

Atmospheric water and graphite lubrication: Insights into surface intercalation and nanoscale confined spaces

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The role of environmental water in graphite lubrication has generated conflicting observations and considerable confusion. Early hypotheses suggested water intercalation between graphene layers, but x-ray diffraction studies revealed no change in interlayer spacing with changing humidity. Conversely, recent Raman spectroscopy studies indicated water intercalation in bilayer graphene under humid conditions. To reconcile these discrepancies, we report density functional theory (DFT) and molecular dynamics (MD) simulations coupled with a reinterpretation of experimental measurements. While DFT calculations reveal softer surface interlayers suggesting potential for water intercalation, MD simulations indicate that such intercalation requires a significant reduction in van der Waals interactions, beyond what surface-induced softening can achieve. Alternatively, if water does intercalate, it likely occurs between the surface layers where graphene interactions are over 80% weaker than in bulk graphite, making such intercalation plausible. Instead, we demonstrate that water forms clusters on the graphene surface, maintaining a stable two-atomic layer structure across a wide temperature range, emphasizing the importance of surface water adsorption. We therefore propose that the lubrication effect is primarily related to the graphene-water interface rather than the graphene-graphene interface. While we do not completely rule out water intercalation, our findings suggest that graphene-water interactions dominate lubrication. These results resolve previous discrepancies by highlighting the role of surface or near-surface water layers over bulk intercalation, underscoring the significance of molecular interactions at the graphene-water interface in confined nanoscale spaces.

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I. INTRODUCTION

The dependence of graphite lubrication on atmospheric water presents a fundamental puzzle in condensed matter physics: while graphite requires environmental moisture to function as an effective lubricant [1], the underlying mechanism remains controversial. This question gained practical importance when the U.S. Air Force discovered a high wear rate for graphitic brushes in electrical dynamos and motors on airplanes at high altitudes. In the 1970s, NASA found that graphite ceased to act as a lubricant in space environments [2]. Environmental water was considered critical in graphite lubrication, as it was believed that water intercalates between graphene layers, enabling sliding [3]. However, in 2000, Watanabe *et al.* reported that the interlayer distance between graphene layers in graphite does not change, based

on x-ray diffraction (XRD) measurements under various humidity levels, suggesting that water does not significantly intercalate between graphene layers [4]. However, more recent Raman spectroscopy results on randomly stacked bilayer graphene under varying humidity conditions show the splitting of the layer breathing mode (LBM) of the bilayer above 22% relative humidity (RH), while above 55% relative humidity, the LBM disappears. Simultaneously, the 2D/G ratio indicates that the bilayer transitions into two monolayers, where the layers no longer interact with each other. The splitting of the LBM was interpreted as partial intercalation of water between the graphene layers, while the disappearance of the LBM was interpreted as complete separation of the graphene layers by water [5]. Considering that average annual relative humidity levels in many regions are above these thresholds—for instance, Northern European countries average around 70–80% humidity, Southern European countries around 60–70%, coastal regions of California about 75%, and southern coastal areas of China around 75–80%, it is evident that unless experiments on bilayer graphene are conducted in low-humidity environments, atmospheric water is likely to intercalate between the layers. Therefore, the Raman experiments reported by Qadir *et al.* [5] strongly suggest that under typical ambient conditions, graphene layers in bilayer graphene can become partially or completely separated by intercalated atmospheric water. To reconcile

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these seemingly contradictory observations, it is crucial to identify the specific properties relevant to each scenario. While several studies have examined water intercalation and adsorption in graphite and graphene—for example, the influence of water on interlayer interactions and frictional behavior has been discussed in Refs. [6–10]—a clear mechanistic understanding of how environmental water governs lubrication remains elusive.

Graphite can be used as either a wet or dry lubricant. In graphitized oil, graphene prevents direct contact between surfaces under extreme pressure, making the friction coefficient of the surfaces themselves irrelevant. Conversely, when graphite is used as a dry lubricant—as in electric motor brushes—the situation involves solid-to-solid contact at discrete points. Although load-bearing contact typically occurs at a limited number of asperities, these contact areas are sufficiently large at the microscopic level for graphene-graphene friction to become significant. The abundant graphite present can fill the low areas between asperities, smoothing the surfaces over time. Furthermore, graphite can also penetrate into the contact surfaces themselves, similar to how, when a hard material slides against a softer one—such as diamond on aluminium—the hard material wears into the soft surface, resulting in abrasion primarily between particles of the hard material [11]. This process is similar to lens grinding, where abrasive materials cause two surfaces to become highly conformal, resulting in extensive surface contact rather than contact at discrete points [12]. Ultimately, given plenty of graphite filling the low areas, the contact surfaces can become so well-matched that contact occurs across the entire interface. In this scenario, the coefficient of friction is largely determined by graphene-on-graphene interactions. Therefore, understanding this interfacial friction is crucial, and it is the focus of our study. Lubrication serves two primary purposes: reducing the friction coefficient at a target interface and reducing wear. A high wear rate does not necessarily indicate an increase in the friction coefficient. Earlier reports found that the friction coefficient between graphene layers could be extremely low [13], while wear rates increased under vacuum conditions [2]. Here, we further narrow our investigation to the impact of ambient water on the friction coefficient at the interface [14]. Graphite lubrication is complex, involving various possible interfaces such as between graphene layers [1], grain boundaries between graphene single crystals [15], between graphite flakes on a larger scale, or between graphene and copper (as in graphitic brushes) [12]. A critical question is the role of environmental water: Why does humidity affect graphite lubrication but not MoS₂ [16], even though all the above seems applicable to both? This paper aims to bridge the gap in understanding the specific conditions and mechanisms by which environmental water affects graphite lubrication but not MoS₂.

