete wetting. The α -phase is more able to wet the solid wall than the β -phase. The partial wetting configuration is energetically favored near the symmetric composition for a deep quench. When the minority phase is more able to wet the surface, droplets of the minority phase move toward the solid wall by diffusional motion, and eventually wet it. The resulting wetting layer is stable for the strongly asymmetric case [8].

Sharp interface limit

First, we consider the situation when the width of the interface is much smaller than the thickness of the cell or thickness of the phase-separated layers. In this case we can neglect the structure of the interface and use the condition of continuity of the stress tensor in the interface region. Then the problem is reduced to the flow of incompressible fluid in a slab geometry with corresponding boundary conditions at the walls and the phase separation boundary

$$\partial_z (\eta(z) \partial_z v) = 0, \quad (1)$$

$$\begin{cases} v_s = 0, & z = 0 \\ v_s = v_b, & \eta_s \partial_z v_s = \eta_b \partial_z v_b, & z = \delta \\ v_b = v_s, & \eta_b \partial_z v_b = \eta_s \partial_z v_s, & z = L - \delta \\ v_b = v & z = L \end{cases} \quad (2)$$

where $v_{b,s}$ denote bulk and surface flow profiles correspondingly. This implies a piece-wise solution

$$v = c_1 z + c_2, \quad (3)$$

where c_1 and c_2 are constants which should be found from the boundary conditions. Finally, for the bulk flow profile we have

$$v_b = \kappa v \left(\frac{\eta_b}{\eta_s} - 1 + \frac{z}{\delta} \right), \quad (4)$$

Then eqn (4) gives the following expression for the slip length

$$b = \delta \left(\frac{\eta_b}{\eta_s} - 1 \right). \quad (5)$$

According to equation (5), to observe boundary slip the viscosity contrast is required. In addition, the layer formed close the walls should be thick enough, since the slip length have the same order of magnitude as the thickness of this layer.

Phase-field approach

The free energy commonly used to study spinodal decomposition can be written as

$$\mathcal{F}_b\{\phi\} = \int d\mathbf{r} \left[\frac{k}{2} (\nabla\phi)^2 + \psi(\phi) - \mu\phi \right], \quad (6)$$

where $\psi(\phi)$ is the free energy of the mixture, $\phi = \phi_\alpha - \phi_\beta$ is the order parameter, $\mu = \mu_\alpha - \mu_\beta$ is the difference of chemical potentials which allows one to tune the average value of the order parameter ϕ , in case of confined systems. The explicit form of the free energy vary depending on the mixture. However, the simple observation that the two phases must coexist implies that there are two minima in the free energy at the respective values of the order parameter of the phase 1 and 2. The most common potentials used are the ϕ^4 potential, equivalent to the potential used to describe Ising ferromagnets [2], and the potential used to describe "regular mixtures" [6, 7].

The ϕ^4 potential allows to obtain analytical solutions for the order parameter profile, but lacks clear interpretation, since possible values of the order parameter ϕ can be outside the $[-1, 1]$ range. The free energy for this model reads

$$\psi_1(\phi) = -\frac{a}{2}\phi^2 + \frac{b}{4}\phi^4. \quad (7)$$

For this model a stationary planar interface is given by

$$\phi = -\phi_b \tanh\left(\frac{z}{2\lambda}\right), \quad (8)$$

where $\lambda = \sqrt{k/2a}$ defines the lengthscale (thickness of the interface) and $\phi_b = \sqrt{a/b}$ is the bulk value of the order parameter. Note, that the chemical potential of the equilibrium interface is zero, since a coexistence of infinitely large domains with positive and negative order parameter requires $\mu = 0$, similar to the condition $H = 0$ for ferromagnets. The surface tension of the interface is

$$\sigma = k \int dz \left(\frac{\partial\phi}{\partial z} \right)^2 = \frac{2}{3} \frac{k\phi_b^2}{\lambda}. \quad (9)$$

For a model describing "regular mixtures" the free energy is given by [6]

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

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

Surface free energy

We assume symmetric walls and use the quadratic approximation for the surface free energy [3, 4]

$$\mathcal{F}_s = \int \left[-\mu_s \phi_s - \frac{1}{2} g \phi_s^2 \right] dS, \quad (10)$$

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

We have assumed that all surface effects are of short range. Therefore f_s depends on the local concentration at the walls only. Because of long range van der Waals forces this is not fully realistic.

