Supporting information for:
Friction of water on graphene and hexagonal
boron nitride from ab initio methods: very
different slippage despite very similar interface
structures

Gabriele Tocci,†,‡,¶ Laurent Joly,§ and Angelos Michaelides*†,‡

Thomas Young Centre, London Centre for Nanotechnology, London WC1E 6BT, United
Kingdom, Department of Chemistry, University College London, London WC1H 0AJ,
United Kingdom, and Institut Lumière Matière, UMR5306 Université Lyon 1-CNRS,
Université de Lyon 69622 Villeurbanne, France

E-mail: angelos.michaelides@ucl.ac.uk

1 Summary

Further details on the computational set up are reported here, along with further infor-
mation on the structure of the liquid film on the two sheets and on the validation results
on the friction coefficient computed using different system sizes, time scales, and a different
ensemble. Also reported are the details of the monomer adsorption energy on the sheets obtained using different codes.

2 Electronic structure Set-up

All the results in the main manuscript have been obtained with the CP2K/QUICKSTEP package (v.2.5). For the calculations of the monomer adsorption we have also performed a careful comparison between the results obtained with CP2K\textsuperscript{S1} (v2.5) and VASP (v5.3.3).\textsuperscript{S2,S3} Because van der Waals dispersion forces are essential to describe the interactions between water and layered materials such as graphene and BN, we use the optB88-vdW exchange-correlation functional.\textsuperscript{S4,S5} CP2K/QUICKSTEP employs a mixed Gaussian and plane-wave basis set and norm-conserving pseudopotentials. We used short range molecularly optimized double-$\zeta$ valence polarized (m-DZVP) Gaussian basis functions, which exhibit a small basis set superposition error, comparable to traditional quadruple-$\zeta$ valence doubly polarized (QZV2P) basis functions.\textsuperscript{S6} Also a 460 Ry cut-off was used for the plane wave expansion. VASP is a plane wave code that uses the projector augmented wave method to treat the core electrons. We used a cut-off of 600 eV for the plane wave expansion and six valence electrons for oxygen ($2s^22p^4$), four for carbon ($2s^22p^2$), three for boron ($2s^22p^1$) and five for nitrogen ($2s^22p^3$). The graphene and BN sheets are modelled using orthorhombic cells with C–C and B–N bond-lengths of 1.422 and 1.449 Å, respectively (see Ref.\textsuperscript{S7}). Calculations in VASP have been performed on $3 \times 5$ orthorhombic cells with a k-point density of $2 \times 2 \times 1$ centered at the $\Gamma$ point. In VASP, using a k-point density of $4 \times 4 \times 1$ changes the adsorption energy of a water monomer on graphene of only 0.3 meV/H\textsubscript{2}O. In CP2K we reproduced the same k-point density by using $6 \times 10$ orthorhombic cells. A vacuum region of 20 Å and a dipole correction along the direction of the vacuum wad used in VASP. In CP2K the sheets have been decoupled from their periodic images along the vacuum according to the method by Martyna and Tuckerman.\textsuperscript{S8}
3 Monomer interaction energies and energy decomposition

In order to provide deeper insights into the corrugation of the free energy profiles shown in Fig. 3 in the main text, we performed a series of extensive calculations of monomer interaction energies. Using the same AIMD set-up described in Section 4, we performed two additional 10-ps long AIMD simulations at 100 K for a water monomer on the (6 \times 10) orthorhombic graphene and BN sheets. To provide an estimate of the potential felt by the water monomer on the sheets, we extracted 4000 configurations to compute the interaction energies of the water monomer with the sheets (the equivalent of 4 ps of the overall trajectories). The interaction energy for a water monomer $E_{\text{int}}$ is defined as $E_{\text{int}} = E_{\text{H}_2\text{O/sheet}} - E_{\text{sheet}} - E_{\text{H}_2\text{O}}$, where $E_{\text{H}_2\text{O/sheet}}$ is the total energy of the composite system and $E_{\text{sheet}}$ and $E_{\text{H}_2\text{O}}$ are the total energies of the isolated sheet and water monomer in gas phase in their non relaxed configuration, respectively. We thus computed a probability distribution of water interaction energies as illustrated in Fig. S1. It can be seen that the total probability distribution (the black bar charts) for BN (Fig. S1(b)) is significantly broader than for graphene (Fig. S1(a)). Specifically, the root mean square of the distribution for BN is twice as large as that for graphene (i.e. 10 meV against 5 meV). This overall demonstrates that indeed the corrugation of the free energy in Fig. 3 in the main text is larger on BN than on graphene because the potential felt by a water monomer on BN is also more corrugated than on graphene.