To address these questions, this work makes three specific contributions: First, we provide a quantitative framework that reconciles the longstanding contradiction between XRD measurements showing no bulk water intercalation and Raman spectroscopy, suggesting water penetration between layers. Second, we demonstrate that the primary lubrication mechanism occurs at the graphene-water interface rather than through intercalation, with water reducing sliding energy bar-

riers from approximately 72 to 22 mJ/m² through induced incommensurability. Third, we explain why graphite requires environmental water for effective lubrication while MoS₂ does not, through systematic analysis of interlayer interaction strengths.

II. COMPUTATIONAL METHODS

For accurate calculations of the out-of-plane stiffness in multilayer graphene, we employed density functional theory (DFT) as implemented in the Vienna *Ab initio* Simulation Package [17] together with projector augmented wave (PAW) pseudopotentials [18] and Perdew-Burke-Ernzerhof (PBE) exchange-correlation potential [19]. The many-body dispersion energy method of Tkatchenko *et al.* was used to include the long-range van der Waals (vdW) interactions [20]. The plane wave cutoff energy was set to 500 eV. Reciprocal space was sampled using a $24 \times 24 \times 1$ *k*-point mesh, which was increased to $24 \times 24 \times 8$ for the graphite case. Our 1×1 DFT cells capture the intrinsic interlayer stiffness that determines the fundamental threshold for water intercalation. Since the required 80% vdW reduction far exceeds any realistic mechanical perturbation, larger supercells would not change our conclusions. The simulation box, composed of *N* Bernal-stacked layers, had in-plane lattice constants of 2.463 Å, and the out-of-plane simulation box dimension was set to $(N - 1) \times 3.2$ Å + 15 Å, corresponding to the initial interlayer distance of 3.2 Å and a vacuum separation of 15 Å. These choices were made to systematically explore the interlayer interaction strength and its influence on water intercalation, following the methodology established in our previous studies on interlayer graphene interactions [21–23].

We first relaxed the models with respect to atomic positions. In the next step, we fixed all interlayer distances but one, which we varied around its equilibrium value. The resulting energy variations were attributed to the elastic stretching of that interlayer binding. We fitted this dependence using a polynomial of the form

$$E(d^{N,ij}) - E(d_0^{N,ij}) = \frac{1}{2} A d_0^{N,ij} (K_{ij} \epsilon_{zz}^2 + K'_{ij} \epsilon_{zz}^3), \quad (1)$$

where $\epsilon_{zz} = (d^{N,ij} - d_0^{N,ij})/d_0^{N,ij}$ describes the strain localized between layers *i* and *j* in the *N*-layer graphene model, and *A* is the cross-sectional area. Here, *K_{ij}* represents the stiffness of the specific interlayer between layers *i* and *j*. The term *K'_{ij}* captures higher-order corrections to the interlayer stiffness, accounting for nonlinear elastic effects. When applying the same approach to graphite (infinite number of layers), we used stacked bilayers with an optimized *c*-lattice constant of 6.798 Å instead of separating them by a vacuum. In graphite, we cannot vary only a single interlayer distance; instead, we apply an affine strain along the *c*-axis — that is, altering every interlayer distance simultaneously. This method yields the bulk interlayer stiffness, corresponding to the elastic constant *c*₃₃ rather than the localized stiffness *K_{ij}*.

The MD simulations were performed with the Large-scale Atomic/Molecular Massively Parallel Simulator [24] using a reactive force field (ReaxFF) potential from Chenoweth *et al.* [25] Although fixed-charge water models such as SPC/E [26], TIP3P [27], and TIP4P/2005 [28] are widely used, they

lack the flexibility required for tuning key parameters (such as interlayer force constants). In contrast, ReaxFF allows for relating interlayer interaction to the probability of water intercalation, and hence exploration of the dominant physical mechanisms at play. Visualizations of the MD snapshots were done using Ovito software [29]. The target temperatures in the MD simulations were set to 300 K using an *NVT* ensemble controlled by a Nosé–Hoover style thermostat [30] and the time step was fixed at 0.3 fs. Energy minimizations were performed using the Polak-Ribiere version of the conjugate gradient (CG) algorithm. Periodic boundary conditions were applied in all three directions, with approximately 20 Å of vacuum separating the layers in the *c* direction.

