

Origin of the isotope effect on solid friction

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Friction of hydrogen passivated surfaces can be reduced by replacing terminating hydrogen atoms with heavier deuteriums. Using molecular dynamics simulations, we show that this experimentally observed isotope effect can be explained quantitatively by small differences in surface coverage, which are due to isotope-dependent bond stabilities. We also demonstrate that a change in vibrational frequencies alone does not account for an isotope-dependent solid friction in our model system.

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I. INTRODUCTION

The ability to reduce friction, adhesion, and wear of two materials in contact is of great technological interest. Poor tribological performance, such as undesired adhesion, has been shown to be a limiting factor for the durability and reliability of micro- or nano-electromechanical systems.¹ An effective method to reduce friction and adhesion is to chemically passivate surfaces with atoms (e.g., hydrogen)² or molecules (e.g., self-assembled monolayers)³. For a review article on the effects of surface chemistry on friction see Ref. [4].

Given that the critical role of (hydrogen) passivation in reducing friction of diamond has been well established both experimentally⁵ and theoretically,⁶⁻⁹ the recent pioneering study by Cannara *et al.*¹⁰ came as a surprise. The authors found that friction can be reduced further by increasing the isotope mass of surface adsorbates. Using atomic force microscopy (AFM), a reduction in friction of about 20% was measured when surfaces were passivated with deuterium (D) instead of hydrogen (H). Despite the potential technological importance of this isotope effect on friction, its origin has not yet been explained convincingly.

The main difference between the isotopes H and D is their mass or inertia. Properties that directly depend on inertia, such as vibrational frequencies and vibrational damping, can consequently also be isotope dependent. In models for vibrational damping, adsorbate atoms transfer energy between surfaces and subsequently this energy is dissipated away from the interface in the form of heat. Vibrational damping has been successfully treated using linear-response theory¹¹ and phenomenological models,¹² which all predict an algebraic scaling of damping with isotope mass. Cannara *et al.*¹⁰, argued that such theories are consistent with the experimentally observed isotope effect on diamond friction, because lighter isotopes collide more frequently with the counterface leading to larger friction. However, as argued in more detail in the main part of this paper, the smaller momentum transferred by lighter isotopes overcompensate this friction increase.

Another argument against applying damping models in a straightforward fashion is that they are in contradiction with friction behavior of solid-solid interfaces, be-

cause vibrational damping theories predict that friction disappears at small sliding velocities. In contrast, solid-solid interfaces exhibit static friction and a weak dependence of kinetic friction on velocity, as for example, in the case of diamond like carbon (DLC).¹³ Moreover, estimates of shear stresses that are based on vibrational damping models are more than six orders of magnitudes smaller than the experimentally measured values for diamond (see section III). For these reasons, we find it desirable that an explanation of the observed isotope effect on solid friction goes beyond the vibrational damping models, i.e., one needs to identify instabilities, which are necessary to produce a static friction¹⁴. Assuming identical chemistry, one then needs to show that the energy dissipated during an instability is larger for H than for D. Unfortunately, we find that the opposite tends to be true for an isolated instability.

What is then the origin of the experimentally observed isotope effect on friction? We propose that it is related to the chemical stability of the passivation layer, which is higher for D than for H and which ultimately leads to higher surface coverage and smaller friction for the heavier isotope. Mass-dependent chemical stability is known to be responsible for the isotope effect in lubrication discovered a few decades ago. For instance, Rebuck *et al.*¹⁵ have shown that performance lifetime of synthetic hydrocarbon lubricants can be increased by deuteration because of the higher oxidation resistance of the C-D bonds as compared to the C-H bonds. Deuterated lubricants are now commercially used.

In this paper we use large scale molecular dynamics (MD) simulations to study the two possible origins of the isotope effect on friction that were discussed so far, i.e., the differences in frequencies of chemisorbed species and the chemical stability of the terminating H (D) atoms. To test the former hypothesis, we perform a set of simulations with identical initial configurations, but with different masses of the terminating H isotopes. The dependence of solid friction on the chemical stability of the terminating atoms is explored by carrying out MD simulations of friction on diamond samples with different H coverages.

II. SIMULATION METHODS

In the reported MD simulations, interactions between atoms are described using the reactive empirical bond-order (REBO) potential.¹⁶ The interaction range of the REBO potential extends as far as the chemical interactions, whereas the van der Waals interactions are not included. We have therefore integrated van der Waals interactions with REBO using a continuous switching function. More details can be found in Ref. 7 and Supplementary Information therein.