Euler-Lagrange equations

In thermal equilibrium the total free energy, $\mathcal{F}_b + \mathcal{F}_s$, must be minimal. Variation of the potential yields an Euler-Lagrange equation together with two boundary conditions at the walls. We will only be interested in one-dimensional solutions, when the order parameter depends only on the z coordinate. Then the resulting profiles are symmetrical around the center of the film, and it is convenient to chose the origin of the coordinates at the symmetry point (see Fig. 3).

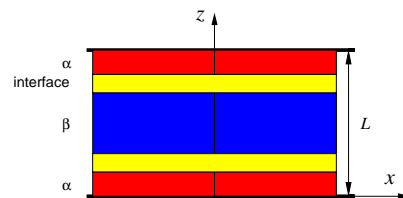


Figure 3 Studied geometry.

The Euler-Lagrange equations and boundary conditions then read

$$k \nabla^2 \phi + a\phi - b\phi^3 + \mu = 0, \quad (11)$$

$$k \frac{\partial\phi}{\partial z} + \mu_s + g\phi_s \Big|_{z=-L/2} = 0, \quad (12)$$

$$\frac{\partial\phi}{\partial z} \Big|_{z=0} = 0. \quad (13)$$

Acknowledgements

We are grateful to R. Evans, K. Kremer, M. Müller for useful discussions. D.A. acknowledges the support of the Alexander von Humboldt Foundation.

Results

Order parameter profiles and phase diagram

To obtain the order parameter profiles the boundary-value problem of Eqs. (11), (12), (13) was solved using the relaxation method [5]. In general, for a fixed set of the parameters, the boundary problem of Eqs. (11), (12), (13) has three different solutions: one is stable, one is metastable, and one is unstable. The *relaxation* method yields only two of them: a *metastable* and a *stable* solution. The unstable solution with the highest free energy has negative response function $\partial\phi/\partial\mu$ and is eliminated by the relaxation method automatically. Typical parameter profiles are shown in Fig. 4.

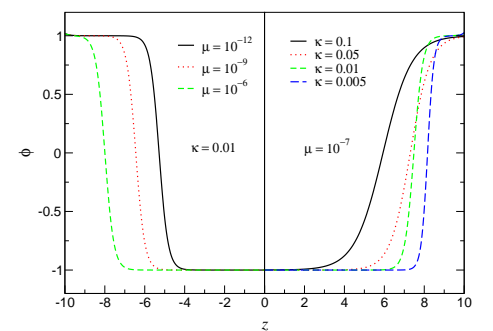


Figure 4 Typical order parameter profiles. Only a half of each profile is shown. Parameters of the potential: $a = b = 0.1$, $L = 20$, $g = -0.0001$, $\mu_s = 0.001$. Left: change of the layer thickness due to the variation of the chemical potential $\mu = 0.01$, $\mu_s = 0.04$. Right: change of the interface thickness λ for a fixed chemical potential $\mu = -10^{-7}$.

To select only stable profiles, we calculated free energy of the mixture, $\mathcal{F}_b + \mathcal{F}_s$ for both solutions and picked up the solution with the lowest free energy. The phase diagram is shown in Fig. 5.

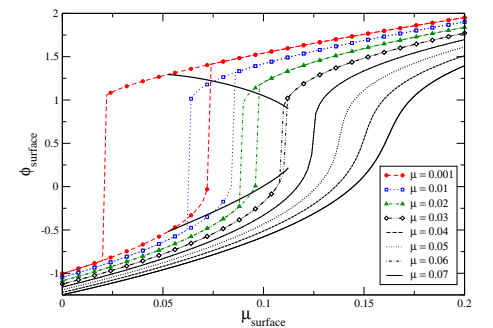


Figure 5 Surface density for different chemical potentials.

Slip length

To calculate velocity profiles, we assumed that the viscosity of the fluid is a function of the order parameter

$$\eta(z) = \eta_1 + \eta_2 \phi. \quad (14)$$

Then the velocity profiles were fitted to obtain slip length (see Fig. 6).

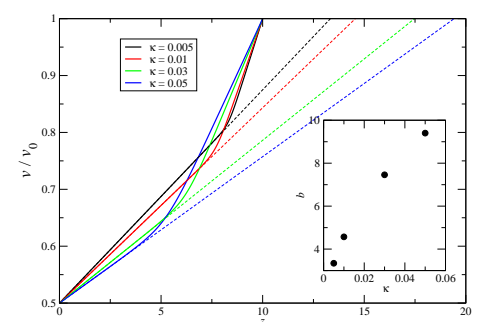


Figure 6 Velocity profiles for a liquid with viscosity contrast 1:3. Inset: corresponding values of the slip length.

Future work

- Slip length as a function of temperature and cell thickness
- Comparison with computer simulation and experiment
- Pressure flow

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