Liquid Slip in Nanoscale Channels as a Rate Process

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Liquids flowing through nanoscale channels can slip; that is, there is a discontinuity in the mean speed between the walls and the first layer of liquid molecules. The mechanisms of slip are unclear. Using numerical simulation, we find an exponential dependence of slip on solvation pressure which can be explained by treating slip as a rate process. Predictions for the temperature and viscosity dependencies of slip agree with published data. Our findings are consistent with a description of slip as due to the propagation of molecular-size vacancies along the solid-liquid interface.

A classical observation in fluid dynamics is the no-slip condition, which finds that the liquid adjacent to a stationary solid boundary is also, on average, stationary. Though this condition remains trustworthy for large-scale flows of Newtonian fluids, recent reviews of physical experiments [1] as well as computer simulations [2] (and additional references in [3]) document that the no-slip condition is not universal. Liquids can slip relative to solids, and slip is especially prominent in small-scale flows. As recently demonstrated in carbon nanotubes, slip can be so large as to yield nearly frictionless flow [4,5]. Another new understanding is that, whereas the no-slip condition is independent of the composition and crystal structure of the channel walls, for nanoscale flows the amount of slip depends on the material parameters of the walls, which can then be utilized to control the amount of slip and hence the flow rate. The prospect of highly slippery surfaces and new means of flow control have encouraged creative ideas for long-standing technological problems of wastewater remediation, purification of power-plant emissions, and other physical and chemical separations. The smallness of nanochannels gives them size- and chemical-exclusion properties but typically at the price of high resistance to flow. Large slip lengths imply greatly reduced resistance, and hence offer the promise to greatly increase separation efficiency in these energy-intensive processes [6–8].

Many of the recent measurements report the amount of slip in terms of the slip length (defined below), averaging over liquid molecules within a broad expanse of the solid-liquid interface, and so smearing out the details of the molecular processes of slip. Consequently, the mechanism(s) by which liquids slip remains unclear. The work described here is motivated by the desire to understand how molecules slip over the solid surface. Advancing our understanding of the physical processes of slip may provide clues to regulating and/or maximizing slip and so would help achieve the envisioned technological advances described above. In this Letter, we present numerical simulation results to provide evidence that slip is a rate process, whose activation energy depends not only on the potential due to the solid, but also on the work done by the liquid environment. Furthermore, the data provided here supports the view that slip is due to the hopping of liquid molecules into molecular-sized vacancies.

We used nonequilibrium molecular dynamics (MD) simulations in a planar Couette geometry. The simulated liquid was *n*-decane using a united atom model (i.e., each molecule is composed of ten monomers connected by rigid bonds) and allowing for both bond bending and torsion. The liquid was sheared by applying equal and opposite speeds to the top and bottom bounding walls. The walls consisted of atoms forming four planes of a face-centered-cubic lattice, where each atom was tethered to its lattice site by a spring potential. Periodic boundary conditions were applied in the flow direction and transverse to the wall-normal direction. All nonbonded interactions were modeled using Lennard-Jones potentials [9]. The liquid was allowed to heat up due to shear, while the temperature of the walls was maintained at 300 K using a Nosé-Hoover thermostat. Following equilibration (see below), simulations were run with a time step of 10^{-6} ns to a minimum duration of 1 ns.

Two methodological aspects differentiate this study from others previously reported. First, preceding the MD simulations, the liquid was allowed to reach equilibrium using grand canonical Monte Carlo simulation. As the chemical potential, rather than, as usually done, particle number, is fixed, this more realistically models the density that would be present in the channel if it were filled from a reservoir at the given temperature. In particular, for fixed reservoir conditions, the density of the channel will vary as the channel height is changed. Second, rather than vary the shear rate by adjusting the wall speed, simulations were run for a range of channel heights from 1 to 3 nm at 0.1 nm intervals and at a constant wall speed of 50 m/s. See [10] for details of the simulation.

The amount of slip is typically quantified in terms of the slip length $L_s = v_s/\dot{\gamma}$. The mean shear rate $\dot{\gamma}$ is determined by fitting a straight line to the velocity profile in the

central part of the channel. The slip speed v_s is determined as the deficit by which $\dot{\gamma}$ extrapolated to the wall lags behind the wall speed.

As the channel height is varied, there is a well-known oscillatory variation in the solvation pressure P, Fig. 1. The oscillatory dependence arises due to the finite size of the liquid molecules, in which liquid "layers" are added only after discrete changes in channel height [11,12]. The "quantum" size is on the atomic scale, rather than the polymer length scale. We also find that the distance between the wall and the adjacent liquid molecules r [13], as well as the slip length, vary in an oscillatory fashion correlated with the changes in solvation pressure, Fig. 2.