Similarly to the experiments of Cannara *et al.*,¹⁰ our model system consists of a diamond-like carbon (DLC) AFM tip and a flat single-crystal diamond sample. Both the tip and the diamond sample are passivated with H isotopes. The MD simulations are carried out at the length scale that is comparable to those encountered in AFM experiments. The DLC tip has a height of 10 nm and a curvature radius of 30 nm. The diamond sample has dimensions of 49.9 nm \times 48.0 nm \times 8.2 nm. The (111) diamond surface is terminated with H isotopes. The AFM tips are prepared by first cutting the desired shapes out of a bulk DLC sample and subsequently by relaxing atomic positions in molecular statics simulations. Surface passivation is accomplished by terminating unsaturated C bonds with H atoms. The AFM tip is then gradually heated to and equilibrated at 300 K. MD simulations of normal loading and lateral sliding are all performed at 300 K. The bottom four layers in each sample are held rigid during these simulations. A Langevin thermostat with an inverse time constant of $\gamma = 0.01\text{s}^{-1}$ is applied to a 1 nm thick layer of atoms, which is adjacent to the rigid layers. Periodic boundary conditions are applied in both lateral directions.

The friction measurements are performed at a number of different tip displacements, which correspond to different normal loads. The DLC tip is sliding in the (2 $\bar{1}\bar{1}$) direction of the sample's surface at a constant velocity of 20 m/s. Simulations are performed at a constant normal displacement. Meanwhile, forces acting on the tip atoms are monitored. The net lateral and normal forces correspond to the instantaneous friction force and the applied load, respectively. Friction force varies consistently with the surface periodicity and a stick-slip behavior is observed. Time-averaged kinetic friction force is calculated for each surface lattice period. The reported value of friction force corresponds to an additional average over 3-8 lattice periods (the exact number is specified in figure captions) and the error bar is defined as a standard deviation from this average.

We have recently employed the same modeling approach to simulate the dependence of the friction force on the applied load for H-passivated diamond samples.⁷ For AFM tips with the curvature radius $R = 30$ nm, simulations yielded shear strength $\tau^H \approx 508$ MPa and contact pressure of 6.12 GPa (measured at 100 nN normal load). These values are consistent with the experimentally observed range of shear stresses (201 MPa to 485 MPa) and mean contact pressures (1.76 GPa to 4.26 GPa) obtained for the same material system, in particular given that the

experimental tip had a slightly larger radius of curvature ($R = 45$ nm).¹⁷

To determine the effect of vibrational damping on friction, we performed simulations of sliding over samples terminated with different hydrogen isotopes. In all of these simulations the systems have identical geometries, identical initial positions of atoms and initial velocities (with the exception of the velocities of the adsorbates). The only differences between the simulations are: (i) the adsorbate mass m (we used values $m = 1, 2, 3, 4, 5, 7$ a.m.u.), (ii) initial velocities of adsorbates, which are scaled by $1/\sqrt{m}$. In the simulations that test the effect of isotope mass on friction (Fig. 1), chemical interactions between atoms are described by the REBO potential without including the long-range van der Waals adhesion. Including van der Waals interactions renders the simulations computationally more expensive, but these interactions are not necessary to test the qualitative dependence of friction on the adsorbate mass.

To quantify the effect of surface coverage on friction, we performed MD simulations where surfaces were terminated with H atoms at 80% and 100% coverage. We have recently shown⁷ that in order to reproduce the sub-linear dependence of friction force on the normal load, long-range van der Waals interactions need to be included in the simulations in addition to the short-range (REBO) interactions. We have therefore included van der Waals interactions in MD simulations with varying coverage so that more direct comparison can be made between simulations and AFM experiments. The surface with 80% coverage is prepared by randomly removing H adsorbates from the 100% terminated surface. System geometries and sliding velocities are identical for simulations with both coverage values.

The sliding velocity of 20 m/s used in our MD simulations may need some additional discussion. While this velocity is comparable to those encountered in a number of applications (e.g., in microelectromechanical systems), it is orders of magnitude higher than the nominal sliding velocity (~ 1.2 $\mu\text{m/s}$) of the AFM tips. This discrepancy between MD and experimental time scales is an outstanding challenge in the field of nanotribology. Nevertheless, we believe our simulations results are comparable to the AFM experiments for the following reasons. The sound velocity in diamond is 6,000 to 9,000 times larger than the MD sliding velocity. Consequently, the heat generated during sliding is effectively dissipated, which is also confirmed by the fact that the temperature gradients in the modeled system are negligible. Additionally, the surface atoms vibrate more than a thousand times between subsequent slip events and therefore it is reasonable to expect that the effects of vibrational damping by adsorbate atoms will be captured in our simulations. Another validation comes from the agreement of the shear strengths and contact pressures calculated from our simulations and from AFM experiments (as discussed in previous paragraphs), which strongly suggests that the dominant energy dissipation mechanism are the same in both, the

MD simulations and experiments, and that velocity dependence of friction is weak in the system under study. Finally, it is worth pointing out that Cannara *et al.*¹⁰ have argued that the actual sliding velocity of the AFM tip in their experiments could be as high as 4 m/s due to the cantilever vibrations, which would imply that MD simulations and experiments explore the same regime of frictional response.