We set the lateral simulation cell dimensions to $\approx 73 \times 63$ Å² for simulations in Fig. 2(a) and $\approx 86 \times 75$ Å² for the other MD simulations, corresponding to 1800 and 2450 carbon atoms per graphene layer, respectively. These dimensions exceed $3 \times$ the typical water clustering length scale (~ 20 Å), ensuring multiple independent water clusters can form without finite-size artifacts. The lateral simulation cell dimensions were chosen based on the specific phenomenon under investigation. For instance, in Fig. 2(a) the cell size was used to capture local interlayer dynamics, whereas larger cells were employed in other cases to accurately resolve water clustering phenomena. The number of water molecules in each simulation was determined by targeting a fixed local water density, thereby allowing us to explore how varying the absolute water content influences intercalation dynamics. The numbers of water molecules in the simulations for Figs. 2(a), 2(b), 3, and 4 were 1440, 101, 1024, and 446, respectively. Specifically, in the simulations for Fig. 2(a), water molecules were placed on both sides of the graphene layers, with initial positions randomly assigned within 8 Å of the carbon atoms. For Fig. 2(b), water molecules were generated randomly between the graphene layers, enforcing a minimum distance between them to prevent overlap; these molecules began to cluster during the MD simulation. In the simulations corresponding to Fig. 3, water molecules were generated 3–13 Å above the graphene sheet at the beginning of the simulation. For Fig. 4, a water layer obtained from the simulation in Fig. 3 was placed between two graphene layers, and the interlayer spacing was optimized before commencing additional simulations.

III. RESULTS AND DISCUSSIONS

A. Surface interlayer softening insufficient for water intercalation

We begin by testing the hypothesis that graphite lubrication occurs primarily at the surface due to water intercalating at surface interfaces, facilitated by the softening of surface layers. First, we performed DFT calculations to examine the interlayer stiffness in multilayer graphene structures. Our calculations reveal that interlayer bonding near the surface is indeed softer compared to interlayers located near the center. As shown in Fig. 1, the graphene interlayer closest to the surface exhibits approximately 6% lower stiffness compared to the interlayer at the center of a ten-layer graphene stack. This softening of the near-surface interlayer interaction supports the hypothesis that water intercalation might occur more read-

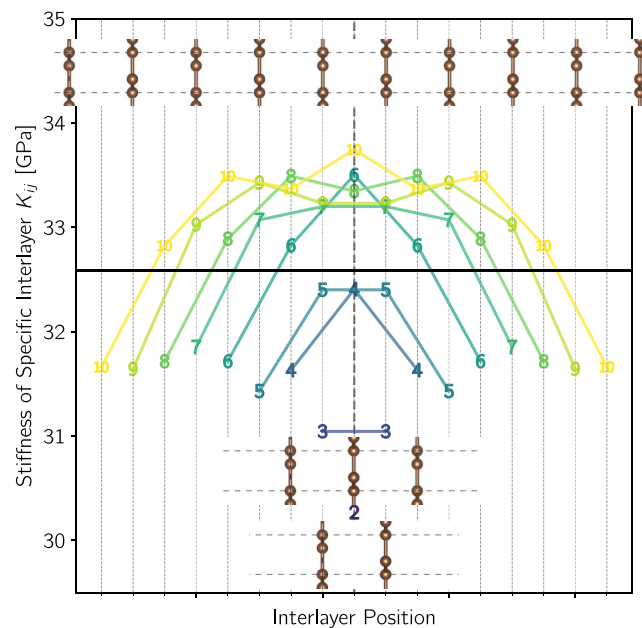


FIG. 1. Interlayer stiffness of each interface in multilayer graphene structures. The DFT calculations were performed for multilayer graphene stacks consisting of two to ten layers. A schematic visualization of the systems with $N = 2, 3$, and 10 layers is shown, with the corresponding stiffness values positioned between the stretched planes. The results show that the interlayer stiffness is reduced for the interfaces closest to the surface compared to those in the center. The solid black line at 32.6 GPa represents the bulk graphite interlayer stiffness calculated by us using DFT (infinite layers), serving as an indication of how the stiffness values converge with increasing layer numbers. This calculated value shows a reasonably good match with the experimental value of 35.7 GPa [33], demonstrating that the calculations are reliable.

ily at these interfaces, potentially contributing to graphite's lubricating properties under humid conditions.

To further understand these findings, we consider experimental measurements of the LBM frequencies. The experimental LBM frequencies for graphite and dry bilayer graphene are 127 cm^{-1} and 97 cm^{-1} , respectively [5,31]. Under a linear chain model with only nearest-neighbor interactions [32], these frequencies correspond to interlayer force constants of approximately $1.2 \times 10^{20} \text{ N/m}^3$ for graphite and $1.3 \times 10^{20} \text{ N/m}^3$ for bilayer graphene. The 23.6% difference in LBM frequencies is thus primarily explained by the collective vibrations described by the linear chain term $\sqrt{1 + \cos(\frac{\pi}{N})}$, where N is the number of layers.