The results shown in Fig. 2 are surprising. The lattice of finite-size solid atoms produces a spatially inhomogeneous force field above the wall. A liquid molecule moving over the wall experiences a fluctuating force best envisioned as a bumpy energy landscape [14]. This molecular-scale potential roughness has been incorporated into a linear-response theory [15] from which it can be shown that slip increases as the amplitude of the variations in potential decrease [16]. This amplitude falls off rapidly with distance above the solid, so it might be expected that if the first liquid layer would be constrained to move in a plane further from the solid, it would experience a smaller variation in potential and so more easily slip. This effect is invoked in describing hydrophobic interfaces, in which the liquid is displaced away from the solid by a "depleted" layer [17] leading to large slip lengths [18,19]. However, the results in Fig. 2 show that rather than increasing as the mean distance r to the first layer of liquid increases, the slip length decreases.

Computer experiments are done largely with liquids at constant density. In such work, once the crystal structure of the solid and the temperature are chosen, the dynamics of slip depends onl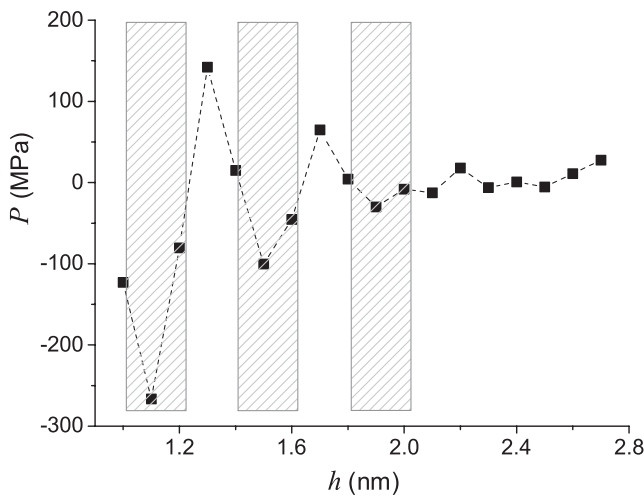y on the wall potential, or the so-called adiabatic potential [20]. In contrast, our numerical experiments were performed at constant chemical potential. To unravel the seemingly contradictory results, we recognize that the energy landscape negotiated by the liquid molecules does not consist solely of the adiabatic potential due to the solid, but also has a component due to the liquid environment. We show that this additional effect can be incorporated if slip is viewed as a rate process.

Consider an equilibrium state G^o and a transition state $G^\ddagger$ where $G = U + PV - TS$ is the Gibbs free energy. The rate from one state to the other is given by [21,22], $k \propto \exp[-\Delta G^\ddagger/(k_B T)]$, where $\Delta G^\ddagger = G^\ddagger - G^o$, k_B is Boltzmann's constant, and T is temperature. If we assume that slip occurs through a rate process, namely $v_s \propto k$, then $v_s(P)/v_s(P_0) = \exp\{-[\Delta G^\ddagger(P) - \Delta G^\ddagger(P_0)]/(k_B T)\}$, where P_0 is a conveniently chosen reference solvation pressure. For a given wall speed, as the channel height is varied, we assume that the adiabatic component U and the entropic term TS are constant, so we are left with

$$\frac{v_s(P)}{v_s(P_0)} = \exp\left[-\frac{(P - P_0)\Delta V^\ddagger}{k_B T}\right], \qquad (1)$$

where $\Delta V^\ddagger$ is the change of volume between the transition state and the equilibrium state. The temperature and solvation pressure are measured for each channel height from our simulation. After fitting a value for $\Delta V^\ddagger$ (see below), the prediction using Eq. (1) can be compared with the slip length data measured from our MD simulation, Fig. 3.

Equation (1) does reasonably well in matching both the amplitude and phase of the oscillatory variations in slip length.
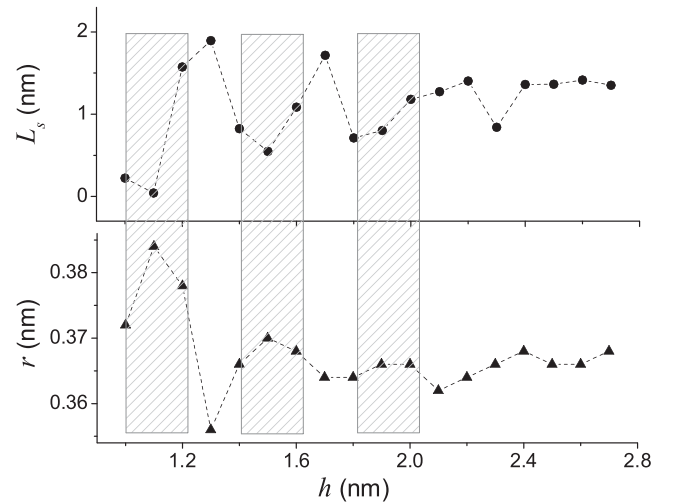

FIG. 1. The solvation pressure P (calculated from our MD simulations using the virial theorem [11]) for channel heights h. Shaded bars are used to highlight periodicity as h is varied.