III. EFFECT OF ISOTOPE MASS ON FRICTION

Cannara *et al.*¹⁰ used a modified version of Persson's theory for adsorbed layers¹² to explain their observed isotope effect in solid friction - and stressed the appealing intuitive argument that because heavier adsorbate atoms collide less frequently with the tip, increasing adsorbate mass will lead to less energy being transferred and dissipated in the sample. However, a heavier atom will also exchange more momentum and thus the invoked picture is not complete. In addition, the theory for adsorbed layers hinges on the fact that the adsorbed layer is less stiff than the substrate. This assumption is violated for both the diamond sample and the DLC tip, where the terminating hydrogen atoms are bonded rigidly to carbon atoms. The rigidity of the C-H bond is exemplified by its large lateral and transversal vibrational frequencies, which have been measured to be 2910-2950 cm^{-1} and 1300 cm^{-1} , respectively.¹⁸⁻²¹

The direct applicability of vibrational damping models to the isotope effect on friction can be ruled out based on the fact that these theories do not apply to solid-solid interfaces that exhibit static friction (see Section I). However, it is yet instructive to pursue the idea of how large the friction force would be if this force could be predicted by a damping theory. An alternative theory to Persson's was developed by Smith, Robbins, and Cieplak.¹¹ The latter approach has the appealing feature that it is a systematic expansion in which the interfacial lateral forces are treated as being the small field. This approach could thus be the appropriate one to pursue, if static and kinetic friction were negligible. While differences in both theories exist regarding the details for the calculation of a damping constant, both approaches can be written in the form

$$\tau = m\eta v\sigma, \quad (1)$$

where τ is the interfacial shear strength, m is the adsorbate mass, η is the damping constant or inverse slip time (which depends on m), v is the interfacial sliding velocity, and σ is the number of adsorbate atoms per surface area. In both mentioned theories (and more generally from first order hydrodynamics), η scales with mass as $1/\sqrt{m}$, ultimately reflecting the fact that lighter atoms make more frequent oscillations, because thermal velocities scale with $1/\sqrt{m}$. This part of the equation is seemingly consistent with the experimentally observed trend

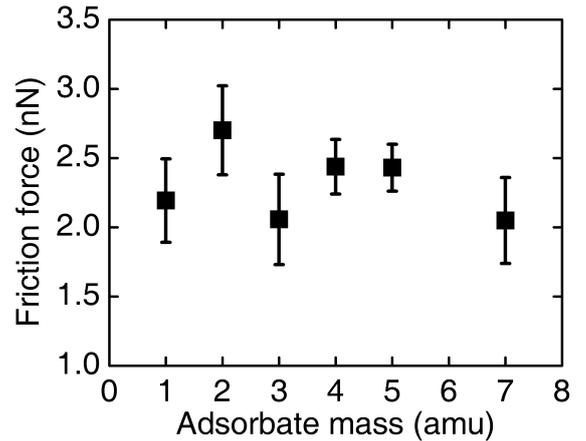


FIG. 1: The effect of isotope mass on friction force. Diamond samples were passivated with H isotopes with masses between 1 and 7 a.m.u. Friction measurements were performed at a load of ~ 50 nN. Friction forces were averaged over eight lattice periods of the sample's surface.

that heavier isotopes lead to less friction. When applying equation (1) to friction experiments, one may be tempted to use the tip mass for m , but the hydrogen or deuterium mass for the estimation of η . It is however unjustifiable to use one value for the mass of a degree of freedom when estimating its kinetic energy (which controls the collision frequencies) and another value when calculating its momentum (or momentum transfer).