We further decomposed the two distributions into components associated to a given adsorption site: if the distance (projected onto the plane of the sheet) between the oxygen of the water and the nearest atom in the sheet is within half of the average bond-length of the atoms in the sheets, then water is defined to be in the top-site, otherwise it is in the center of the hexagon. It can be seen that the distributions for BN are more skewed than those for graphene. In particular, there is a high probability for the top-N site between $-138 \text{ eV/H}_2\text{O}$ and $-125 \text{ meV/H}_2\text{O}$, illustrating that water on the top-N site is relatively...
unfavorable. On the other hand, water is more favorable in the center of the BN hexagon and on the top-B site, showing pronounced tails with interaction energies between −170 and −152 meV/H₂O. Also, on graphene the tail of the distribution at relatively unfavorable interaction energies for water on the top site is more pronounced than that for water in the center of the hexagon, while at more favorable interaction energies (about −155 meV/H₂O) the tail of the distribution for water in the center of the hexagon is more pronounced. However, the tails of the distributions for graphene are less pronounced than those for BN. Overall, Fig. S1 presents a quantitative picture for the corrugation of the potential felt by a water monomer on the graphene and BN sheets, that is consistent with Fig. 3 in the main text.

Now we show that our results on the interaction energies relating to the corrugation of water on the two sheets are reliable although they span a range of a few tens of meV. Table S1 compares the values of the interaction energies of a water monomer on graphene and on BN for different adsorption sites, using different codes (i.e. VASP and CP2K) and different dispersion corrected functionals (i.e. PBE-D2 and optB88-vdW). The results obtained using VASP and the optB88-vdW functional (\(E_{int}^{\text{VASP}}\)) are for the structures shown in Fig. 3 in the main text, while the interaction energies obtained with CP2K and using the PBE-D2 or optB88-vdW functional result from an average over ten different configuration per site. The ten different configurations have been obtained by rotating and translating the water monomer with respect to the reference sites in Fig. 3 in the main text, with shifts in the height and in the directions parallel to the sheets of ±0.1 Å, and full rotations, e.g. including structures with the dipole parallel and perpendicular to the sheets. The absolute value of the interaction energy for a given site may show a dependence on the functional used and the level of accuracy may not be in the meV range. However, Table S1 shows that the differences in interaction energies are accurate at the meV scale because they are essentially the same between the two sites for a given functional (within 3 meV). This argument is supported by results for water on graphene using the random phase approximation (RPA). We observe
Figure S1: Probability distribution of interaction energies for a water monomer on (a) graphene and (b) BN (non normalized). The overall probability distribution is decomposed into the sum of the distributions for water on the top-site and in the center of the hexagon (see text). The figure shows that the probability distribution of water on BN is broader and it indicates that BN is more corrugated. It also demonstrates that the more favorable sites are for water in the center of the hexagons (for BN also on the top-B site), while the top site is less favorable (for BN the top-N site). This provides a picture of the corrugation of water on the two sheets that is consistent with that of Fig. 3 in the main text.

A difference of about +12 meV between water in the center of the hexagon and on the top-C site, in agreement with the RPA result, which shows a 16 meV difference between the two.

The interaction energy of water in the center of graphene for the configuration shown in Fig. 3(c) in the main text as obtained with VASP is of $-147 \text{ meV/H}_2\text{O}$, and it is 11 meV more stable than water on the top-C site (see Fig. 3(d) in the main text). In the case of BN, however, the VASP interaction energy for water in the center of the hexagon (Fig. 3(e) in the main text) is $-180 \text{ meV}$, and it is 36 meV more stable than water on the top-N site.
(Fig. 3(f) in the main text), indicating a larger corrugation than graphene. A similar trend is observed if the interaction energies are obtained from an average over the 10 different water configurations per site, and using a different functional or code. Indeed, water in the center of the hexagon of graphene is always about 10 meV more stable than water on the top-C site, while on BN a larger difference in the stability between the two sites is observed, around 35 meV. This illustrates that the potential of the water monomer on BN is more corrugated regardless of the functional or code used.