FIG. 2. The slip length L_s and the distance between the first liquid layer and the wall r for different channel heights h. The distance r is the mean distance between the wall and the first layer of liquid molecules [13]. For different channel heights, as r increases, L_s decreases. The shaded bars are located as in Fig. 1, to highlight the periodicity.
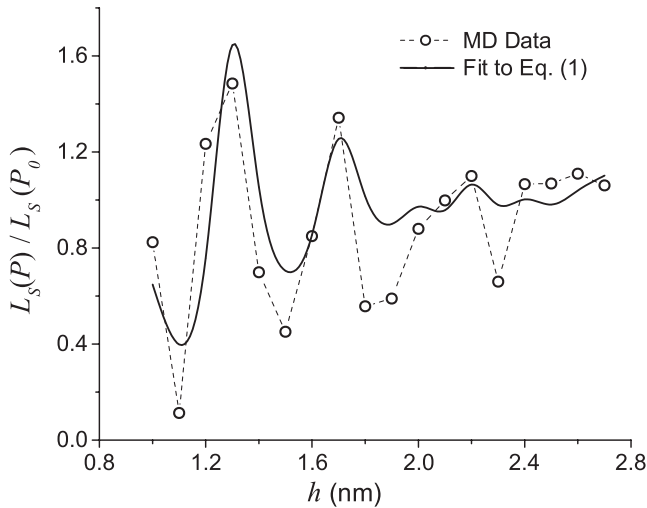
FIG. 3. Comparison of slip length measured from our MD simulation to the value predicted using Eq. (1) and converted to slip length using $L_s = v_s/\dot{\gamma}$. $f = 0.80$ was fit to the data.
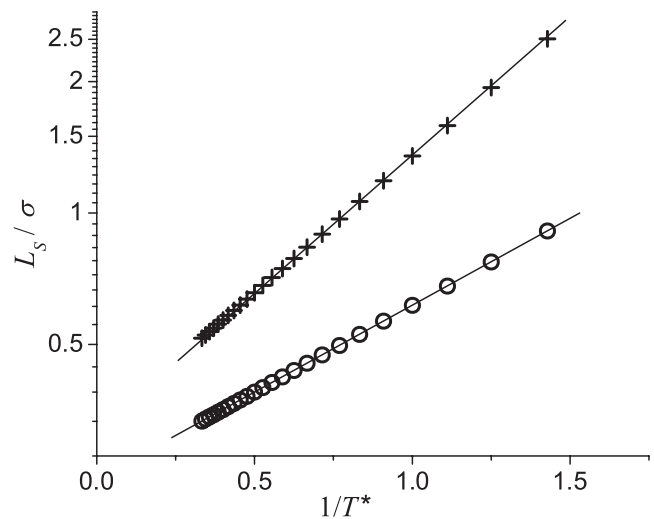

FIG. 4. The MD data of [24] (symbols) for two liquid densities compared with the least-squares fit for a rate process $L_s \propto \exp(B/T^*)$ (solid curves). T^* is the reduced temperature as defined by [24], and we find $B = 1.44$ (0.92) for the upper (lower) curve with $R^2 = 0.993$ (0.996).

A physical scenario can be ascribed to this rate process. With no applied shear, liquid molecules are most stable in the valleys of potential energy located between the solid lattice sites [14]. When shear is applied, liquid molecules move from one equilibrium site (valley) to another, needing to cross a pass of higher energy. The highest energy encountered is assigned $G^{\ddagger}$ and that in the equilibrium state G^o. The downstream hopping of a liquid molecule from one lattice site to another is equivalent to the upstream hopping of a vacancy: as a molecule hops into an unoccupied downstream site, its upstream initial position becomes vacated. The slip speed v_s is given by the mean number of vacancies times their mean rate k of hopping times the length per hop. We assume that the number of vacancies is at most weakly dependent on the pressure and shear rate [23], and so, as assumed above, find that $v_s \propto k$. The change in volume can now be estimated as follows. Following [22], we consider that the volume of the vacancy in the transition state is smaller than that in the equilibrium state, hence the negative sign in $\Delta V^{\ddagger} = -f(4\pi/3) \times (\sigma_{PW}/2)^3$, where $0 \leq f$ and σ_{PW} is the polymer-wall (PW) Lennard-Jones size parameter [9].