In our estimate for the damping forces at the given experimental conditions, we will use consistent masses entering the various expressions on the right-hand-side of equation (1), i.e., in our calculations we use the mass of a H atom $m_H = 1.66 \times 10^{-27}$ g, the mass of D equal to $m_D = 2m_H$, the nominal sliding velocity of the AFM tip equal to 1.2 μ m/s (from Ref. 10), the surface density of adsorbates $\sigma = 1.6 \times 10^{19}$ m^{-2} , and the damping coefficients for H and D equal $\eta_H = 1700$ THz and $\eta_D = 1075$ THz, respectively (also from Ref. 10). We estimated the contribution to shear strength from vibrational damping to be ~ 54 Pa and ~ 69 Pa for H- and D-terminated diamond surfaces, respectively. These values are orders of magnitude lower than the ~ 200 MPa measured in the ultra high vacuum (UHV) environment or ~ 1000 MPa in dry nitrogen environment.¹⁰

The above discussion confirms that the isotope effect on solid friction cannot be explained by directly applying vibrational damping models.^{11,12} However, it is still possible that adsorbate vibrations have an indirect effect on friction: Whenever several competing energy minima are accessible after an instability occurred, the energy minimum where the system comes to a halt can depend on the damping and thus, in principle, solid friction can have non-trivial dependences on inertia of individual atoms. Because of the complex energy landscape, it is not known

a priori whether in this scenario heavier isotopes would exhibit lower friction or not. To investigate this possibility, we performed large-scale MD simulations of AFM experiments and we calculated friction force as a function of the adsorbate mass. All H isotopes were treated as chemically identical, that is their chemical interactions with other atoms in the system were independent of the isotope mass. The results of MD simulations carried out at a normal load of 50 nN are shown in Fig. 1. The statistical errors are sufficiently small and the range of isotope masses sufficiently large to rule out a (significant) trend in the friction with isotope mass, which is expected from the Prandtl-Tomlinson theory of solid friction at low sliding velocities.^{14,22}

IV. EFFECT OF COVERAGE ON FRICTION

Having shown that a simple vibrational damping scenario is not a likely origin of the isotope effect on solid friction, we will now investigate the role of chemical stability of the surface terminating atoms. We argue that D terminated surfaces will have a higher surface coverage mainly due to the higher stability of D as compared to H atoms. The isotope dependence of desorption rates is known as the kinetic isotope effect (KIE) and its existence has been well established for hydrogenated and deuterated Si.^{23,24} While specific mechanisms underlying the KIE constitute an active area of research, one may argue that the higher attempt frequency of the H atom and its higher zero-point energy as compared to D are important reasons for the experimentally observed smaller chemical stability of H. For the latter reason, we expect initial coverages to differ between H and D already, but will yet focus on the KIE in our quantitative analysis.

In Cannara's studies¹⁰ of the isotope effect on friction, the KIE could possibly take place during the sample preparation (which in some cases involved abstraction of previously chemisorbed species), and/or during high temperature annealing (some samples were annealed for a few hours in vacuum at 770K), and/or during sliding of the AFM tip. The latter effect might be, however, unlikely if the applied load is low.²⁵ To test our hypothesis that surface coverage effects are responsible for the experimentally observed isotope effect in friction, we will focus our discussion on a specific example of the KIE that results from high temperature annealing. It needs to be determined what concentration of vacancies in the surface H layer can be achieved due to thermal desorption and how this concentration will affect friction.

Although a direct comparison of desorption rates during thermal annealing of H- and D- terminated diamond is still lacking, the similarity of the Si-H and C-H bonds strongly suggest that the KIE of carbon-based solids is similar to that of silicon. Indeed, the differences in reaction rates of C-H and C-D containing systems have been observed in abstraction and reaction dynamics experiments.²⁶⁻²⁸ It has been shown that breaking

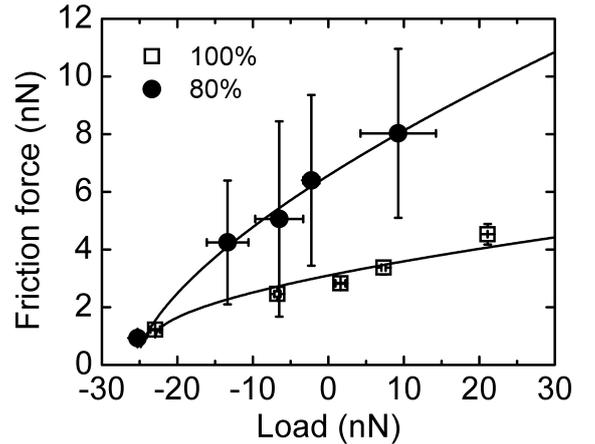


FIG. 2: Friction force vs. load for 100% and 80% surface coverage. Friction is averaged over 3-9 lattice periods of the diamond surface. Error bars correspond to standard deviations of forces averaged over one surface lattice constant.

of the C-H bonds occurs twice²⁶ to 4-6 times^{27,28} faster than that of C-D bonds. Based on these results, we will use conservative limits of the H/D desorption ratio to be between 2 and 4 for our system of interest.

