Negative Differential Friction Predicted in 2D Ferroelectric In$_2$Se$_3$ Commensurate Contacts

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At the macroscopic scale, the friction force ($f$) is found to increase with the normal load ($N$), according to the classic law of Da Vinci–Amontons, namely, $f = \mu N$, with a positive definite friction coefficient ($\mu$). Here, first-principles calculations are employed to predict that, the static force $f$, measured by the corrugation in the sliding potential energy barrier, is lowered upon increasing the normal load applied on one layer of the recently discovered ferroelectric In$_2$Se$_3$ over another commensurate layer of In$_2$Se$_3$. That is, a negative differential friction coefficient $\mu$ can be realized, which thus simultaneously breaks the classic Da Vinci–Amontons law. Such a striking and counterintuitive observation can be rationalized by the delicate interplay of the interfacial vander Waals repulsive interactions and the electrostatic energy reduction due to the enhancement of the intralayer Se–In ionic bonding via charge redistribution under load. The present findings are expected to play an instrumental role in design of high-performance solid lubricants and mechanical-electronic nanodevices.

1. Introduction

Friction is one of the most important and significant problems in science and technologies,[1,2] which may play an instrumental role in diverse systems that cover from macroscopic equipment,[3] through the nanometer contacts in nanomachines[2,4] to biological molecular motors.[5] At the macroscopic scale, friction force ($f$) normally increase with increasing normal load ($N$) according to Da Vinci–Amontons law, namely, $f = \mu N$, with a positive definite friction coefficient ($\mu$), and the friction force $f$ is independent on other factors, such as apparent contact area, sliding velocity, etc. However, such a classic law has been demonstrated to breakdown at the microscopic scale. Research of recent decades has identified that microscopic friction becomes very complex and sensitive to various factors, such as temperature,[6–9] sliding velocity,[3,8–13] size effects,[14–17] surface roughness,[3,18,19] Moreover, frictions via electronic and magnetic dissipations,[20–23] radiative heat transfer,[6,24] and quantum effects[25,26] have also been respectively revealed.

In contrast to liquid lubrications, which may fail in some extreme conditions,[27,28] structural superlubricity has emerged as a new promising remedy for the reduction of friction,[29,30] which generally originates from the effective cancelation of lateral forces with incommensurate rigid crystalline contacts[31,32] due to the lattice mismatch and thus significantly reduces the energy barriers of motion.[33–35] Such an intriguing phenomenon was originally predicted three decades ago in nanoscale homogeneous graphitic contacts[36] and later termed superlubricity,[37] where the friction exhibits peak and superlow feature in commensurate and incommensurate contacts, respectively. However, only recent experiments have unambiguously observed the proposed superlubricity in various 2D material incommensurate van der Waals (vdW) junctions, including homogeneous contacts of graphite nanoflake-graphite,[38] heterojunctions of graphitic-hexagonal boron nitride (hBN),[39] and graphene-MoS$_2$.[40] More intriguingly, adhesion-dependent negative friction coefficients of chemically modified graphite was reported recently in experiment.[40,41] Note that, here the negative friction coefficient could be more rigorously expressed as negative differential friction (NDF), coined by analogy with another two very popular concepts of negative differential resistance[42,43] and negative...
2. Results and Discussion

2.1. Properties of 1QL-In$_2$Se$_3$ and 2QL-In$_2$Se$_3$ Systems

First, the calculated lattice constant of In$_2$Se$_3$ is 4.11 Å and the optimized thickness of In$_2$Se$_3$ is about 6.8 Å,[54] in close agreement with previous calculations[54] and experimental results.[55,56] As shown in Figure 1a,b, the significantly different interlayer spacing between the Se layer and the two In layers and the in-plane centrosymmetry breaking of the 1QL In$_2$Se$_3$ result in spontaneous out-of-plane (≈0.1 eÅ) and in-plane (≈2.4 eÅ) electric polarizations.[54] 

Then, we identify the preferred high-symmetry stacking modes of the homogeneous contact. As shown in Figure 1, for 2QL In$_2$Se$_3$ commensurate contacts, in the out-of-plane direc-

