Chemistry and collective fluctuations dictate fluid slip at atomically smooth boron nitride and carbon aqueous interfaces

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Despite essentially identical crystallography and equilibrium structuring of water, nanoscopic channels composed of hexagonal boron nitride and graphite exhibit an order-of-magnitude difference in fluid slip. We investigate this difference using molecular dynamics simulations, demonstrating that its origin is in the distinct chemistries of the two materials. In particular, the presence of polar bonds in hexagonal boron nitride, absent in graphite, leads to Coulombic interactions between the polar water molecules and the wall, and thus to an enhanced effective solid-liquid friction. We demonstrate that this difference is manifested in the long wavelength, collective density fluctuations in the confined water and accounts for the high conductivities of graphitic channels. Based on this observation, we propose a novel scaling relationship for the slip length, anticipated to be valid in the presence of atomically smooth interfaces.

Nanofluidics is the basis for emerging membrane-based desalination and blue energy generation technologies.11,17 The viability of such technologies is limited by the attainable efficiency of flow generation and power conversion.7 The frictional dissipation, characterized by the degree to which fluid slips past a solid-liquid interface, thus enters as a fundamental parameter in need of molecular characterization.2 Two paradigmatic materials in this context are hexagonal boron nitride (HBN) and layered graphite (GR), which, while crystallographically identical, exhibit nearly an order-of-magnitude difference in slip, independent of macroscopic geometry.9,15 In order to rationalize this difference, we have employed molecular dynamics simulations of channels composed of HBN and GR, finding that the origin of the difference is in the distinct chemistries of the two materials. The polar bonds of HBN, relative to GR, afford stronger adhesive interactions with the water. This difference is manifested in long wavelength, collective density fluctuations, offering a novel perspective on slip for atomically smooth interfaces.13,15,18

The no-slip condition, ubiquitous in macroscopic fluid mechanics,11,19,20 posits that the tangential velocity in the vicinity of a wall exactly vanishes. However, in nanofluidics, one must allow for the finite slip of fluid past a solid boundary, reflecting a deviation of nanoscale fluid transport from classical macroscopic hydrodynamic theory due to the predominance of interfacial effects. This finite slip is characterized by the slip length, which relates the average fluid velocity \( \langle q(z) \rangle \) in the vicinity of a wall to the velocity gradient normal to the wall \( \partial_z \langle q(z) \rangle \) via the partial-slip boundary condition

\[
\langle q \rangle_{\text{wall}} = b \partial_z \langle q(z) \rangle_{\text{wall}},
\]

where \( \langle q \rangle_{\text{wall}} \) is the fluid velocity at the wall. The slip length is a coefficient of proportionality with the unit of length and may be interpreted geometrically as the distance beyond the wall at which the fluid velocity extrapolates to zero.19

Understanding the molecular origins of slip in nanometric confinement has captured consistent attention over the last few decades,11,15,21–23 yet there is no satisfactory theoretical prediction for the slip length from fundamental microscopic parameters of the fluid and material. In addition to this fundamental theoretical challenge, the presence of large slip lengths in certain materials, for example graphene and carbon nanotubes,14,15,21 presents the promise of designing high efficiency membranes for desalination and blue energy generation. A greater degree of fluid slip translates to diminished frictional energy dissipation and hence to greatly enhanced flow generation or power conversion for a given input of electrical or osmotic energy.21,25

In order to study slip in HBN and GR, we use molecular dynamics simulations. Figure 1A shows snapshots of our systems. We consider HBN and GR channels of \( L \approx 6 \) nm in width, defined as the distance between the center-of-mass location of the interior wall layers. The channels are bounded by two fixed walls of area \( A \approx 3 \times 3 \) nm², each composed of three atomic layers. The channel widths are adjusted such that the bulk density \( \bar{\rho} \approx 1 \) g/cm³. Periodic boundary conditions are imposed in all three directions, with a vacuum layer of roughly 1.5 nm beyond the walls to ensure that the periodic images of the channel do not interact with one another. The channels are filled with \( N = 2000 \) TIP4P/2005 water molecules, with rigid geometries imposed by the SHAKE algorithm.24 Lennard-Jones parameters for the \( sp^2 \) carbon in GR are taken from the Amber96 force field25 and those for boron and nitrogen in the HBN simulations are taken from Ref. 29. The Lennard-Jones parameters for carbon, boron, and nitrogen are very similar,
reflected the similar corrugations in the short-range repulsive wall interactions. Lennard-Jones parameters for heteroatomic interactions are determined using Lorentz-Berthelot mixing rules. Additionally, owing to the polar bond present in HBN, the boron and nitrogen atoms have formal charges of ±1.05e, respectively, which interact Coulombically with the polar water molecules.