We estimate the rate of change in the surface coverage based on the desorption rate of H from (100) diamond determined in isothermal desorption experiments. The isothermal desorption experiment reported the energy barrier for H desorption of 1.69 eV and the pre-exponential factor of $3.2 \times 10^5 \text{ s}^{-1}$ (Ref. 29). At 770 K (the annealing temperature in the experiments on diamond) the desorption rate of H equals $2.53 \times 10^{-6} \text{ s}^{-1}$. The same experimental study²⁹ also reported that the desorption of H from diamond follows the zeroth-order kinetics at temperatures below 800°C, i.e., the change of coverage can be calculated as the desorption rate multiplied by the annealing time. We estimate that 2-5 hours of annealing will lead to desorption of approximately 2-5% of H atoms from a diamond surface, assuming the coverage at the start of annealing is 100%. The difference in surface coverage between H- and D- passivated diamond surfaces can be as high as 4%.

MD simulations have previously shown that increasing the number of surface dangling bonds on diamond and DLC leads to a significant increase in friction force.^{30,31} However, contact geometries considered in these modeling studies (e.g., two flat surfaces or small tip radii with frozen atomic coordinates) are different from those used in the experiments of Cannara *et al.*¹⁰ and therefore a direct quantitative comparison of results is challenging. To quantify the effect of surface coverage on friction, we performed MD simulations of AFM tip sliding across diamond surfaces passivated with H at coverages of 80% and 100%. The dependence of the friction force on normal load for both values of surface coverage is shown in

Fig. 2. The significance of error bars is explained in the figure caption. As expected, a lower surface coverage results in a larger friction force at the same normal load.

To determine shear strength from MD simulations, we fit the friction-load data shown in Fig. 2 to the Maugis-Dugdale model,³² which is derived from continuum mechanics theories. More specifically, we employ a fitting procedure developed by Carpick, Ogletree, and Salmeron (COS)³³ that has been used in experimental studies^{10,17} and in our previous simulations.⁷ Although the breakdown of continuum models at the nanoscale has been demonstrated,^{7,34,35} fitting to these models provides a convenient way to compare simulation results to experimental data. In the fitting we use the effective elastic modulus of $E^* = 303$ GPa, which was obtained from the equation $E^* = ((1 - \nu_1^2)/E_1 + (1 - \nu_2^2)/E_2)^{-1}$. In this equation $E_1 = 348$ GPa and $E_2 = 1330$ GPa are the Young's moduli of DLC and diamond, respectively. The corresponding Poisson's ratios are $\nu_1 = 0.33$ and $\nu_2 = 0.11$. All the elastic constants were directly calculated in separate MD simulations. In the fits to continuum models, the pull-off force was constrained at the value measured directly in the sliding simulations. The shear strengths τ estimated from the fitting are 540 MPa and 1920 MPa for the 100% and 80% coverage, respectively. This analysis shows that surface coverage has a dramatic effect on τ .

The question remains as to what coverage differences, Δn , are required to account for the measured ratio of shear strengths τ^H/τ^D of 1.26. To estimate Δn we linearly interpolate shear strengths calculated for coverages $n = 80\%$ and 100% . The linear dependence of friction on coverage is justified by our less expensive MD simulations carried out in the absence of van der Waals interactions for coverages 80%, 85%, 90%, 95%, and 100% (see Section VI). We estimate that $\Delta n \approx 2\%$ would suffice to induce the experimentally observed isotope effect on solid friction, which is a number that would be difficult to detect experimentally. If the thermal desorption during annealing in UHV was the only place where the KIE takes place (which likely is not the case), then it would take only 3.3 to 6 hours of annealing time at 770 K to yield $\Delta n \approx 2\%$ for the H/D desorption ratios of 4 and 2, respectively. These values are consistent with the 2-3 hours of annealing time reported in Ref. 10.

Of course, when H or D desorption occurs before sliding, surfaces are likely to reconstruct and/or attract new terminations (i.e., oxygen) to eliminate the dangling bonds. If the relaxations take place on longer time scales, then they will not be well captured by our simulations, which in turn will result in an overestimation of the friction enhancement due to unpassivated bonds. However, as we make very conservative assumptions otherwise, it is reasonable to assume that our calculations are appropriate to estimate the order of magnitude of the effects of dangling bonds on wearless friction. It is also important to point out that we do not see wear in any of our simulations (i.e., wear due to dangling bonds ripping out atoms

from the counterface, structure deterioration, or formation of wear debris). Consequently, the mechanisms of friction observed in our simulations are the same as those that occur in experiments in the regime of wearless friction. Therefore, it is reasonable to use the shear strength obtained for the 80% coverage to estimate shear strengths for the case where the density of dangling bonds on the surface is lower, e.g., for the surface coverage of 98%. Finally, it is known that replacing H with more reactive species, such as oxygen, leads to an increased adhesion and friction both on Si³⁶ and on diamond³⁷ surfaces. If the dangling bonds are re-passivated with O, then the H-terminated surface will have a higher concentration of O atoms than the D-terminated surface, which supports our hypothesis that the isotope effect on solid friction is due to the chemical stability of surface terminated species. Thus our study can be viewed as an estimate of how shear strength would change in the presence of dangling bonds and/or reactive species.