Our DFT results include higher-order neighbor interactions not captured in the simple linear chain model, contributing to the observed 6% difference between surface and middle interlayers and explaining the slightly higher elastic constant c_{33} of graphite compared to bilayer graphene shown in Fig. 1. Note that while the linear chain model assumes uniform force constants, the stiffness variations in Fig. 1 come from our DFT calculations with higher-order interactions. For our study, we focus on interlayer stiffness rather than spacing when discussing water intercalation, as stiffness directly

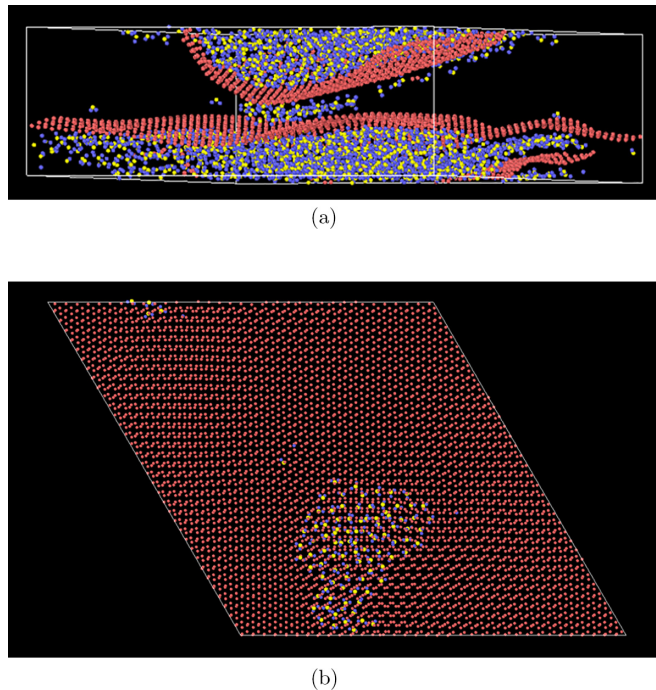


FIG. 2. (a) MD simulation snapshot with interlayer interactions reduced to 20% of the graphite vdW strength, enabling water intercalation. Carbon, hydrogen, and oxygen atoms are shown in red, blue, and yellow, respectively; the lateral dimensions are approximately $73 \times 63 \text{ \AA}^2$. (b) MD simulation snapshot illustrating water forming clusters between infinitely large graphene layers, which prevents water escape through edges; the graphene layers are relaxed similarly as in (a).

influences interlayer interactions that affect the likelihood of water molecules entering these layers.

B. Water intercalation

We aimed to demonstrate that water intercalation occurs exclusively at the surface interfaces due to softening because such intercalation would not be detectable by XRD results if it only occurred at the surface rather than in the bulk. However, our molecular dynamics (MD) simulations did not support this hypothesis. This was a systematic computational experiment to identify the intercalation threshold. Instead, the MD runs indicate that water intercalates in a bilayer graphene model (where a finite-sized graphene ribbon sits on an infinitely large graphene layer) only when the interlayer vdW interactions are manually reduced to below 20% of the normal strength in graphite. As shown in Fig. 2(a), at this significantly reduced level of vdW forces, the top graphene ribbon begins to roll up from the edges and eventually separates from the bottom layer after some time. This behavior suggests that the 6% softening (e.g., retaining 94% equivalent of its strength in bulk) at the surface interlayer, observed in our DFT calculations, is insufficient to facilitate water intercalation, thus challenging the initial hypothesis regarding its relevance to graphite lubrication. We note that the graphite interlayer cleavage energy is approximately 0.37 J/m^2 [34], and delamination can be achieved

under extreme conditions such as high shear rates in liquid-phase exfoliation [35] or through applied surface charges [36]. However, such conditions involve external energy input far exceeding what ambient water alone can provide. Under the conditions relevant to graphite lubrication—ambient humidity and typical contact pressures—the vdW interactions remain intact and water does not spontaneously intercalate. Local mechanical perturbations such as surface curvature or finite flake edges could potentially weaken interlayer interactions, but our simulations show these effects remain far below the 80% reduction threshold required for water intercalation.

Next, we aimed to answer whether water, once intercalated at the surface interfaces (perhaps during the formation of the surface), can remain there. Our findings indicate that water tends to move out of the interface, regardless of the initial amount of water intercalated between the graphene layers or the presence of vacancy sites in the graphene. Vacancy sites were introduced by selectively removing carbon atoms from the graphene lattice, thereby mimicking experimentally observed defects. Notably, water does not accumulate at these vacancy sites. To investigate whether edge passivation might facilitate water intercalation, we introduced atomic hydrogen into the system. This allows us to assess whether hydrogen functionalization at the graphene edges influences the migration or trapping of water molecules. As the number of hydrogen atoms increased, we observed hydrogen binding at the edges of the graphene. However, this edge functionalization did not facilitate the intercalation of either hydrogen or water. This result stood even when we varied the size of the graphene ribbon. These simulations directly address edge chemistry effects, demonstrating that even functionalized edges do not facilitate sustained water intercalation, confirming that edge effects are not the dominant pathway for water entry in microscale graphite. Naturally, water remains trapped if it cannot find an edge to escape, such as when placed between two infinitely large graphene layers. In this scenario, water forms clusters, as shown in Fig. 2(b). In macroscopic graphite, however, water molecules would perceive the nearest edge as effectively infinitely far away, facilitating cluster formation. Hence, it is possible for water to form clusters without sensing and moving to an edge.

