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Review Article

Molecular Hydrodynamics of the Moving Contact Line in Two-Phase Immiscible Flows

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Abstract. The no-slip boundary condition, i.e., zero fluid velocity relative to the solid at the fluid-solid interface, has been very successful in describing many macroscopic flows. A problem of principle arises when the no-slip boundary condition is used to model the hydrodynamics of immiscible-fluid displacement in the vicinity of the moving contact line, where the interface separating two immiscible fluids intersects the solid wall. Decades ago it was already known that the moving contact line is incompatible with the no-slip boundary condition, since the latter would imply infinite dissipation due to a non-integrable singularity in the stress near the contact line. In this paper we first present an introductory review of the problem. We then present a detailed review of our recent results on the contact-line motion in immiscible two-phase flow, from molecular dynamics (MD) simulations to continuum hydrodynamics calculations. Through extensive MD studies and detailed analysis, we have uncovered the slip boundary condition governing the moving contact line, denoted the generalized Navier boundary condition. We have used this discovery to formulate a continuum hydrodynamic model whose predictions are in remarkable quantitative agreement with the MD simulation results down to the molecular scale. These results serve to affirm the validity of the generalized Navier boundary condition, as well as to open up the possibility of continuum hydrodynamic calculations of immiscible flows that are physically meaningful at the molecular level.

Key words: Moving contact line; slip boundary condition; molecular dynamics; continuum hydrodynamics.

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1 Introduction

The no-slip boundary condition, i.e., zero relative tangential velocity between the fluid and solid at the interface, serves as a cornerstone in continuum hydrodynamics [3]. Although fluid slipping is generally detected in molecular dynamics (MD) simulations for microscopically small systems at high flow rate [2, 8, 39, 41], the no-slip boundary condition still works well for macroscopic flows at low flow rate. This is due to the Navier boundary condition which actually accounts for the slip observed in MD simulations [2,8,39,41]. This boundary condition, proposed by Navier in 1823 [30], introduces a slip length l_s and assumes that the amount of slip is proportional to the shear rate in the fluid at the solid surface:

$$\mathbf{v}^{slip} = -l_s \mathbf{n} \cdot \left[(\nabla \mathbf{v}) + (\nabla \mathbf{v})^T \right],$$

where $\mathbf{v}^{slip}$ is the slip velocity at the surface, measured relative to the (moving) wall, $\left[(\nabla \mathbf{v}) + (\nabla \mathbf{v})^T\right]$ is the tensor of the rate of strain, and $\mathbf{n}$ denotes the outward surface normal (directed out of the fluid). According to the Navier boundary condition, the slip length is defined as the distance from the fluid-solid interface to where the linearly extrapolated tangential velocity vanishes (see Fig. 1). Typically, l_s ranges from a few angstroms to a few nanometers [2,8,39,41]. For a flow of characteristic length R and velocity U, the slip velocity is on the order of Ul_s/R. This explains why the Navier boundary condition is practically indistinguishable from the no-slip boundary condition in macroscopic flows where $v^{slip}/U \sim l_s/R \to 0$.

It has been well known that the no-slip boundary condition is not applicable to the moving contact line (MCL) where the fluid-fluid interface intersects the solid wall [11,12,20] (see Fig. 2 for both the static and moving contact lines). The problem may be simply stated as follows. In the two-phase immiscible flow where one fluid displaces another fluid, the contact line appears to "slip" at the solid surface, in direct violation of the no-slip boundary condition. Furthermore, the viscous stress diverges at the contact line if the no-slip boundary condition is applied everywhere along the solid wall. This stress divergence is best illustrated in the reference frame where the fluid-fluid interface is time-independent while the wall moves with velocity U (see Fig. 2b). As the fluid velocity has to change from U at the wall (as required by the no-slip boundary condition) to zero at the fluid-fluid interface (which is static), the viscous stress varies as $\eta U/x$, where η is the viscosity and x is the distance along the wall away from the contact line. Obviously, this stress diverges as $x \to 0$ because the distance over which the fluid velocity changes from U to zero tends to vanish as the contact line is approached. In particular, this stress divergence is non-integrable (the integral of $1/x$ yields $\ln x$), thus implying infinite viscous dissipation.

Over the years there have been numerous models and proposals aiming to resolve the incompatibility of the no-slip boundary condition with the MCL. For example, there have been the kinetic adsorption/desorption model by Blake [4], the fluid slip models by Hocking [19], by Huh and Mason [21], and by Zhou and Sheng [43], and the Cahn-Hilliard-van der Waals models by Seppecher [38], by Jacqmin [24], and by Chen *et al.* [7]. In the kinetic adsorption/desorption model by Blake [4], the role of molecular processes was investigated. A deviation of the dynamic contact angle from the static contact angle was shown to be responsible for the fluid/fluid displacement at the MCL. In the slip model by Hocking [19], the effect of a slip coefficient (slip