V. DISCUSSION AND CONCLUSIONS

Before concluding, it may be worth investigating alternative explanations for isotope effects on friction. It is particularly important to consider a regime where friction is due to elastic instabilities, but where bonds do not yet break, i.e., where chemistry does not yet take place. In classical systems, there is no significant dependence of attainable shear stresses on isotope mass, because (formulae on) shear strengths and shear stresses are related to the potential energy surface but not to inertia.¹⁴ Lack of dependence on inertia is characteristic not only of shear strength, but also of analogous physical quantities, such as Peierls-Nabarro barriers for dislocation motion and kink energies in the Frenkel Kontorova model.³⁸ Shear strength may become inertia-dependent once one considers quantum mechanical effects, which are not entirely negligible at room temperature for Si-H or C-H bonds. The situation is captured qualitatively by the quantum Frenkel Kontorova model, which consists of a quantum-mechanical elastic string that is dragged over a rigid, corrugated substrate. In this model, lighter atoms turn out to produce less friction, because they tunnel more easily through the corrugation barriers.³⁹

We would like to argue that the same trend would be found for any real system, in which no bonds were broken. Thus, including elastic instabilities and quantum-mechanical effects does not explain the observed isotope effect on solid friction, because as shown here these phenomena would lead to friction force being independent of the adsorbate mass or friction force being lower for lighter adsorbates.

It is a well established (classical) theory that solid friction in the small-velocity limit is related to the energy dissipated during instabilities: Whenever a degree of freedom becomes unstable due to an external force, it quickly pops forward to another minimum in the potential en-

ergy landscape, typically to the next minimum available. The situation is sketched in Fig. 3, where the energy dissipated during such a (classical) “pop” is indicated by ΔE_{cla} .

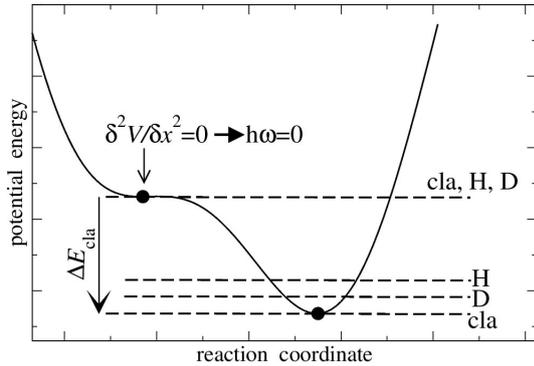


FIG. 3: Schematic representation of the amount of energy dissipated when a degree of freedom becomes unstable. The solid line describes the potential energy V surface as a function of a reaction coordinate x . Dashed lines correspond to energy levels at the instability point and at the new potential energy minimum in a purely classical picture (denoted as cla) and with quantum mechanical corrections (denoted as H and D). ΔE_{cla} indicates the amount of energy dissipated due to the instability in a classical picture. More detailed discussion of externally driven instabilities can be found in Ref. 14 (see Fig. 8 in that reference).

When estimating the quantum effects to the lowest order, one would add a harmonic excess energy of roughly $\hbar\omega$, where \hbar is the Planck’s constant divided by 2π , and ω is related to the curvature of the potential, $(\partial^2 V / \partial x^2)$, and the mass m , via $\omega = \sqrt{(\partial^2 V / \partial x^2) / m}$. At the instability point, such corrections disappear, while in the newly acquired equilibrium position, the harmonic quantum corrections are larger for lighter isotopes. As a consequence the dissipated energy is larger for heavier isotopes and if this contribution to friction was dominant, then surfaces terminated with heavier isotopes would have a larger friction.

More sophisticated quantum corrections would also address the question of when the instabilities are invoked, as the “pops” tend to occur slightly before the instability point is reached, e.g., due to thermal fluctuations or quantum mechanical tunneling. Incorporating these corrections would further increase the isotope effect, as the H atom would more easily tunnel through a barrier (quantum mechanically) and in a classical picture, H would have the higher attempt frequency to escape from the old (meta)stable site to the new stable site. While this discussion is rather qualitative, it appears obvious that for an “isolated” or “elementary” instability, one has to expect more energy dissipated for deuterium than for hydrogen, again leading to a larger friction for surfaces terminated with heavier isotopes.