Figure 1B shows a single layer of HBN and GR. Experimentally, the interatomic spacings in the two lattices are found to be essentially identical (1.42 Å in GR and 1.45 Å in HBN) and are set to 1.42 Å in the simulations. The interlayer spacings are set to 3.39 Å for GR and 3.33 Å for HBN. The HBN and GR layers are arranged according to their equilibrium stackings—AA’ stacking for HBN and AB (Bernal) stacking for GR—and are kept rigid. All simulations were performed in LAMMPS in the NVE ensemble after equilibrating for approximately 5 ns with a Langevin thermostat at T = 298 K. The total length of all production runs used is approximately 60 ns.

The identical crystal structures lead to strikingly similar equilibrium water structures. We illustrate this with the density profiles, shown in Fig. 1C. Despite their hydrophobicity, both materials induce a strong layering of water in the vicinity of the solid-liquid interface, with a contact density that is slightly higher for HBN than GR. The orientational structure of water is also similar in the two materials, with both showing a preferential orientation of water in the vicinity of the interface such that the O-H bonds are orientated parallel to the wall. These aspects of the equilibrium water structure are also observed in ab initio simulations, indicating that these force field parameters accurately parameterize the solid-liquid interaction.

To characterize the flow properties in these channels, we compute their permeability to water. We examine two related quantities indicating the ease with which fluid flow is generated by the application of a pressure gradient ∂z,p: the mobility M(z) and hydraulic conductivity L. The mobility encodes the shape of the average velocity profile ⟨q(z)⟩ induced by an applied pressure gradient, while the hydraulic conductivity indicates the magnitude of the average velocity ⟨Q⟩ = (1/L) ∫ dz ⟨q(z,t)⟩.

The definitions and corresponding Green-Kubo relations for these two quantities are given by

\[ M(z) = \beta V \int_0^{t_N} dt \langle q(z,t)Q(0) \rangle, \quad (2) \]

and

\[ L = \frac{\langle Q \rangle}{-\partial_z p} = \frac{1}{L} \int_0^L dz M(z) = \beta V \int_0^{t_N} dt C_{QQ}(t). \quad (3) \]

In these expressions, \( \beta \equiv 1/k_B T \) is the inverse of the temperature times Boltzmann’s constant, \( V = AL \) is the channel volume, \( q(z,t) = (L/N) \sum_{i=1}^N v_{i,z}(t) \delta[z - z_i(t)] \) is the instantaneous molecular velocity at z and \( Q(t) = (1/L) \int_0^L dz q(z,t) \) its average over the channel height. The function \( C_{QQ}(t) \equiv \langle Q(t)Q(0) \rangle \) appearing in Eq. 3 is the average velocity autocorrelation, and the times \( t_N \) appearing in Eqs. 2 and 3 are taken long enough that the integrated correlation functions have plateaued, but not so long that they have begun to decay to zero. This decay at long times is a reflection of the finite lateral extent of these systems, and evaluating the Green-Kubo relation at the plateau time is the standard procedure in such scenarios.

Care must be taken in determining the fluid volume in which to apply the above Green-Kubo relations. In particular, since we will ultimately connect these results to a hydrodynamic model of the fluid flow, we must properly partition the fluid volume into three subregions: a hydrodynamic region where the bulk viscosity applies, and two contact regions in the vicinity of the walls. This partitioning amounts to determining the location of the hydrodynamic interface, the plane at which the boundary condition given in Eq. 1 is applied. An analysis by Chen et al. has shown that the hydrodynamic interface coincides closely with the second density peak for fluids in the vicinity of either hydrophobic or hydrophilic walls, and we take this as our operational definition of
The profiles of mobility $M(z)$ obtained from Eq. [2] with fits to the Poiseuille solution (Eq. [4]) indicated by the dashed red lines. B) The average molecular velocity autocorrelations $C_{QQ}(t)$, and their integrals $\tau_P(t)$ (inset). The shaded vertical regions in panel A indicate the contact regions. The error bars indicated here and in Fig. [B] are obtained by binning our data into equal-length trajectories and calculating the standard error of the means obtained for each bin.