Now, starting from the optimized most stable stacking configuration of O-O(AP), we analyze the energy profile of the interlayer sliding along two typical commensurate pathways, i.e., [110] and [100] directions, where the bottom Se atoms of the top QL (Se$_{top}$) are displaced straightly from A site, over B and C, to the second-nearest neighboring A, and directly displaced from an A site to the nearest neighboring A site, as respectively shown in Figure 1c. To mimic the experimental investigations of friction as performed on other 2D materials,[13] when sliding the top QL In$_2$Se$_3$, relative to the bottom QL, the X, Y, and Z coordinates of the bottom-two layers of atoms in the bottom QL In$_2$Se$_3$ are fully fixed, and the energy profile of the commensurate contact is optimized by displacing the top QL In$_2$Se$_3$ every 0.3 Å along the proposed directions with fixing X and Y coordinates of the top two layers atoms.[34] That is, in the constrained sliding pathways,
Z direction of the top-two layers and X, Y, and Z directions of the six intermediate layers can be fully relaxed under external load.

The calculated energy profiles of the three stable commensurate contacts of O-O(AP), I-O(P), and I-I(AP) along the [110] pathway under three representative loads, i.e., $N = 0.00$, 1.1, and 2.2 GPa, are presented in Figure 2a–c, respectively. Two distinct features can be observed: i) In all the three contacts, during the whole sliding period, two local maxima of energy are identified, with the highest energy maximum ($E_{\text{max}}$) occurred when Se BT is slid to around the A site; ii) With the external $N$ increasing, the $E_{\text{max}}$ can be slightly pass over the A site, and the lowest energy minimum ($E_{\text{min}}$) may be shifted from B site to C, as found in the case of I-I(AP) with $N = 2.2$ GPa. Correspondingly, we present the activation energy barrier ($E_{\text{bar}}$) of the interlayer sliding subject to different loads in Figure 2d–f, for O-O(AP), I-O(P), and I-I(AP), respectively. Here, we define the $E_{\text{bar}}$ as the energy difference between the $E_{\text{max}}$ and $E_{\text{min}}$. Dividing the $E_{\text{bar}}$ by the sliding distance,\[64]\ we can estimate the friction force $f$ during the sliding. Very interestingly, the three types of commensurate contacts possess very contrasting $E_{\text{bar}}$ curves as a function of load $N$, as shown in Figure 2d–f. Specifically, for O-O(AP), the $E_{\text{bar}}$ decreases with $N$ increasing, namely, the differential friction coefficient $\mu = \Delta f / \Delta N < 0$ can be identified in a fairly large load regime up to 2.2 GPa applicable in recent experiments on 2D material contacts.\[34,45]\ Here, we emphasize that the NDF in the present load regime is also confirmed by further calculations performed by using HSE+D3 and optPBE-vdW schemes, as detailed in Figure S2 in the Supporting Information. However, $\mu > 0$ is observed when $N$ is beyond 2.2 GPa. Note that, here the predicted overall variation of friction with normal load is estimated to be about several $nN$ according to the definition.\[34]\ Importantly, the variation of the friction within 0–2.2 GPa reaches up to about 6.4%. Therefore, we expect that the NDF in the present work can be probed by the elaborate experiments.\[38]\ Moreover, we have also calculated the differential friction coefficients $\mu = \Delta f / \Delta N$ for all the three representative systems. As shown in Figure 3a–c, it is very clear that for the case of O-O(AP), the friction coefficient $\mu$ is indeed negative in the load regime of $0 < N \leq 2.2$ GPa, with a maximum absolute value of 0.015 at 2.2 GPa; for the case of I-O(P), $\mu$ is negative (with relatively small absolute values) in the load regime of $N \leq 1.10$ GPa; In contrast, for I-I(AP), $\mu$ is positive and increases up to the maximum absolute value of about 0.04 at 2.2 GPa, beyond which the calculated $\mu$ begins to decrease with the load, corresponding to the $\alpha$-to-$\beta$-like structural distortion. These findings provide strong evidence that the electric dipole can serve as an important degree of freedom to modulate the differential friction coefficient of In$_2$Se$_3$ interlayer commensurate sliding, i.e., from $\mu < 0$, through $\mu \approx 0$, to $\mu > 0$.