Finally, we demonstrate that the BN sheet is more corrugated than graphene is not only due to electrostatic interactions between water and the B and N atoms, but because electronic structure effects including electronic exchange and kinetic energy. In order to determine the energetic contributions that give rise to such an increase in the corrugation of the BN sheet, we perform the following decomposition of the mean interaction energy $E_{\text{int}}$:

$$E_{\text{int}} = E_{\text{vdW}}^{\text{int}} + E_{\text{int}}^{\text{lc}} + E_{\text{int}}^{X+Es+T}, \quad (1)$$

where $E_{\text{vdW}}^{\text{int}}$, $E_{\text{int}}^{\text{lc}}$, $E_{\text{int}}^{X+Es+T}$ are the average contributions to the mean interaction energy coming from the van der Waals dispersion, the local correlation, and the sum of exchange ($X$), electrostatic ($Es$) and electron kinetic energy ($T$) terms, respectively. Specifically, $E_{\text{int}}^{X+Es+T}$ is expressed as the sum of the contributions from the exchange energy, the Hartree energy, the ion-ion term, and of the single-particle Hamiltonian term which includes the electron-ion and the single-particle kinetic energy (see Ref. $S1$). The results of this decomposition are shown in Table S1. While the van der Waals and local correlation terms for the different configurations of water on graphene and BN differ of 3 meV at most, there is a significant change in the $E_{\text{int}}^{X+Es+T}$ term, which contributes to the corrugation of water on the two sheets and is more pronounced for BN. We can estimate a value of the corrugation due to exchange, electrostatic and electron kinetic energy terms by taking the difference between the less stable state and the more stable state: for graphene, we obtain $E_{\text{int}}^{X+Es+T}(\text{GRA}_{\text{top-C}}) - E_{\text{int}}^{X+Es+T}(\text{GRA}_{\text{center}})=$
+11 meV/H$_2$O; while for BN $E_{int}^{X+E_s+T}$(BN$_{top-N}$)$-E_{int}^{X+E_s+T}$(BN$_{center}$)= 25 meV/H$_2$O.

Table S1: Interaction energies (in meV) for a water monomer on graphene and on boron nitride on two main sites, i.e. in the center of the hexagon (GRA$_{center}$ and BN$_{center}$) and on top of a carbon atom for graphene (GRA$_{top-C}$), and on top of a nitrogen atom for boron nitride (BN$_{top-N}$). The interaction energies obtained with VASP ($E_{int}^{V\text{ASP}}$) correspond to the snapshots illustrated in Fig. 3 in the main text, while the other values of the interaction energies have been obtained from CP2K and result from an average over ten different configurations of water for each site. Apart from the interaction energy obtained using the PBE-D2 functional ($E_{int}^{PBE-D2}$), the other values have been obtained using the optB88-vdW functional. Also shown is the decomposition into different contributions of the mean interaction energy $E_{int}$ for the ten different configurations per site. It can be seen that the relative differences between the interaction energies on each site are the same regardless of the functional or code used, although the differences in the interaction energies themselves are on the meV scale. The term $E_{vdW}$ is the contribution coming from the average van der Waals dispersion, the term $E_{lc}$ indicates the contribution from the local correlation and $E_{int}^{X+E_s+T}$ indicates the sum of exchange, electrostatic interactions and electronic kinetic energy. The larger difference between the two interaction energies on BN compared to graphene arises from the $E_{int}^{X+E_s+T}$ (25 meV for BN against 11 meV for graphene), and not from the van der Waals and the local correlation which differ by only 3 meV at most.

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<th>$E_{int}^{V\text{ASP}}$</th>
<th>$E_{int}^{PBE-D2}$</th>
<th>$E_{int}^{vdW}$</th>
<th>$E_{int}^{lc}$</th>
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4 Ab initio and force field MD simulations set-up

AIMD simulations of liquid water films on graphene and hexagonal BN have been performed with the CP2K/QUICKSTEP package using the electronic structure set-up described earlier. To assess the validity of our results on the friction coefficient we performed a series of AIMD and force field molecular dynamics (FFMD) simulations with varying system sizes, time scales and ensembles, both in the canonical and in the microcanonical ensemble. Specifically, the results reported in the main text are for 40 ps long AIMD simulations in the canonical ensemble on systems composed of 6 $\times$ 10 graphene and BN orthorhombic cells and 400 water molecules. Here, we compare the results in the main text with those obtained from AIMD simulations on 3 $\times$ 5 BN and graphene cells containing 100 water molecules performed
both in the canonical and in the microcanonical ensemble, and which are 70 and > 40 ps long, respectively. Using the $3 \times 5$ cells we also performed a test using H masses instead of D. The initial conditions for the microcanonical runs were obtained from the equilibrated positions and velocities of the canonical runs. Further, we computed the friction coefficient obtained from FFMD trajectories which are up to 10 ns long.