The most straightforward comparison of our results to those obtained in experiments and other computational studies is in terms of the slip length. We can extract estimates of the slip length from our data by connecting our results to a hydrodynamic model of the pressure-induced flow – namely, the Poiseuille solution to the Navier-Stokes equations subject to the partial-slip boundary condition in Eq. [1] for the flow field generated by a uniform pressure gradient. The Poiseuille solution gives for the mobility and conductivity

$$M_P(z) = \frac{L_{hyd}^2}{2\eta} \left[ \left( \frac{b}{L_{hyd}} \right)^2 + \frac{z}{L_{hyd}} - \left( \frac{z}{L_{hyd}} \right)^2 \right],$$

and

$$L_P = \frac{L_{hyd}^2}{12\eta} \left( 1 + 6 \frac{b}{L_{hyd}} \right).$$

As we have an independent method of estimating $L_{hyd}$ from the density profile and $\eta$ for the water model is known, the only unknown in both of these equations is the slip length $b$. We obtain two estimates of the slip from the measured value of the conductivity and a fit of the mobility profile to Eq. [4]. We give the results of these estimates in Table I. The values obtained from the two estimation methods are consistent for both materials, giving a slip length of $\sim 6$ nm in HBN and $\sim 40$ nm in GR. These values are consistent with what is known theoretically and experimentally of slip lengths in smooth hydrophobic materials and they agree quantitatively with previous experimental and computational results. They also illustrate the approximately order-of-magnitude difference in slip characteristics between the two materials.

When fitting our mobility profiles to Eq. [4] we assume the known bulk viscosity of TIP4P/2005 water at 298 K, $\eta = 0.855$ mPas$^{-1}$. This assumption is appropriate because we have partitioned the channel volume into regions dominated by the wall interaction and by the viscous fluid-fluid interaction, and the bulk viscosity holds in the latter region. The validity of this approach is

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confirmed by our results for the mobility in HBN (Fig. 2A), where we see that the curvature of our fit determined by the bulk viscosity (Eq. 3) matches the curvature measured in our simulations within the statistical uncertainty. The profile obtained in GR appears to be essentially flat because the high degree of slip in GR leads to large equilibrium fluctuations in the velocity, making it difficult to converge the mobility profile.

We may measure the slip directly, rather than extracting it as a fit parameter when comparing our data to a hydrodynamic model of the flow. To do so, we must consider the interfacial friction coefficient \( \lambda \), defined by \( \langle F_{\text{wall}} \rangle /A = -\lambda \langle q \rangle \rvert_{\text{wall}} \), where \( F_{\text{wall}} \) is the total force of the wall on the fluid. This parameter may be related to the slip length through a force balance \(-\langle F_{\text{wall}} \rangle /A = \eta \partial_z \langle q(z) \rangle \rvert_{\text{wall}}\). This gives \( \lambda = \eta / b \), relating the slip length to the ratio of interfacial and bulk dissipation. The Green-Kubo relationship for \( \lambda \) is \[ \lambda = \frac{\beta}{A} \int_0^{t_N} dt \ C_{FF}(t) = \frac{\beta}{A} \langle F_{\text{wall}}^2 \rangle \tau_F(t_N), \]

where we have introduced the wall-force autocorrelation \( C_{FF}(t) \equiv \langle F_{\text{wall}}(t) F_{\text{wall}}(0) \rangle \). As in the Green-Kubo relations for the mobility and conductivity, it is necessary to evaluate the integral of \( C_{FF}(t) \) at a plateau time \( t_N \). We observe from Eq. 6 that the interfacial friction coefficient may be decomposed into a static contribution \( \langle F_{\text{wall}} \rangle \) and a dynamic contribution \( \tau_F(t_N) \equiv \int dt \ C_{FF}(t) / C_{FF}(0) \).

We show the results for \( C_{FF}(t) \) for water on HBN and GR in Fig. 2C. The estimates of the slip length are obtained from the wall-force variances and the normalized integrated autocorrelations \( \tau_F(t_N) \), and our results are reported in Table 1. The estimates are consistent with those obtained from the conductivity and mobility, demonstrating that we are accurately quantifying the fundamental difference in frictional characteristics between these materials. We note that, when normalized by the static contribution, the two curves very nearly collapse, indicating that the primary contribution to the difference in frictions is due to the wall-force variance, consistent with previous results. There is also an apparent secondary dynamic contribution, revealed by the distinct relaxations of the autocorrelation curves for times less than roughly 1 ps. This dynamic contribution is more clearly illustrated by examining the normalized integrated autocorrelations. The dynamic contribution is then obtained as the difference in the plateau values of these two curves, corresponding to a relaxation time \( \tau_F \) that is about 20% smaller in HBN than in GR, compensating some of the static difference.