In summary, we used MD simulations to show that vibrational damping by adsorbate atoms has either a negligible contribution to friction or this contribution is mass independent. We also demonstrated that small changes in surface coverage have a large effect on solid friction. We propose that the kinetic isotope effect on friction is due to a difference in desorption rates of the isotopes, which leads to a difference in surface coverage. Our study suggests that using heavier isotopes will prevent degradation of surface passivation due to exposure to environment and possibly due to sliding. We propose several experiments that would verify the hypothesis presented in this paper. Ideally, the ratio of desorption rates for H and D from diamond surfaces would be measured directly in isothermal desorption experiments. Alternatively, friction measurements on samples annealed for different lengths of time or different annealing temperatures could be compared to confirm the correlation between friction and desorption.

Acknowledgments

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- ¹ M. P. de Boer and T. M. Mayer, MRS Bulletin **26**, 302 (2001).
- ² R. J. A. van den Oetelaar and C. F. J. Flipse, Surf. Science **384**, L828 (1997).
- ³ U. Srinivasan, M. R. Houston, R. T. Howe, and R. Maboudian, Journal of Microelectromechanical Systems **7**, 252 (1998).
- ⁴ I. Szlufarska, Chandross, and R. M., Carpick, J. Phys. D **41**, 123001 (2008).
- ⁵ A. Erdemir, Surf. Coat. Technol. **146**, 292 (2001).
- ⁶ G. T. Gao, P. T. Mikulski, G. M. Chateaufneuf, and J. A. Harrison, J. Phys. Chem. B **107**, 11082 (2003).
- ⁷ Y. Mo, K. T. Turner, and I. Szlufarska, Nature **457**, 1116 (2009).

- ⁸ Y. Qi, E. Konca, and A. T. Alpas, Surf. Sci. **600**, 2955 (2006).
- ⁹ G. Zilibotti, M. C. Righi, and M. Ferrario, Phys. Rev. B **79**, 075420 (2009).
- ¹⁰ R. J. Cannara, M. J. Brukman, K. Cimatu, A. V. Sumant, S. Baldelli, and R. W. Carpick, Science **318**, 780 (2007).
- ¹¹ E. D. Smith, M. O. Robbins, and M. Cieplak, Phys. Rev. B **54**, 8252 (1996).
- ¹² B. N. J. Persson, *Sliding Friction: Physical Principles and Applications* (Springer, Berlin, 2000), 2nd ed.
- ¹³ J. A. Heimberg, K. J. Wahl, I. L. Singer, and A. Erdemir, Appl. Phys. Lett. **78**, 2449 (2001).
- ¹⁴ M. H. Müser and M. O. Robbins, Adv. Chem. Phys. **126**, 187 (2003).

- ¹⁵ N. D. Rebeck, A. A. Conte Jr., and L. Stallings, *ASLE Transactions* **20**, 108 (1977).
- ¹⁶ D. W. Brenner, O. A. Shenderova, J. A. Harrison, S. J. Stuart, B. Ni, and S. B. Sinnott, *J. Phys.-Cond. Mat.* **14**, 783 (2002).
- ¹⁷ G. T. Gao, R. J. Cannara, R. W. Carpick, and J. A. Harrison, *Langmuir* **23**, 5394 (2007).
- ¹⁸ B. D. Thoms and J. E. Butler, *Surface Science* **328**, 291 (1995).
- ¹⁹ T. Anzai, H. Maeoka, A. Wada, K. Domen, C. Hirose, T. Ando, and Y. Sato, *Journal of Molecular Structure* **352**, 455 (1995).
- ²⁰ C. L. Cheng, J. C. Lin, H. C. Chang, and J. K. Wang, *Journal of Chemical Physics* **105**, 8977 (1996).
- ²¹ L. V. Zhigilei, D. Srivastava, and B. J. Garrison, *Surface Science* **374**, 333 (1997).
- ²² L. Prandtl, *Z. Angew. Math. Mech.* **8**, 85 (1928).
- ²³ B. G. Koehler, C. H. Mak, D. A. Arthur, P. A. Coon, and S. M. George, *J. Chem. Phys.* **89**, 1709 (1988).
- ²⁴ T. C. Shen, C. Wang, G. C. Abeln, J. R. Tucker, J. W. Lyding, P. Avouris, and R. E. Walkup, *Science* **268**, 1590 (1995).
- ²⁵ Private communication with R.W. Carpick, R. J. Cannara, and M. J. Brukman.
- ²⁶ D. D. Koleske, S. M. Gates, B. D. Thoms, J. N. Russell, and J. E. Butler, *J. Chem. Phys.* **102**, 992 (1995).
- ²⁷ K. B. Wiberg and L. H. Slauch, *J. Am. Chem. Soc.* **80**, 3033 (1958).
- ²⁸ R. A. Lynch, S. P. Vincenti, Y. T. Lin, L. D. Smucker, and S. C. Subba Rao, *J. Am. Chem. Soc.* **94**, 8351 (1972).
- ²⁹ M. McGonigal, M. L. Kempel, M. S. Hammond, and K. D. Jamison, *J. Vac. Sci. & Technology A* **14**, 2308 (1996).
- ³⁰ J. A. Harrison, C. T. White, R. J. Colton, and D. W. Brenner, *MRS Bulletin* **18**, 50 (1993).
- ³¹ G. T. Gao, P. T. Mikulski, and J. A. Harrison, *J. Am. Chem. Soc.* **124**, 7202 (2002).
- ³² D. Maugis, *J. Colloid Interface Sci.* **150**, 243 (1992).
- ³³ R. W. Carpick, D. F. Ogletree, and M. Salmeron, *J. Colloid Interface Sci.* **211**, 395 (1999).
- ³⁴ B. Luan and M. O. Robbins, *Nature* **435**, 929 (2005).
- ³⁵ B. Luan and M. O. Robbins, *Phys. Rev. E* **74**, 026111 (2006).
- ³⁶ Y. Liu and I. Szlufarska, *Phys. Rev. B* **79**, 094109 (2009).
- ³⁷ S. Dag and S. Ciraci, *Phys. Rev. B* **70**, 241401 (2004).
- ³⁸ F. R. N. Nabarro, *Mat. Sci. Eng. A* **2344-236**, 67 (2007).
- ³⁹ F. R. Krajewski and M. H. Müser, *Phys. Rev. Lett.* **92**, 030601 (2004).