We also use FFMD to obtain equilibrated configurations for the AIMD runs. FFMD have been performed using the GROMACS 4.5 package where the electrostatic interactions have been accounted for using the particle mesh Ewald method. The rigid SPC/E model for water and a Lennard-Jones potential to describe the water-surface interactions have been employed according to the works of Werder et al. on a water droplet on graphene and Won et al. for the study of water transport in BN nanotubes. The Lennard-Jones parameters from Refs. are $\sigma_{OO} = 3.166 \ \text{Å}$, $\varepsilon_{OO} = 0.6502 \ \text{kJ/mol}$, $\sigma_{CC} = 3.214 \ \text{Å}$, $\varepsilon_{CC} = 0.2363 \ \text{kJ/mol}$, $\sigma_{BB} = 3.453 \ \text{Å}$, $\varepsilon_{BB} = 0.3971 \ \text{kJ/mol}$, $\sigma_{NN} = 3.365 \ \text{Å}$, $\varepsilon_{NN} = 0.606 \ \text{kJ/mol}$, where the water-surface interaction parameters are obtained using the standard mixing rules.

We use 1 fs timestep and deuterium masses for the hydrogens in the AIMD to enable stable simulations to be performed with a 1 fs timestep. This results in an energy drift of at most 0.011 meV/(ps×atom). The first 5 ps of AIMD are used for equilibration and the remaining time for analysis. Equilibration has been performed for the initial 4 ps using the Bussi-Donadio-Parrinello thermostat, after which we switched to the Nosé-Hoover chain thermostat. To partially compensate for the lower diffusivity of water with the optB88-vdW functional a target temperature of 330 K was used. In order to test the effect of replacing H with D on the friction coefficient, we performed a further 20 ps long AIMD in the NVT ensemble using hydrogen masses instead of deuterium with a 0.5 fs timestep.
5 Orientation of water molecules with respect to the sheets

In the main text we showed how the density and number of H-bonds profiles in the liquid film are very similar for water on graphene and on hexagonal BN. We also computed the probability distributions of the angles between the water dipole moment and the vertical direction from the sheets to detect any possible difference in the orientation of the water molecules between the two systems. The results of this analysis are shown in Fig. S2. Again

![Figure S2: Probability distribution of the angle $\varphi$ between the water dipole and the vertical direction as a function of the height from the sheet for (a) graphene (GRA) and (b) BN. The colour scale goes from red (large probability) to blue (low probability). The same criterion as in Fig. 1 in the main text is used for the distance of a water molecule from the sheet. The snapshots in (a) illustrate three different possible orientations of a water molecule.](image)

the similarity between the two system, as evinced from Fig. S2(a) and (b) is striking. Water in the contact layer orients with its dipole predominantly tangential to the sheets, as previously reported for water on hydrophobic surfaces or for water confined between graphene sheets or for water droplets on graphene and BN.\textsuperscript{S19–S21} Indeed, the majority of molecules in the contact layer orient their dipoles around $60^\circ$ and $100^\circ$, while there is a scarce probability of molecules pointing up opposite to the sheets ($\varphi = 0^\circ$) or down, towards them ($\varphi = 180^\circ$).
In the depletion region, at a height of about 5 Å, there is instead a uniform distribution of the dipoles. Affected by the pronounced reorientation of waters in the first layer, molecules in the second layer orient with their dipoles between 30° and 150°. After the second layer the distribution of angles becomes more homogeneous. Yet, because of the presence of the two interfaces (i.e. with the sheets and the vacuum) within just a 2 nm thick film, a region where the distribution is completely homogeneous and bulk-like is not observed.

6 Validation results on the friction coefficient

As a validation of the results on the friction illustrated in the main text we show in Fig. S3 the values of $\lambda_{GK}(t)$ (defined in the main text) obtained from the different simulation setup and models of the two interfaces as described before. Specifically, the various curves in Fig. S3(a) extracted from the AIMD trajectories demonstrate that the value of the friction coefficient on BN is always about 3 times larger than that on graphene. Indeed, the results are not affected significantly by performing the AIMD in the microcanonical (NVE) ensemble instead of the canonical (NVT) ensemble, nor are they affected by using a smaller $3 \times 5$ orthorhombic cell as opposed to the $6 \times 10$ cell.