C. Water structure on graphene surface

Since the XRD experiment showed that the average interlayer spacing in graphite does not change with humidity, a popular interpretation has been that graphite lubrication is due to water adsorbed on the graphene surface [4]. Understanding of this phenomenon advanced significantly when Akaishi *et al.* reported that water forms a two-atomic-layer structure on the graphene surface [37]. Complementing this, Morstein *et al.* [14] demonstrated that environmental water prevents cold welding between graphite surfaces under extreme conditions. Our work addresses a distinct question: How does water reduce friction under ambient conditions where cold welding does not occur? We demonstrate through three targeted investigations that the surface water bilayer is functionally critical: (1) thermal stability across 300–380 K confirms relevance to operating conditions, (2) persistence on curved surfaces validates applicability at asperity contacts, and (3) quantification

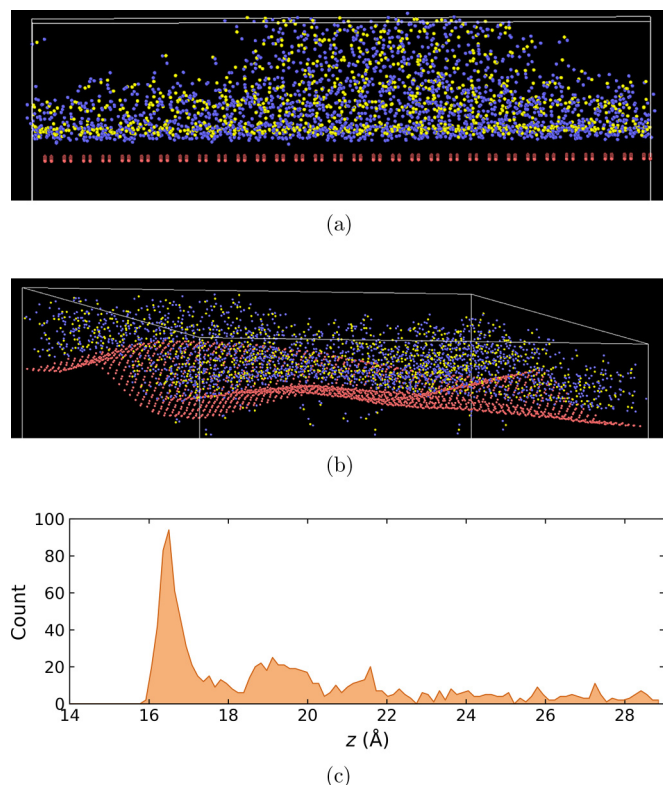


FIG. 3. Snapshots from the MD simulation showing the double-layer water structure intact both (a) on a flat graphene surface and (b) on a relaxed, realistically curved graphene plane at 300 K. Red, blue, and yellow balls represent C, H, and O atoms, respectively. (c) Hydrogen density profile for a flat surface along the z direction. The primary peak near the graphene surface and secondary features at larger distances indicate the two-layer water structure persists at room temperature, with thermal broadening of the peaks.

of the 70% reduction in sliding barriers establishes the graphene-water interface as the dominant friction mechanism. The properties of this layered water are markedly different from those of bulk water, fundamentally altering the surface properties of graphene in the presence of water. For instance, although graphene is intrinsically hydrophilic, it appears hydrophobic due to the presence of the adsorbed water layers [37]. This finding contradicts the previous theory that the incapability of water intercalation between graphene layers is due to the hydrophobic nature of graphene. Inspired by this report, we used MD simulations to investigate the effects of temperature, humidity (amount of water in the environment), and the flexibility of the graphene plane on the stability of the water double-layer structure using MD. Our results indicate that this double-layer structure remains stable over a wide temperature range, from 300 K to 380 K (near water's boiling point). At 300 K, we compared scenarios with a flat graphene plane and a relaxed plane that showed realistic curvatures. We found that the water layers remained intact even on the flexible surface. The comparison is shown in Fig. 3. The presence of a stable double-layer water structure is further substantiated by the hydrogen density profile, which shows identifiable peaks corresponding to the two water layers, with thermal broadening expected at room temperature.