Evidence for slip as a rate process is also found in the literature. A recent study presents slip length as a function of temperature [24]. Under the assumption that the shear rate in their Couette flow does not change appreciably as temperature is varied, we find that their data fits the expected exponential form of a rate process, Fig. 4.

The formulation of Kramers [25] is expressly concerned with rate processes in solution. Kramers shows that rate is proportional to the bulk viscosity. Using molecular dynamics simulations, the slip of polymer solutions with a range of viscosities is reported in [26]. This data as well as that from physical experiments using sucrose solutions of dif-

ferent viscosities [27] show the predicted linear dependence on viscosity, Fig. 5.

It may be seen as surprising that polymer slip is due to vacancies. However, the slip length versus shear rate curves for the polymer solutions presented in Fig. 3 of
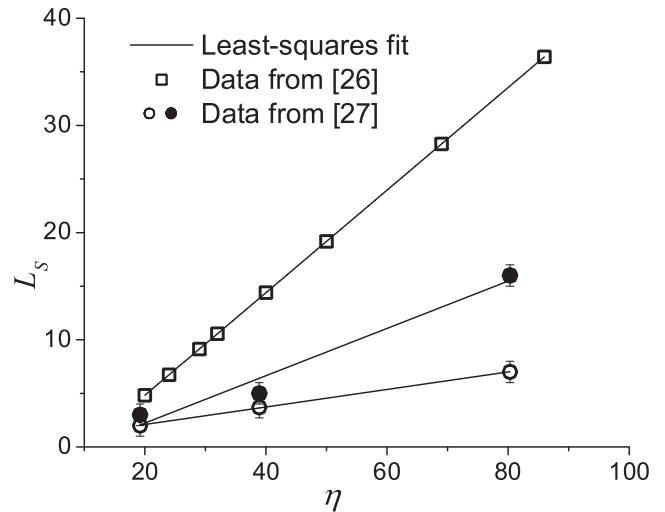

FIG. 5. Slip length L_s shows the predicted linear dependence on viscosity η. For the MD data for polymeric solutions [26] (squares), η and L_S are the nondimensional viscosity $\times 10$ and slip length, respectively, as defined in [26]. The physical experiments of [27] use sucrose solutions at low (7300 nm/s, closed circles) and high (11 900 nm/s, open circles) rates of driving. For their data, the values along the abscissa are in centipoise, the slip length is in nanometers, and error bars are from [27]. The coefficients of determination, from top to bottom, are $R^2 = 0.997, 0.969, 1.000$.

[26] collapse onto a single curve with single monomer data, as shown in Fig. 4 of [26]. The analytic form of this curve is, furthermore, identical to that found for simple liquids [28]. The authors of [26] "support the view that [slip behavior] ... for simple fluid systems [is] more generally applicable to polymeric systems." It seems, then, not unreasonable that the slip mechanism should similarly encompass both simple and polymeric liquids. Less direct evidence is also provided by x-ray reflectivity, in which sheared polymers appear to disentangle and lie down along the substrate [29], as suggested by molecular layering experiments [30,31].

Following LeChatelier's principle, high pressures can accelerate the rate to the transition state. Treating slip as a rate process incorporates the work done by the solvation pressure. This treatment allows us to make sense out of what otherwise seems to be contradictory observations. On the one hand, it is expected that since the potential due to the solid falls off rapidly with distance above the solid, liquid molecules lying further from the solid would slip more easily. At fixed solvation pressure, this is a correct observation. However, channels of varying height filled from the same reservoir will vary in their solvation pressure, leading to flows with different amounts of slip. In comparing these cases, the work done by the liquid can lead to the opposite result of the constant density case, in which proximity to the solid facilitates slip.

In conclusion, a consequence of the discreteness of molecules is that the liquid molecules have energetically preferred configurations. In order for slip to occur, the liquid molecules must leave these stable sites. We have shown that in addition to overcoming the adiabatic solid potential, there is another component to the energy landscape, namely, the work supplied by the solvation pressure of the liquid environment. The effects of solvation pressure may be quantitatively accounted for by treating slip as a rate process. The physical process which accommodates the data is one in which liquid molecules hop downstream along the liquid-solid interface, or, equivalently, vacancies hop upstream.

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