To test the effect of a heavier water mass on the friction coefficient, we also performed AIMD simulations using light water (H$_2$O) instead of heavy water (D$_2$O) for the interface with graphene. The friction computed using H$_2$O (labelled GRASMALL(H$_2$O) in Fig. S3), is not significantly different from that extracted using D$_2$O (GRASMALL(D$_2$O) in Fig. S3) and within the error bars indicated in the main text, i.e. $\lambda = (9.6 \pm 2.0) \times 10^4 \text{N s m}^{-3}$. Although we could not detect any significant effect in the friction due to the change in the light atom mass, we cannot rule out the presence of isotopic effects in the friction resulting from a change from light water to heavy water. For instance, it is known that the viscosity of light liquid water is different from that of heavy water likely because of nuclear quantum effects. However, inclusion of nuclear quantum effects in our simulations to investigate
Figure S3: Validation results on the friction coefficient $\lambda_{GK}$ of liquid water on graphene (GRA) and on BN computed from AIMD (a), and FFMD trajectories (b). In (a) GRA$_{BIG}$ (D$_2$O) and BN$_{BIG}$ (D$_2$O) refer to $\lambda_{GK}$ extracted from the simulations performed on the large 6 × 10 cells and using D masses instead of H (as reported in Fig. 2 in the main text). GRA$_{SMALL}$ (D$_2$O) and BN$_{SMALL}$ (D$_2$O) refer to simulations performed in the smaller 3 × 5 cells and GRA$_{NVE}$ (D$_2$O) and BN$_{NVE}$ (D$_2$O) refer to simulations on this same cell performed in the NVE ensemble. GRA$_{SMALL}$ (H$_2$O) refers to simulations performed in the NVT ensemble on the 3 × 5 cell and using H masses instead of D. In (b) we show using FFMD that the friction coefficient is already converged if computed over a trajectory of 50 ps (GRA$^{FFMD@50\text{ps}}$) as opposed to the full 10 ns (GRA$^{FFMD}$). (b) also shows that the increase in the friction between graphene and BN is sensitive to the particular force-field used and that even by assigning point charges to B and N atoms extracted from AIMD, the friction on BN is only less than twice as that of GRA (see BN$^{FFMD\text{charges}}$).

Isotopic effects on the friction coefficients at the two interfaces is beyond the scope of this work and left for further studies.

Further, using the FFMD results we demonstrate in Fig. S3(b) that the friction coefficient is already converged if is computed over a trajectory of 50 ps as opposed to the full 10 ns. It is also clear from Fig. S3(b) that FFMD cannot reproduce the 3-fold increase in the friction coefficient on BN and that the particular value of the friction is sensitive to the details
of the force field used. Indeed, an increase in the friction coefficient on BN is observed if electrostatic interactions between the water and the BN sheet are included by assigning point charges to the B and N atoms of $-0.35e$ and $+0.35e$, respectively, as obtained from a Mulliken analysis (see the curve labelled BN$^{\text{FFMD charges}}$). However, the increase in the friction coefficient from graphene to BN with point charges on the B and N atoms is less than 2-fold, suggesting again that the 3-fold increase on BN resulting from the analysis of the AIMD trajectories arises from specific electronic structure effects.

7 Validation results on the free energy profile

We demonstrate that the friction coefficient from FFMD is very similar between graphene and BN because the corrugation in the free energy is also very similar as opposed to the results obtained from AIMD. Indeed, Fig. S4 illustrates that the level of corrugation is very similar between the two systems ($\approx 10$ meV), which is why the friction coefficient obtained from FFMD is also very similar. In Fig. S5 we compare the free energy profiles extracted from half the AIMD trajectory used for analysis with those extracted from the full trajectory. The different profiles display the same features and level of corrugation, indicating that the values of the free energy corrugation extracted from Fig. 3 and discussed in the main text are converged.

References


Figure S4: Free energy profile of water within the contact layer of the liquid projected onto the graphene (a) and BN (b) primitive unit cells obtained from force field molecular dynamics (FFMD). The free energy profiles are smoother than those obtained from *ab initio* molecular dynamics (see Fig. 3 in the main text) and most importantly they present a very similar corrugation. The friction between liquid water and graphene and between liquid water and BN obtained from FFMD is very similar because of the very similar free energy corrugation of the two contact layers. The energy scale is kept the same as Fig. 3 in the main text.


(S6) VandeVondele, J.; Hutter, J. Gaussian basis sets for accurate calculations on molecular
Figure S5: Comparison between the free energy profiles of water within the contact layer of the liquid projected onto the graphene and BN primitive unit cells extracted from half the AIMD trajectory used for analysis ((a) and (b)) and from full AIMD trajectory ((c) and (d)). The free energy profiles obtained over half the trajectory display the same corrugation and features as those extracted over the full trajectory.


(S10) Grimme, S. Semiempirical GGA-type density functional constructed with a long-range


