A Universal Molecular-Kinetic Scaling Relation for Slip of a Simple Fluid at a Solid Boundary

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Abstract

Using the observation that slip in simple fluids at low and moderate shear rates is a thermally activated process driven by the shear stress in the fluid close to the solid boundary, we develop a molecular-kinetic model for simple fluid slip at solid boundaries. The proposed model, which is in the form of a universal scaling relation that connects slip and shear rate, reduces to the well known Navier-slip condition under low shear conditions, providing a direct connection between molecular parameters and the slip length. Molecular-dynamics simulations are in very good agreement with the predicted dependence of slip on system parameters, including the temperature and fluid-solid interaction strength. Connections between our model and previous work, as well as simulation and experimental results are explored and discussed.
**Introduction** — Fluids under nanoscale confinement can exhibit a number of remarkable transport properties, including anomalous flow rates [1–3], diffusion [4], and heat transfer [5]. Nanofluidic engineering exploits these phenomena for the development of novel materials for clean water [6] and energy [7] among other applications. Modeling the dynamics of nanoconfined fluids requires a detailed understanding of the effect of the fluid-solid interface on transport [8–11].

Slip at the fluid-solid interface is, perhaps, the most ubiquitous of these phenomena and has received considerable attention (see, for example, [11–16]). In the case of dilute gases, the functional form of the slip relation as well as slip coefficients can be calculated via asymptotic expansions of the Boltzmann equation [17, 18]. In dense liquids such analytical treatments are not possible; however, strong empirical evidence exists that the slip relation is of the same form as the dilute case, namely

\[ u_s = \beta \frac{\partial u}{\partial \eta} \bigg|_b \]  

which is referred to as the Navier slip condition, after Navier [19] who first proposed it. In this expression, \( u_s \) is the slip velocity (difference between the fluid velocity at the boundary and the boundary velocity), \( u \) is the flow velocity in the direction parallel to the boundary, and \( \eta \) is the wall normal in the direction pointing into the fluid; the subscript “b” denotes the boundary location.

Most research in the dense-fluid arena has thus focused on investigating the properties of the slip length \( \beta \). Of particular note is the work of Thompson and Troian [11] which showed that molecular-dynamics (MD) data for the slip length could be described well by an expression of the form \( \beta = \beta_0 \left(1 - \frac{\dot{\gamma}}{\dot{\gamma}_c}\right)^{-1/2} \) (where \( \beta_0 \) is the slip length at low shear rates, \( \dot{\gamma} \) denotes the shear rate, and \( \dot{\gamma}_c \) is a constant), suggesting that the slip length obeys some form of critical dynamics. Other notable work [20, 21] has instead established that slip exhibits many of the hallmarks of a thermally activated process, at least for simple fluids in contact with atomically smooth boundaries. In other words, despite some progress, complete and predictive models of fluid slip based on ab-initio (molecular) considerations have yet to be fully developed. The goal of the present work is to present a physically motivated model for slip at the interface between a simple fluid and a molecularly smooth solid that is able to unify existing work and explain our, as well as previous, simulation results.

**Theory** — Thermally activated transport can be modeled using an extension of the Eyring theory of reaction rates [22, 23], which relates the drift velocity of fluid molecules to their hopping over the potential wells generated by nearby layers of molecules. Eyring used such an approach to develop a theory for the viscosities of dense fluids [23], while Blake and Haynes [20] used it to
model contact-line motion as a molecular-kinetic process. More generally, for a fluid in contact with a solid, this drift velocity can be written in the form

$$u_d = \frac{2l_j}{\tau_0} \exp\left(-\frac{V}{k_B T}\right) \sinh\left(\frac{f_d l_j^2}{2k_B T}\right)$$  \hspace{1cm} (2)

where $l_j$ is the characteristic length scale of jumps, $\tau_0$ is a characteristic time scale for jump attempts, $V$ is the potential barrier associated with the fluid-solid interaction potential, $k_B$ is Boltzmann’s constant, and $f_d l_j$ is the force per molecule acting on the fluid molecules [24] causing this drift.

To make further progress, we use the observation that the force on the molecules at the fluid-solid boundary responsible for the drift is the shear stress in the fluid at this location, $\mu (\partial u / \partial \eta)\big|_b$, where $\mu$ denotes the viscosity. The insight that at the fluid-solid boundary, despite the failure of the no-slip condition (and possibly the Navier-Stokes description itself), the force on the boundary (per unit area) is still given by $\mu (\partial u / \partial \eta)\big|_b$ was first articulated by Maxwell [25] on his way to predicting the presence of slip at a gas-solid interface. Since then, asymptotic solutions of the Boltzmann equation [17] have rigorously shown that this assertion yields the correct slip expression, even though Maxwell was not aware of the kinetic boundary layer corrections [17] that need to be added to the velocity field; these corrections require the derivative $(\partial u / \partial \eta)\big|_b$ to be taken only on the Navier-Stokes (bulk-flow) component of the flow field [18].

