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Combining atomistic and continuum simulations of contact-line motion

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In this paper we show that molecular dynamics simulation results for contact-line motion can be accurately reproduced by fully continuum simulations. The problem considered is flow of two immiscible fluids in a two-dimensional channel. Molecular dynamics is used to capture correctly the contact-line dynamics from basic principles. Continuum boundary conditions are extracted from the molecular solution in the vicinity of the contact point where the classical hydrodynamic theory fails. Finite element simulations of the same problem subject to these boundary conditions accurately reproduce the molecular results.
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The moving contact-line problem [1,2] has been one of the few problems that has defied conclusive theoretical analysis over the years [3]. The main reasons for this lie in the multiscale nature of the problem, but also the apparent breakdown of the local hydrodynamic theory in the vicinity of the contact point [2]. Experimental data are unable to characterize fully the molecular processes involved in the contact-line dynamics, because they are limited by resolution to the determination of an apparent contact angle θ_a [2] which is the macroscopically ''perceived'' (coarse grained) angle between the two-fluid interface and the solid wall. Due to the significant curvature of the interface at molecular distances from the wall, the apparent and dynamic contact angles can be appreciably different.

Analytical [4,1] or numerical [5] solutions of the moving contact-line problem have been obtained by taking advantage of the relative insensitivity of the far-field solution to the exact contact-line dynamics. The logarithmic (with distance from the contact line) singularity present in the Navier-Stokes model of the contact-line problem is relieved by relaxing the no-slip boundary condition close to the contact line. Various slip models are introduced, the most popular of which is the Navier condition, albeit for purely historical reasons. The dynamic contact angle θ_d, which enters as a boundary condition in the dynamical equations of motion, requires an additional assumption; it is usually taken to have the same value as the static contact angle, although there is no physical justification for this assumption.

Molecular dynamics (MD) simulations have recently been used to treat the moving-contact, line problem [2,6,7]. Those simulations are, however, limited to very small systems (~5000 molecules) and cannot, by themselves, be used to treat macroscale problems. They can, however, be used as a means for developing physical models of the contact-line behavior for use in macroscale (continuum) descriptions, or for the calibration of already existing molecular-kinetic models [3].

Low cost, accurate numerical solutions can be readily obtained by correctly addressing the two stumbling blocks in the way to simulating the contact-line problem: slip in the vicinity of the contact line, and the value of the dynamic contact angle. The present paper reports advances in this front: MD simulations have been used to extract information at the molecular level which serves as input for finite element simulations. The agreement between the molecular and continuum results indicates that reliable continuum-based approximations, that correctly capture the contact-line dynamics, exist.

In the only previous attempt to develop further an understanding of the physical processes occurring at the contact line [2,7] in terms of appropriate continuum boundary condition choice, the continuum model was not correct: the interface was treated as a rigid flat wall. In the above formulation the interface shape and hence the apparent contact angle were not allowed to vary, the dynamic contact angle

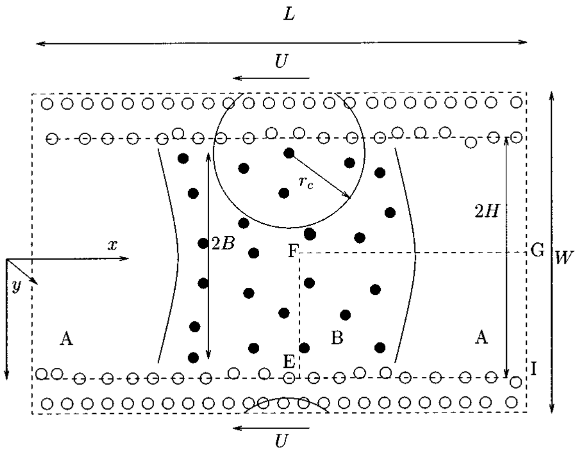

FIG. 1. Problem geometry. Wall molecules are denoted by open circles, and fluid *B* molecules are shown by dark circles (not to correct density for clarity). EFGI is the continuum simulation box and r_c is the interaction cutoff length.

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was fixed at an arbitrary 45°, and the capillary forces were not included; the simulation was, effectively, a Couette flow in a semi-infinite channel which is blocked at one end by a wall at an angle of 45° to the flow. In our study we utilize a full moving geometry finite element simulation of the Stokes equations, with the appropriate variational treatment for the surface tension interaction between the two fluids.