To summarize the MD results from the above two sections, our simulations utilized a preset ReaxFF potential [25], allowing for reactive behavior by dynamically modeling bond formation and breaking. This approach enables the carbon (C), oxygen (O), and hydrogen (H) atoms to interact flexibly according to the ReaxFF rules, with the amounts of atoms/molecules, their initial locations and temperature as inputs, and all other properties as outputs. We found that water molecules are adsorbed onto the graphene surface without forming covalent bonds, creating a stable two-layer structure where the planar H_2O molecules are approximately parallel to the graphene plane, in agreement with Akaishi *et al.* [37], as shown in Fig. 3(a). We confirmed the stability of this two-layer structure across various temperatures and humidity levels. Introducing more water, as in Fig. 2(a), resulted in only the first two layers forming stable structures; no additional layered structures were observed beyond the first two. The water adsorbed on the top surface does not penetrate and intercalate between the graphene layers. Available water molecules from the ambient can intercalate only when the graphene-graphene interlayer potential is reduced by over 80%. When trapped between graphene layers, water migrates as intact H_2O molecules before forming a compact layer. No dissociation into $(\text{OH})^-$ and H^+ ions was observed in our simulations.

While our simulations use fixed numbers of water molecules rather than controlling humidity directly, the stable two-layer water structure we observe is consistent with experimental observations under typical ambient humidity conditions ($>50\%$ RH). The key insight is that this surface water structure forms readily and remains stable, regardless of the specific humidity level above this threshold.

D. Friction coefficient of graphite sliding

Next we used literature data to extract the friction coefficient from experiments performed under ambient conditions to identify the relevant interface to graphite lubrication. Given that most laboratories worldwide have an average RH well above 50%, it is safe to assume the abundant presence of environmental water in these experiments. It is important to note that the friction coefficients reported in many superlubrication studies, where friction is minimized along specific crystallographic directions, are not directly applicable to general graphite lubrication performance [38,39]. In typical applications of graphite as a lubricant, such as in graphitic brushes, sliding occurs along all directions between graphene layers, necessitating an understanding of friction across all possible orientations. While single-crystal graphite allows for orientation-dependent sliding and could exhibit superlubricity along specific crystallographic directions, practical lubrication scenarios require knowledge of friction over the full range of angles. Even when setting aside the complexities introduced by grain boundaries and defects, capturing the friction behavior over all angles remains a challenge. Atomic force microscopy measurements typically cover limited directions and small areas, restricting the ability to comprehensively assess friction characteristics necessary for applications involving multidirectional sliding. To address this limitation, we identified one published all-angle experiment involving

bulging monolayer and bilayer graphene [40]. In this experiment, the authors placed a monolayer of graphene on SiO₂ with prepatterned holes. They then pressurized the holes and measured the Raman spectra of graphene over one hole and surrounding areas. They interpreted their data as indicating that there was no interfacial sliding in their experiment. We reinterpret their data as follows: Beyond the hole, the strain decreases approximately linearly from 13.8% (of the maximum strain) at the edge of the hole (radius 2.5 μm) to zero at the radius where slipping occurs (4.5 μm). This strain gradient of 400 m^{-1} , obtained from the shift of the G mode (GM), results in a constant friction shear stress of 0.15 MPa across this region, through the 2D in-plane stiffness of graphene [41]. Assuming a friction coefficient between graphene and SiO₂ of 0.2, we derive a normal stress between graphene and SiO₂ of 0.75 MPa. This stress is significantly larger than ambient pressure and likely results from the adhesive van der Waals forces between graphene and SiO₂. The authors also conducted the same experiment on bilayer graphene, but the data is more complex to interpret. However, it suggests a normal stress of approximately 3 MPa between the bilayer graphene, assuming a friction coefficient between graphene layers of 0.02 [42].

We then investigated whether the estimated interlayer (graphene-SiO₂ in the case of monolayer and graphene-graphene in bilayer) adhesion matches our calculations in order of magnitude to determine if they indeed represent the relevant interface determining the shear stress observed in the experiments. We previously performed DFT calculations to obtain the interlayer potential change with interlayer spacing, fitted the calculated potential with a Lennard-Jones potential [23], and extracted the vdW stress from the attraction term of the potential between graphene layers in bilayer graphene and graphite in vacuum. The results yielded values of 2.9 GPa for bilayer graphene and 5.6 GPa for graphite. The significant discrepancy between these calculations and the experimental results—by 3 to 4 orders of magnitude—suggests that the graphene-SiO₂ or the graphene-graphene interface might not be the relevant interface determining the friction in the experiments. Alternatively, the normal stress between graphene layers at the leading edge could be reduced by 3 orders of magnitude from the normal graphene-graphene vdW forces due to factors such as water adsorption at the top surface. It is also noteworthy that the friction coefficient could be 3 orders of magnitude smaller than the assumed 0.02 to reconcile DFT results with experimental findings. However, such values typically occur only at specific angles, known as superlubrication. Therefore, we consider it more likely that the relevant interface is graphene water. As quantified in Sec. III B, mechanical perturbations and edge effects cannot achieve the 80% vdW reduction required for intercalation nor explain the primary friction mechanism.