A useful framework for understanding the static and dynamic contributions to the interfacial friction coefficient is obtained by treating the force on the fluid from the fixed walls as an external potential. In this case, we may rewrite \( C_{FF}(t) \) in terms of the instantaneous molecular density \( \rho(r,t) = \sum_i \delta(|r-r_i(t)|) \) as

\[ C_{FF}(t) = \int d\mathbf{r} \int d\mathbf{r}' \partial_i \mathbf{U}(\mathbf{r}) \partial_j \mathbf{U}(\mathbf{r}') \langle \rho(\mathbf{r},t) \rho(\mathbf{r}',0) \rangle, \]

where \( \mathbf{U} \) is the interaction potential between a single water molecule and the wall. Decomposing this expression into Fourier modes in the plane parallel to the interface and inserting it into Eq. 6 we obtain

\[ \lambda = \beta \int_0^{t_N} dt \sum_k k^2 \int dz \left[ \hat{U}_k(z) \right]^2 \rho(z) S_{2d}(k,z), \]

neglecting correlations among different \( z \) values. This allows us to rewrite the Fourier decomposition of the density correlation as \( \rho(k,z) S_{2d}(k,z) = \sum_{i,j=1}^N \exp(-ik|x_i(t) - x_j(0)|) \delta(z - z_i(t)) \) where \( S_{2d}(k,z) \) is a two-dimensional time-dependent structure factor conditioned on a value of \( z \). We have assumed that the Fourier amplitude of the potential \( \hat{U}_k(z) \) exists and exploited the isotropy of the contact-layer, observed previously and confirmed in our own simulations, to identify a dependence in each on the magnitude of \( k \) parallel to the wall.

We see from Eq. 8 that the dynamic contribution is determined by the relaxation of fluctuations in the density field while the static contribution is determined by a convolution of the solid-liquid interaction and the fluid structure. As noted, however, the water structures observed in HBN and GR are essentially identical. The minor quantitative difference in the short wavelength structuring is not enough to contribute to the dramatic difference in slips, as the perpendicular and in-plane density distributions near the wall are nearly identical for the two materials. We probe the solid-liquid interactions by examining the reversible work necessary to dewet water from the interface. This calculation is done by placing a thin probe volume \( v \) of large cross-sectional area in the vicinity of the interface and calculating the probability \( P_\text{rev}(N) \) of observing \( N \) particles in this volume. The reversible work \( w_\text{rev} \) associated with fully evacuating the probe volume is then obtained as \( \beta w_\text{rev} = -\ln P_\text{rev}(N = 0) \) in the limit of large \( v \), this reversible work would report directly on the solid-liquid interactions.

We consider a probe volume \( v = 2 \times 2 \times 0.3 \text{ nm}^3 \) placed at the solid-liquid interfaces in the two channels and compute \( P_\text{rev}(N) \) via the indirect umbrella sampling and weighted histogram analysis methods. The results

<table>
<thead>
<tr>
<th>slip length (nm)</th>
<th>HBN</th>
<th>GR</th>
</tr>
</thead>
<tbody>
<tr>
<td>conductivity</td>
<td>5.71 ± 0.18</td>
<td>39.9 ± 2.13</td>
</tr>
<tr>
<td>mobility</td>
<td>5.95 ± 0.16</td>
<td>41.7 ± 2.13</td>
</tr>
<tr>
<td>force</td>
<td>6.81 ± 0.10</td>
<td>40.4 ± 0.54</td>
</tr>
</tbody>
</table>

TABLE I. Slip length estimated in HBN and GR using each of the three methods discussed in the text. Error bars indicate the standard error of the mean.
are indicated in Fig. 3A. We observe that density fluctuations in both materials exhibit Gaussian statistics in the vicinity of the mean particle number. Such fluctuations are characteristic of the bulk fluid. Far from the mean, the distributions exhibit fat tails, deviating far from bulk statistics and from each other. The greater likelihood of observing spontaneous evacuation of the probe volume in the vicinity of the interface than in the bulk is an indication that both materials are indeed hydrophobic.

Such fat-tailed behavior is known to be a reflection of long wavelength density fluctuations and it is thus only in these long wavelengths, interface-forming fluctuations, and not in the short wavelength corrugation of the fluid structure, where the difference between the materials is manifested. Quantitatively, we find the change in the free energy needed to dewet the HBN interface exceeds that of GR by approximately 5 k_B T/\text{nm}^2, indicating that the solid-liquid interaction in HBN is much stronger than that in GR. Because HBN is composed of distinct atoms with unequal electronegativities, the polar B-N bond results in formal charges on the boron and nitrogen centers. Such an effect is absent in GR, as it is composed only of identical carbon atoms. The large solid-liquid interaction in HBN reflects the corresponding Coulombic interactions between the wall and surrounding water.