We begin with a MD simulation of the immiscible fluid displacement problem: one fluid displaces a second fluid in a two-dimensional channel of length L and width $2H$ (Fig. 1). The width of the channel is determined by the average location of the first layer of wall molecules (Fig. 1). However, the volume occupied by the fluid is less due to the finite repulsive core of the interaction potential between the walls and the fluid. We will denote the thickness of the ''fluid region'' by $2B$. Our simulations closely resemble those of Thompson and co-workers [2,7] for comparison purposes. The main differences are that Poiseuille instead of Couette velocity profiles are examined, and that the wall molecules are not bound to lattice sites through springs but instead they interact with all the other system molecules through interaction potentials. It is convenient to study this problem in the reference frame of the moving interface: in this reference frame the interface does not move, and the walls of the channel move with speed $-U$ (where U is the speed with which the interface advances in the laboratory frame) in the x direction.

Unless otherwise stated, all quantities will be expressed in reduced units using $\sigma=\sigma_{\mathrm{Ar}}=3.4\,\text{Å}$ for length, $m=m_{\mathrm{Ar}}=40\,\text{amu}$ for mass, $\varepsilon/k_b=\varepsilon_{\mathrm{Ar}}/k_b=119.8\,^{\circ}\text{K}$ for temperature, and $\tau=(m\sigma^2/48\varepsilon)^{1/2}=3.112\times10^{-13}\,\text{s}$ for time. Here σ_{Ar} and $\varepsilon_{\mathrm{Ar}}$ are the parameters of the Lennard-Jones potential for argon [8], m_{Ar} is the mass of the argon atom, and τ is the characteristic time for argon. The interaction potential was truncated at the rather conservative cutoff length $r_c=3\sigma$. The simulation box is a fully periodic MD domain of size $(L\times D\times W)=(57.05\sigma\times5.56\sigma\times15.29\sigma)$ in the x, y, and z directions, respectively.

The molecular model for the two fluids is the same as in Refs. [2,7]; the argon molecules are divided into two subspecies: subspecies A and B. These two subspecies (1280 molecules each) are completely identical because they have the same self-interactions and interactions with the walls of the system; they are, however, immiscible because the potential interaction between them is repulsive. We have taken $\delta=1$ [7] such that at the temperature ($T=1.4$) and density ($\rho=0.81\sigma^{-3}$) of the simulation $\gamma=3.9\pm0.2\varepsilon/\sigma^2$ [7]. Each of the two parallel, isothermal, walls bounding the fluid is modeled by 600 wall molecules arranged in a two-layer fcc structure in the x-y plane. The combined thickness (along the z direction) of the two walls is greater than the interaction potential cutoff ($W-2H>r_c$), so that the fluid molecules do not ''see'' their images across the walls. The mass of the wall molecules is $m_W=2m$; all other parameters are similar to the ones in Ref. [2].

After an equilibration period of 640τ, samples are taken for a further 2720τ. The flowfield is recovered by averaging the instantaneous molecular velocities in rectangular bins spanning the x-z plane. The sizes of the bins are 1.43σ along the x direction and 1.53σ along the z direction. The resulting statistical errors for the velocity are expected to be less than $0.002\sigma/\tau$.

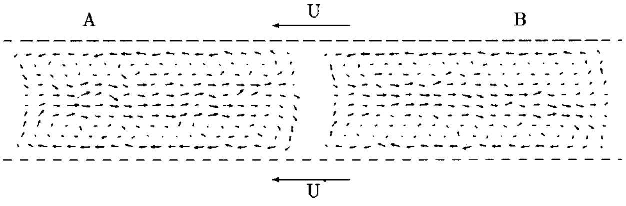

FIG. 2. Flowfield for Poiseuille configuration. Both walls move with velocity $-U=-0.017\sigma/\tau$.

In continuum terms the behavior of the above molecular system is equivalent to two fluids with the same density and viscosity (equal to bulk values for liquid argon); the fluids, however, are immiscible with a surface tension coefficient γ which can be calculated from molecular techniques [7]. Additionally, the two fluids interact with the two bounding walls in exactly the same way, and therefore, the static contact angle (θ_s), by symmetry arguments, has to equal 90°. Also note that the periodic boundary conditions imposed on the MD simulation for reasons of computational simplicity result in two two-fluid interfaces.