E. Impact of water on interlayer friction

While Sec. III B demonstrated that water does not spontaneously intercalate between graphene layers under normal conditions, we now examine a hypothetical scenario: If water molecules were trapped between layers during surface preparation or at defects, how would this affect sliding friction? We investigate how the graphene-water interface improves

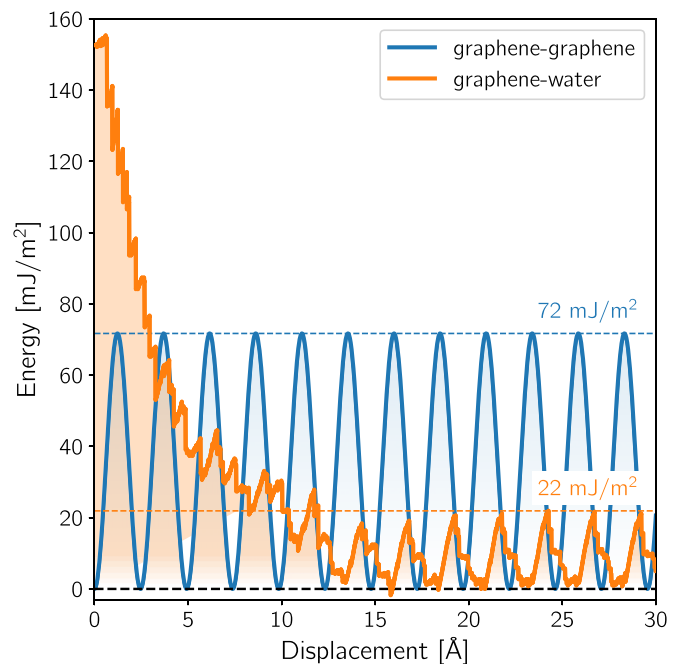


FIG. 4. Calculated potential energy surface vs horizontal displacement along the zigzag $\langle 1\bar{1}00 \rangle$ direction of the top graphene layer for the optimized bilayer Bernal-stacked graphene (blue line) and the optimized structure with a single water layer adsorbed on a graphene layer, followed by another graphene layer on top (orange line).

lubrication compared to the graphene-graphene interface. Due to the restriction of maintaining a periodic structure, it is challenging to calculate the all-angle friction. Therefore, we calculate the energy barrier for sliding one layer of graphene along a single direction. For the graphene-water interface investigation, we first introduce a water layer adsorbed on the bottom graphene layer, as shown in Fig. 3(a). Then, we place another graphene layer on top, mimicking the scenario where water intercalates during the formation of the surface interface. The vertical spacing is then optimized, and we horizontally shift the top layer while calculating the corresponding energy profile.

As illustrated in Fig. 4, after a running-in period, sliding graphene on a water layer requires overcoming an energy barrier of approximately 22 mJ/m^2 (orange line), whereas sliding graphene on a graphene layer requires overcoming a barrier of approximately 72 mJ/m^2 (blue curve). It is important to note that in the case of graphene-on-graphene sliding, the energy barrier is significantly dependent on the sliding direction due to the commensurate nature of the lattice structures. Different sliding directions can yield varying energy barriers, which could influence the overall frictional behavior.

However, in our simulations of graphene-on-graphene sliding, the layers are perfectly commensurate, as indicated by the blue curve in Fig. 4 with its perfect 2.5 $\text{\AA}$ periodicity. This commensurability means that as the top layer is displaced, all atoms simultaneously move over the energy barriers, resulting in synchronized peaks and troughs in the potential energy surface. In reality, slight mismatches or strains between the layers can lead to *incommensurability*. For example, applying

a small tensile strain of 1% to one graphene layer results in 99 units of the strained layer aligning with 100 units of the unstrained layer. This loss of commensurability causes the energy barriers for sliding to become misaligned across the interface. As one region goes uphill in energy during sliding, another region elsewhere goes downhill, effectively averaging out the energy barriers. Consequently, the overall potential energy surface becomes significantly flatter, leading to a large reduction in the sliding energy barrier [43]. This phenomenon is analogous to the behavior of dislocations in metals, where misalignment within the crystal lattice reduces the energy barriers for deformation. In metal crystals, dislocations introduce regions where atomic planes are offset, allowing atoms to move past one another with less energy than would be required to shift an entire plane simultaneously. This misalignment means that while some atoms are moving into higher-energy positions, others are moving into lower-energy ones, effectively canceling out energy peaks and troughs.

The presence of intercalated water promotes incommensurability by inhibiting strain transfer between the graphene layers. Our calculations show that introducing a water layer reduces the energy barrier for sliding from approximately 72 mJ/m^2 (dry graphene-graphene interface) to 22 mJ/m^2 (graphene-water interface), as illustrated by the orange line in Fig. 4. Additionally, when comparing the sliding energy barrier to the normal stress implied from friction experiments under ambient conditions, we find a significant discrepancy. The calculated sliding energy barrier corresponds to approximately 11.78 meV per carbon atom, whereas lifting the layers by a fraction of an angstrom under a normal stress of 3 MPa yields an energy per atom of only about 0.0049 meV . This indicates that under typical normal stresses encountered in experiments, it is energetically more favorable for the graphene layers to slide over each other rather than to separate.