To understand the compensating dynamic contribution to the friction, we consider the wavelength dependence of the density fluctuations in the contact layer. We probe the dynamics of the density field in the vicinity of the wall by examining the integral relaxation time of the intermediate scattering function calculated in the contact layer. We define

\[ \tau_{\rho}(k) = \frac{1}{S_2(k, \mathbf{0}|z_c)} \int_0^\infty dt S_2(k, t|z_c) \]  

and use a definition of the contact-layer as including \( z_c \) values up to the second peak in the density distribution in Fig. 3A. From Eq. 8 we see that the integral wall-force relaxation time \( \tau_F \) scales with the relaxation time of the density field \( \tau_{\rho} \), a fact that has been confirmed in \textit{ab initio} simulations.

We show the integral relaxation time \( \tau_{\rho} \) for the two interfaces in Fig. 3B. At intermediate wavenumbers, \( 1.5 \lesssim k \lesssim 5 \text{ Å}^{-1} \), the relaxation time in HBN exceeds that in GR, with the two becoming essentially equal as \( k \to \infty \). This behavior reflects the fact that at very short wavelengths comparable to or smaller than the mean intermolecular separation, fluctuations of the density field involve only single particles undergoing self-diffusion. The dominance of self-diffusion at short wavelengths is confirmed by the dashed red line in Fig. 3B, which indicates the diffusive relaxation time \( \tau_{\rho}^{-1} = D_s k^2 \) associated with the self-diffusion coefficient \( D_s = 0.21 \text{ Å}^2 \text{ps}^{-1} \) of TIP4P/2005 water at 298 K. We find that at very small wavenumbers, the relaxation time in HBN is smaller than that in GR, consistent with its stiffer static density response and the ordering observed in the wall-force autocorrelations. The ratio of the relaxation time in HBN to that in GR does not approach the value of 0.8 inferred from Fig. 3C except for \( k \lesssim 0.5 \text{ Å}^{-1} \), or wavelengths on the order of 1 nm or larger. In accordance with our observations of the origins of the static difference, we find from this dynamic analysis that the difference in frictional properties between the materials is reflected in long wavelength collective fluctuations of the density field. This dominance of long wavelength fluctuations is a reflection of the fact that we are considering atomically smooth walls exhibiting negligible corrugation in the potential of mean force. We may contrast this observed dominance of collective fluctuations with the common assumption that short wavelength fluctuations dominate the slip response.

If we suppose that the dominant response is not directed at the wall but a few atomic diameters away,
consistent with the assumption that the solid-liquid interaction is dominated by the long-range attractive portion.\textsuperscript{19} Then all wavevectors consistent with our periodic boundary conditions are permitted in Eq. \ref{eq:8}. From our observations, we assume that the $k \to 2\pi/\sqrt{A} \approx 0$ response dominates. If we write $S_{2d}(k, \ell | z) = S_{2d}(k, 0 | z) \exp\left[-tk^2D_c(k)\right]$ and take the small $k$ limit, we find a scaling relation for $b$,

$$b^{-1} \sim \beta \rho \frac{U^2}{\eta D_c(0^+)}.$$  \hspace{1cm} (10)$$

where $U$ is the laterally averaged attractive solid-liquid interaction with characteristic lengthscale $\ell$, and we have taken $S_{2d}(k, 0 | z) \to 1$, and $\rho(z) \approx \tilde{\rho}$. This scaling relation highlights that the frictional response is dictated primarily by the strength of the laterally averaged interaction, with a secondary dynamic contribution from the long-wavelength collective dynamics of the density field. This further suggests the possibility that atomically smooth walls like the ones considered here represent a regime distinct from that previously considered in the literature.\textsuperscript{19} In which the frictional response is dominated by the magnitude of the solid-liquid interaction, rather than the corrugation of the wall.

Our results indicate the crucial importance that material chemistry is expected to exert on flow properties in nanoconfinement, and they suggest that relatively moderate changes in chemistry can have profound implications for the slip length even within crystallographically similar materials. In this study, we have investigated atomically smooth channels and illustrated the particular role of Coulombic interactions in increasing the scale of interactions between water and HBN over that of water and GR and the importance of collective density fluctuations. These findings suggest that surface charge adsorption on chemically activated crystallals should likewise have a dramatic effect on fluid slip. This influence is in addition to the key role surface charge plays in the generation of boundary-driven flow and conversion of osmotic energy into useful electrical or mechanical work.\textsuperscript{21,27}

This is particularly relevant in light of recent results highlighting the difference in charge adsorption mechanisms in GR and HBN and the large surface charges obtainable in activated HBN.\textsuperscript{14,15} Accordingly, investigating the interplay between defects, surface charge, and fluid slip is a key next step in the design of ideal materials for bio energy generation.

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