Writing $f_d l_j = \mu \Sigma_{FL}^{-1} (\partial u / \partial \eta)\big|_b$, where $\Sigma_{FL}$ denotes the areal density of fluid molecules at the fluid-solid interface [26], we obtain

$$u_s = \frac{2l_j}{\tau_0} \exp\left(-\frac{\alpha \epsilon}{k_B T}\right) \sinh\left(\frac{l_j \mu}{2\Sigma_{FL} k_B T} \dot{\gamma}\right)$$  \hspace{1cm} (3)

where $\alpha = V / \epsilon$ is a geometrical factor that depends on the solid structure and fluid-solid interaction potential, and $\epsilon$ is the energy scale for fluid-solid interactions. It immediately follows that in the small-shear-rate limit, $\dot{\gamma} \ll \frac{2\Sigma_{FL} k_B T}{l_j \mu}$, Eqn. (3) linearizes to the Navier-slip condition (1), with

$$\beta = \frac{2l_j}{\tau_0} \exp\left(-\frac{\alpha \epsilon}{k_B T}\right) \frac{l_j \mu}{2\Sigma_{FL} k_B T}.$$

In other words, contrary to the continuum approach where $\beta$ is to be determined by experiments, the molecular-kinetic approach provides a direct connection between the slip length and the governing molecular parameters.

**Simulations** — To assess these ideas, we performed non-equilibrium MD simulations of a Lennard-Jones (LJ) fluid [27] of density $\rho_{ave}$, atomic mass 16 g/mol, length scale $\sigma = 3.15 \text{Å}$, and
energy scale $\varepsilon_f = 0.15 \text{ kcal/mol}$, in a plane-Couette setup of channel width 50 Å, with periodic boundary conditions in all directions. Simulations were performed using the LAMMPS code [28]. Our results and subsequent discussion will be expressed in terms of standard LJ non-dimensional quantities [27], namely, $\sigma$ for length, $\varepsilon_f$ for energy, and $\tau \equiv (m\sigma^2/\varepsilon_f)^{1/2}$ for time.

The fluid is confined between two rigid sheets of graphene at fixed z-coordinate, which move in opposite directions at fixed velocity $u_w$. In each simulation, after an equilibration period of $3 \cdot 10^3$ with a Nosé-Hoover thermostat [29] at a temperature of 5 (unless otherwise specified), fluid velocities are averaged over a total of $6 \cdot 10^3$ to obtain a velocity profile as a function of z-coordinate (to reduce variance in low-signal simulations [30], averaging was extended to $3 \cdot 10^4$ if $u_s \leq 0.01$). In order to verify each of the dependences in Eqn. (3), we measure the slip velocity as we systematically vary the shear rate, the temperature, and the fluid-solid interaction strength. All simulations are performed with $\gamma \tau < 0.07$; it is well known that simple fluids have shear-rate-independent viscosity [11, 31] in this regime. We determine the slip velocity by fitting a line to the fluid velocity profile far away from the solid boundaries (which can induce strong inhomogeneities in the fluid density [8, 26]) and extrapolating to the locations of the walls.

FIG. 1. Scaled slip velocity as a function of scaled shear as measured in MD simulations. The scaling predicted by Eqn. (3) is shown as the dashed green line.

**Validation** — Figure 1 shows that MD simulation results (with fixed choice of solid, temperature, and fluid-solid interaction strength) can be scaled using the form $u_s = u_0 \sinh(\dot{\gamma}/\dot{\gamma}_0)$, as
FIG. 2. Scaled slip velocity as a function of scaled shear for experiments performed via atomic force microscopy (AFM), surface-force apparatus (SFA), and near-field laser velocimetry (NFLV). The scaling predicted by Eqn. (3) is shown as the dashed green line.

suggested by Eqn. (3). Here, \( u_0 \) and \( \dot{\gamma}_0 \) are constants that are determined for each dataset using a non-linear fit to (3). The scaling law prediction is remarkably accurate both for our in-house simulations (maximum deviation 8%) as well as results from the literature [11, 32]. In fact, (3) is also able to describe well the slip velocities measured in a wide range [33–35] of experiments (see Fig. 2) involving aqueous solutions, alkanes, and polymeric fluids.

We now investigate the other major factors affecting slip predicted by Eqn. (3), namely, the temperature and the fluid-solid interaction strength. For the temperature dependence, shown in Fig. 3, we find strong fits \( R^2 \geq 0.96 \) to the form

\[
u_s \propto \exp \left( \frac{c_1}{T} + \frac{c_2}{T(c_3 + c_4/T)} \right)
\]

(4)

where the \( c_1 - c_4 \) are fitting constants; this form was arrived at by noting the leading-order temperature dependence of \( \Sigma_{FL} \) reported in [26], and that the exponentially decaying component of the hyperbolic sine has negligible impact on the fits over this range (affects \( R^2 \) by less than 0.01). The mild dependence of the two plots on the liquid density reflects the fact that \( \Sigma_{FL} = \Sigma_{FL}(\rho_{ave}, T) \) (see [26] for a discussion).