This significant reduction in the sliding energy barrier due to incommensurability and the presence of water enhances lubrication at the graphene-water interface compared to the dry graphene-graphene interface. It also parallels our earlier observations where the normal stresses obtained from DFT calculations for dry graphene interfaces are several orders of magnitude higher than those observed experimentally [23]. This discrepancy suggests that the graphene-water interface, where water adsorption leads to incommensurability and reduced interlayer interactions, is more relevant in determining friction behavior. This water-induced incommensurability provides the fundamental explanation for why graphite requires environmental water for effective lubrication while MoS_2 does not. In graphite, adjacent layers naturally align in commensurate stacking (AA or AB) with strong interlayer interactions, causing all atoms to experience energy barriers simultaneously during sliding. Water disrupts this perfect alignment, creating regions where some atoms move uphill while others move downhill, dramatically reducing net friction. In contrast, MoS_2 achieves low friction without water due to its fundamentally weaker interlayer interactions (shear strength $\sim 25 \text{ MPa}$ versus $62\text{--}140 \text{ MPa}$ for graphite) [33,44,45] and larger interlayer spacing ($6.2 \text{ \AA}$ versus $3.35 \text{ \AA}$) [16,46]. These weak interactions mean that (1) even commensurate MoS_2 layers have lower sliding barriers than graphite and (2) incommensurability is readily achieved

through minor perturbations like thermal fluctuations or surface roughness, without requiring water's assistance [47]. This mechanism represents a fundamental design principle for layered lubricants: achieving low interlayer interaction strength either through water-induced disruption (graphite) or inherently weak van der Waals forces (MoS_2). The reduction in energy barriers due to water mirrors the beneficial impact of environmental humidity reported in other systems, such as in the frictional contact between amorphous carbon doped with silicon and alumina [48].

Returning to the aim of the paper, these results partially bridge the gap in understanding the specific conditions and mechanisms by which environmental water affects graphite lubrication. The three key aspects to reconcile are: (i) graphite requires water to be lubricative, unlike other layered materials such as MoS_2 [16]; (ii) XRD shows that the average interlayer spacing in graphite does not change with humidity; and (iii) Raman spectroscopy reveals the splitting of LBM in bilayer graphite above 22% RH and the disappearance of LBM, along with a significant drop in the 2D/G ratio, above 55% RH. It is evident that graphite lubrication originates from the surface (including the surface interlayers) because water, which only affects the surface, is essential [14]. Water certainly adsorbs on the top surface. Regarding whether water intercalates between the surface interlayers, two possible theories could reconcile all observations: water does not intercalate, suggesting the Raman results were misinterpreted, or intercalation occurs within the surface interlayers where graphene interlayer interactions are over 80% weaker than the graphene-graphene vdW interactions in graphite. This latter theory is plausible, especially considering that the interlayer attraction in bilayer graphene is only about half of that in graphite. Either way, the relevant interface for graphite lubrication is graphene-water rather than graphene-graphene.

IV. CONCLUSION

In this study, we investigated the influence of environmental water on the lubrication properties of graphite, providing significant insights into the interactions between water molecules and graphene layers. DFT calculations revealed that the surface interlayers of multilayer graphene are softer than the central layers, suggesting a potential for water intercalation at these surface interfaces. However, MD simulations demonstrated that effective water intercalation would require a substantial reduction in vdW interaction strength, which the observed 6% softening does not achieve. Consequently, water tends to move out of interlayer spaces, forming clusters when it cannot escape, and does not significantly intercalate into the bulk.

Instead, the stability of a two-atomic-layer water structure over a wide temperature range ensures the presence of at least one graphene-water interface in the presence of atmospheric water. Friction coefficients derived from ambient condition experiments indicate that the graphene-water interface plays a more crucial role in lubrication than the graphene-graphene interface. The significant discrepancy between theoretical vdW forces and experimental shear stresses, combined with a comprehensive consideration of all existing observations, supports this conclusion. Additionally, energy barrier calculations

demonstrated that a water layer reduces the sliding energy barrier from approximately 72 mJ/m^2 for graphene-graphene interfaces to about 22 mJ/m^2 for graphene-water interfaces. While we focus on pristine interfaces to identify the primary mechanism, real graphite presents additional complexity including grain boundaries and defects where water dissociation could provide secondary passivation. Our work establishes that: (1) surface water layers form stably and reduce friction via incommensurability, (2) bulk intercalation requires conditions unlikely under normal operation, and (3) edge and defect contributions are 3 to 4 orders of magnitude smaller than interfacial friction for micrometer-scale flakes.

These results underscore that the graphene-water interface is the dominant mechanism for graphite lubrication rather than direct graphene-graphene interactions. This enhanced understanding explains why graphite serves as an effective lubricant and highlights the broader implications of molecular interactions at graphene-water interfaces in confined nanoscale environments.

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DATA AVAILABILITY

The data that support the findings of this article cannot be made publicly available due to their excessive size. All information needed for their reproduction has been shared in the paper. The data are available upon reasonable request from the authors.

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