The flowfield is generated by forcing the fluid into the Poiseuille parabolic profile far away from the two-fluid interface. Various studies [5,9] have verified that the flowfield relaxes to the above profile at distances greater than $2.5H$. We have thus ensured that the distance between the two two-fluid interfaces is greater than $5H$, such that forcing of the flow would be possible. The Poiseuille profile is a zero-mass-flux profile because the simulation takes place in the reference frame of the moving interface. The velocity profile was imposed through the method developed in Ref. [10]. The exact details of this technique for the contact-line case can be found in Ref. [11]. We have ensured that the method of imposing the flowfield is consistent with previous reports of similar work, by comparing the results of the above method with results obtained using gravity as the driving force for the fluid motion [6]. The results of the two simulation methods for the same U are indistinguishable within the statistical accuracy of the simulations.

The Capillary number ($\mathrm{Ca}=\mu U/\gamma$) is based on the wall velocity (U). We also define x_c as the distance along the wall measured from the contact point. We need to differentiate between U and $U_f=u_x$ ($x_c>2.5H,z=B$), the fluid velocity along the wall at distances from the contact line large enough that slip is negligible; they differ due to the non-negligible ratio (7%) of σ to the channel transverse dimension ($2H$). If the fluid reached all the way to the walls, we would have $u_x(x_c>2.5H,z=H)=U$; that is, the extrapolation of the fluid velocity for $x_c>2.5H$ to $z=H$ indicates negligible slip. The fluid velocity closest to the walls will be denoted $u_f(x_c)=u_x(x_c,z=B)$, and hence $U_f=u_f(x_c>2.5H)$.

Figure 2 displays the flowfield obtained from the simulation of the immiscible fluid displacement problem. The walls move in the x direction with $-U=-0.017\sigma/\tau$, and the Capillary number based on the wall velocity is $\mathrm{Ca}=0.059$. The fairly repulsive potential interaction between the two fluids results in a gap on the order of 1σ between the two fluids.

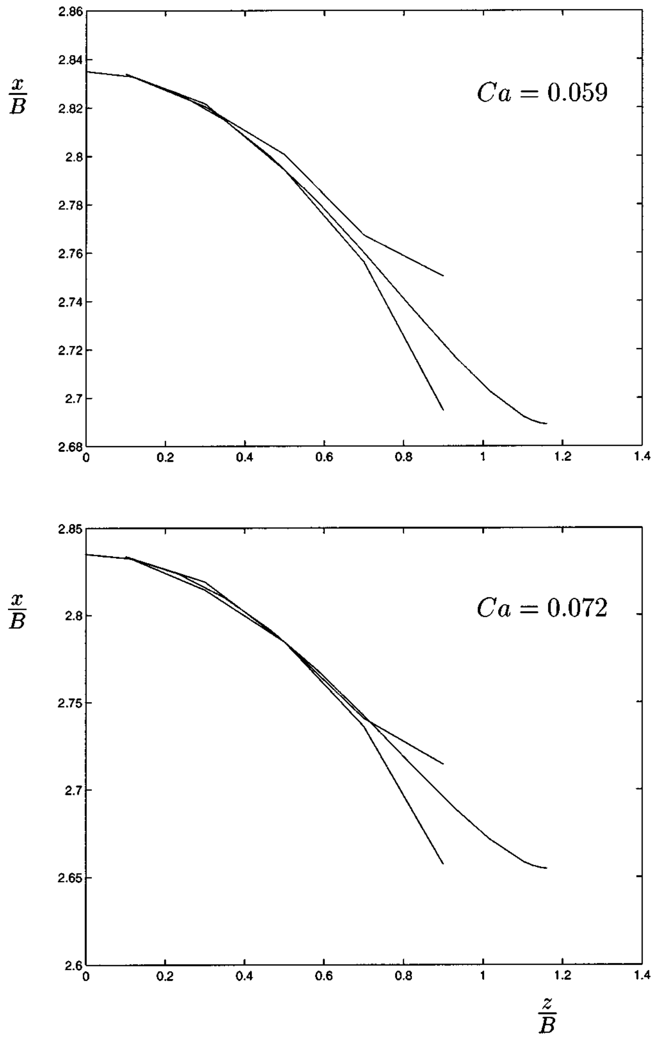

FIG. 3. Comparison between molecular and finite element (line that extends to $z=1.16$) interface shapes with $\theta_d=\theta_s=90°$ assumed in the finite element simulation.

More realistic potentials, or alternatively the simulation of a fluid and its vapor, would result in significantly more diffuse interfaces that would require modeling assumptions for the exact definition of their location. We thus preferred this slightly artificial interaction which we believe does not affect the generality of our conclusions, since the surface tension associated with it can be calculated.