In excellent agreement with Eqn. (3), we also find that the slip velocity decays exponentially
FIG. 3. Slip velocity as a function of temperature for high- and low-density fluids ($u_w = 0.25$), where the change in non-dimensional temperature is effected by changes in the dimensional temperature ($\epsilon$ is held constant at 1). For both densities, the results from MD simulation show strong agreement with the dependence in (4).

with the fluid-solid interaction strength (see Fig. 4). Interestingly, the dependence on the liquid density is negligible over the simulated range of $\epsilon$ (in fact, both data sets are jointly well fitted by the same exponential decay). Physically, as $\epsilon$ increases, the fluid is increasingly “locked” into the potential wells. In the limit of complete locking, we expect to observe a no-slip condition ($u_s \to 0$ as $\epsilon \to \infty$), which is consistent with Fig. 4.

It is worth noting that the present model agrees closely with and sheds further light upon earlier theories and experiments on liquid slip. For example, Eqn. (3) predicts that at fixed temperature, in the small-shear-rate limit, slip is linear in the bulk viscosity. This is in good agreement with the Green-Kubo analysis by Barrat and Bocquet [15, 36], who found the same scaling; this observation also agrees qualitatively with the predictions of the variable-density Frenkel-Kontorova model [14]. The strength of this result is even clearer after careful comparison with experiments that probe the effect of varying both the viscosity and the shear rate [33] across the transition into the non-linear regime. The data of Craig et al., included in Fig. 2, show both a transition to the non-linear regime as the shear rate is increased at fixed viscosity, but also that the controlling factor for this transition is the product of viscosity and shear rate. Analyzing their experimental data in terms of the product of these two factors, one finds quantitative agreement (within 14% error) with
FIG. 4. Slip velocity as a function of fluid-solid interaction strength for high- and low-density fluids ($u_w = 0.125$). For both densities, the results from MD simulation show strong agreement with the exponential decay predicted by Eqn. (3).

the predictions of [3] (see Fig. 2).

Equation (3) also corroborates, and improves upon, earlier work focused on the relationship between slip and wettability. Both MD simulations [11, 37] and experiments [38, 39] have found that slip tends to increase as the fluid becomes less wetting (as the energy scale $\varepsilon$ of fluid-solid interaction decreases). More specifically, MD simulations strongly suggest that $du_s/d\varepsilon < 0$ and $d^2u_s/d\varepsilon^2 > 0$, i.e. slip decays as a convex function of $\varepsilon$, which is predicted by Eqn. (3). In fact, our model can be interpreted as a natural regularization of the inverse-quadratic dependence proposed in Eqn. (16) of [15], $u_s \propto 1/\varepsilon^2$, in the sense that (while both predict convex decay of slip in the wetting limit) Eqn. (3) predicts increasing but bounded slip in the non-wetting limit, clearly a more physically motivated result.

Equation (3) may also be used to provide a connection between slip and fluid layering at the fluid-solid interface [26]; this connection was first studied by Barrat and Bocquet [15]. By recognizing that the areal density $\Sigma_{FL} = \rho_{FL} h_{FL}$, where $h_{FL}$ is the thickness of the first fluid layer and $\rho_{FL}$ is the density of the first fluid layer [26], we find that $du_s/d\rho_{FL} < 0$, in agreement with the theory by Barrat and Bocquet [15]. In fact, linearizing Eqn. (3) in the small-shear-rate limit suggests $u_s \propto 1/\rho_{FL}$, which matches the scaling proposed in [15].

Conclusions and Outlook — We have proposed and validated a general scaling relation describ-
ing slip of simple fluids at smooth solid boundaries. The model builds upon the observation that slip is a thermally activated process, proposed by others [20] and more firmly established by recent careful studies [21]. The proposed model is found to be in excellent agreement with MD simulations as well as experimental data; the latter even extends to moderately complex fluids. Although the power-law relation proposed in [11] also exhibits good agreement with MD simulations, Eqn. (3) has the advantage of being associated with a clear physical model of the slip process and does not suffer from a slip-length divergence at finite shear rates.

In this Letter we have limited our investigation to the case $\mu \neq \mu(\dot{\gamma})$, which for LJ fluids corresponds to $\dot{\gamma} \tau \lesssim 0.07$. It is worth emphasizing that, from a practical perspective, this low to moderate shear-rate regime covers virtually all nanofluidic engineering applications (for channels of nanoscale dimensions and typical fluids, this condition corresponds to flow velocities $\lesssim O(10^3)$ m/s). On the other hand, we note that shear thinning in the large-$\dot{\gamma}$ limit typically results in a behavior of the type $\mu \propto \dot{\gamma}^{-1}$ for simple fluids [40], suggesting that it is possible that Eqn. (3) could be used to describe slip even at high shear rates where $u_s$ is known to exhibit a plateau [32].

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