VI. APPENDIX: LINEAR DEPENDENCE OF SHEAR STRENGTH ON COVERAGE

In Section IV we argued that the dependence of shear strength τ on coverage n can be approximated by a linear function. Data shown in Fig. 2 was obtained from MD simulations of sliding where both the short-range and van der Waals interactions were present between the AFM tip and the diamond sample. Because such simulations are computationally expensive and they converge slowly,

only simulations for 80% and 100% have been performed. To confirm that friction properties can be linearly interpolated between 80% and 100% coverages, we have car-

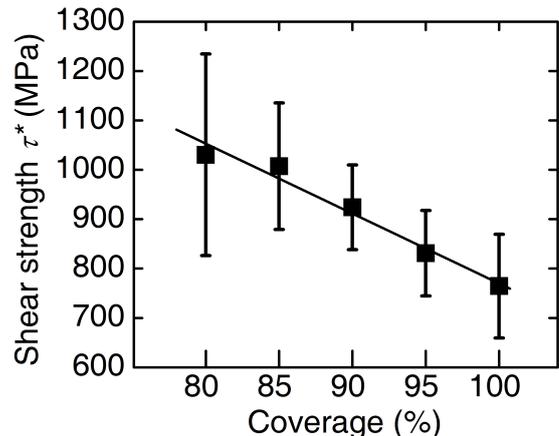


FIG. 4: Interfacial shear strength τ^* as a function of H coverage of the diamond surface. Simulations are performed at a normal load of 51 nN. Friction is averaged over 6 periods of the surface lattice and the error bars correspond to the standard deviation of forces averaged over one surface lattice constant.

ried out additional simulations of sliding friction in the absence of van der Waals interactions. These simulations are computationally less expensive and therefore we were able to perform simulations for more values of n . Figure 4 shows the calculated shear strength τ^* plotted as a function of H coverage. The interfacial shear strength τ^* has been calculated directly from MD simulations as dF_f/dA , where F_f and A are the friction force and the contact area, respectively. A is calculated using a method described in Ref. 7. In contrast to τ^* , τ reported in Section IV was obtained from fitting to continuum models. Continuum contact mechanics models are not valid at the small length scales considered in our study, nevertheless we used these models for adhesive contacts to make a quantitative comparison to the AFM data. Data shown in Fig. 4 confirms that shear strength increases linearly with decreasing surface coverage.

The linear dependence of shear strength on coverage is further justified by the fact that all the simulations are carried out in the wearless regime of friction and therefore the same energy dissipation mechanisms control friction at 80% and at higher coverage values. Specifically, the dominant mechanisms underlying friction in our simulations are elastic instabilities (where no bond is formed across the interface) and formation/breaking of H-C bonds across the interface. Even in the case of bond formation, no atoms are pulled out by the sliding counterface and no surface deterioration is observed.