Due to the periodic boundary conditions in the streamwise direction, there are two two-fluid interfaces; in one, fluid A advances into fluid B, and in the other, fluid B advances into fluid A. Because the gap between the two fluids is not constant but varies as a function of z, we defined each two-fluid interface using two lines: each line represents the envelope of the average (in time) extreme excursions of one fluid in the streamwise direction. For example, at the interface where fluid A is advancing into fluid B, one line represents the mean maximum excursion of fluid A and the other line represents the mean minimum excursion of fluid B. In Fig. 3 we retain both lines to indicate the molecular interface shape, but we reduce their gap at the centerline of the channel to zero, to facilitate comparison of both their relative curvatures as well as with the continuum results. Note that the two lines diverge close to the wall indicating that the accomodation of the shearing from the wall requires the gap between the two fluids to increase. This is clearly a molecular phenomenon that cannot be captured by a continuum simulation.

We have used our MD simulations to obtain a model of the slip along the wall close to the contact line. We have found that a simple exponential fit of the form

$$u_f(x_c)=U_f(-1+e^{(-0.47|x_c|)}), \qquad (1)$$

adequately describes the slip profile along the wall [11].

Our finite element simulations use the fully variational formulation developed in Refs. [11,12], and a moving geometry to capture fully the dynamics of the two-fluid interface. The technique uses an isoparametric finite element solver with a structured mesh that is refined to mesh sizes at least one order of magnitude smaller than the slip length close to the contact point for complete resolution of the slip profile. We have used the Crouzeix-Raviart elements [11,12] in order to capture the pressure discontinuity at the two-fluid interface. The simulation was performed in the Stokes limit since the Weber number ($\mathrm{We}=\rho U^2 H/\gamma$) that measures the effect of the inertia forces with respect to the capillary forces was always less than 0.02. Previous work [13,14], both analytical and computational, indicates that for a Weber number of 0.01 the error in neglecting the inertial terms is less than 1%. The error associated with the MD procedure is estimated to be 5–10 %.

The finite element simulations utilize the molecular slip model of Eq. (1) on EI (Fig. 1). Symmetry boundary conditions are applied on FG, and the Poiseuille zero-mass-flux profiles on EF and GI. The dynamic contact angle was taken to be equal to the static (90°); our aim is to examine the validity of this assumption that is usually found in the literature [2]. Note that the continuum simulation extends to $z=1.16B=1H$; in other words, the continuum wall is identified with the first layer of wall molecules (see Fig. 1). On the other hand, the molecular interface shapes can only be defined for $0\leqslant z\leqslant 1B$ because they are limited to the volume occupied by the fluid; furthermore the last data bin is centered on $z=0.9B$. Although it may be argued that the gap between the wall and the fluid belongs to neither, this definition was preferred because of its ability to capture the fluid behavior in the best continuumlike way: the agreement is excellent in the region away from the walls where continuum fluid mechanics is adequate. Close to the walls purely molecular effects are present, but the agreement is still very good.

Despite the fact that the Navier condition

$$\sigma_{xz}(x_c)=-\frac{\mu}{\varepsilon}[U+u_x(x_c,z=H)], \qquad (2)$$

where ε is the slip length, is the most popular of the slip models used, we found that in this case it could not be used with satisfactory results; this indicates that it indeed does not contain the correct physics involved in the vicinity of the contact line. Its inadequacy stems from the fact that it introduces slip by setting a limit on the maximum allowable stress close to the wall. If the slip length is of the order of the channel width ($\varepsilon\sim H$), Eq. (2) implies that significant slip will be present for the whole length of the slipping wall, which is not the case in our simulations.

This study has shown that, excluding purely molecular effects which are observable only at the microscopic level, continuum methods can reproduce moving contact-line dynamics given correct ‘‘boundary conditions’’ (in our case molecularly derived) for the slip profile along the channel wall and the dynamic contact angle. For the set of fluid-wall interactions of our study, we find that the assumption that the dynamic contact angle is approximately equal to the static angle is correct. Although a systematic study of the effect of the interaction parameters on the above results has not yet been completed, we believe that the parameters used in this study are quite general and not pathological in any way: variations in the interaction parameters, for example, are expected to affect the magnitude of the slip length but not the ability of our continuum model to reproduce the molecular results.

Additionally, this work has shown that the molecular input required in a continuum simulation is localized to within one slip length from the contact point, and suggests that hybrid algorithms which utilize MD in the vicinity of the contact-point and continuum techniques for the far-field solution are indeed feasible.

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