2.1.2. Origin of the Negative Differential Friction Coefficient $\mu$

To rationalize the above intriguing findings, we decompose the calculated $E_{\text{bar}}$ ($\mu$) into two terms which are contributed purely by vdW interactions ($E_{\text{bar-vdW}}$) and electrostatics interactions ($E_{\text{bar-ES}}$),\[51–53]\ as shown in Figure 2g–i for O-O(AP), I-O(P), and I-I(AP).

\[\text{Figure 2. a–c) Load dependent sliding energy profiles, d–f) Sliding energy barriers ($E_{\text{bar}}$) along [110] pathway as shown in Figure 1c. The contribution of the $E_{\text{bar}}$ by vdW corrections ($E_{\text{bar-vdW}}$) and electrostatics interactions ($E_{\text{bar-ES}}$) are analyzed in g–i). a), d), and g): O-O(AP); b), e), and h): I-O(P); c), f), and i): I-I(AP). In d–f), the interface separation distance $d$ of the $E_{\text{max}}$ configuration of the three contacts are also presented.}\]
respectively. Clearly, the negative (quasizero) \( \mu \) and attribute the left portion of the reduction of the \( E \) (I-O(P)) can be ascribed to the more significant (quasi-identical) within \( \approx \) totally reversed trend in the same load regime, i.e., decreases in dominating the NDF of the ferroelectric 2D material In\(_2\)Se\(_3\) into demonstrating the critical role of the electrostatic interactions analysis in Figure S4 in the Supporting Information. These findings, the \( E_{\text{vdW}} \) exhibits totally reversed trend in the same load regime, i.e., decreases within \( \approx 0-2.2 \) (1.65) GPa, and increases beyond 2.2 (1.65) GPa, respectively. Clearly, the negative (quasizero) \( \mu \) of O-O(AP) (I-O(P)) can be ascribed to the more significant (quasi-identical) reduction of the \( E_{\text{vdW}} \) which compensates the raise of the \( E_{\text{vdW}} \). More detailed analysis in Figure S3 in the Supporting Information show that the Ewald energy and exchange correlation potential dependent on the charge transfers and charge redistributions under load dominate the \( E_{\text{vdW}} \) reduction and negative friction. For I-I(AP), in the whole load regime of \( \approx 0-3.3 \) GPa, the \( E_{\text{vdW}} \) exhibits monotonous decrease which nevertheless is insufficient to compensate the monotonous increase of the \( E_{\text{vdW-ES}} \) leading to a reversed sign of the \( \mu \), i.e., \( \mu > 0 \).

2.1.3. Role of Interlayer vdW Interactions Verses Intralayer Electrostatic Interactions

Here we emphasize that though NDF arises from the decreased sliding potential corrugation with increased normal load is also observed in other systems,[45-48] however, such NDF is dominated by van der Waals interactions in the attractive regime of the interfacial separation above its equilibrium.[46,48] However, in our findings, the vdW interactions increase, rather than decrease the potential corrugation with the load increasing, very probably due to the fact that the interlayer distances are reduced to the sharp repulsive regime of the interfacial vdW interactions, as supported by the smallest interfacial separations in the OO(AP) and detailed analysis in Figure S4 in the Supporting Information. These findings demonstrate the critical role of the electrostatic interactions in dominating the NDF of the ferroelectric 2D material In\(_2\)Se\(_3\) vdW commensurate contact. Moreover, as detailed in Figure S5 in the Supporting Information, the increase of the friction under load beyond 2.75 GPa in O-O(AP) is accompanied with a structure distortion of the top QL In\(_2\)Se\(_3\) in the \( E_{\text{max}} \) state, and an \( \alpha \) to \( \beta \) phase transition is observed beyond 3.3 GPa. Such a transition results in energy increases, due to the higher energy of the \( \beta \) phase than \( \alpha \), by about 0.01 eV for the 1QL In\(_2\)Se\(_3\) under the present pressure regime, as also detailed in Figure S6 in the Supporting Information. For I-O(P), such a structural distortion and phase transition begins from relatively small critical load, around 1.65 GPa. However, no significant phase transition is observed in both the \( E_{\text{max}} \) state of I-I(AP) contact and \( E_{\text{min}} \) states of all the three systems.

To illustrate the underlying mechanism of the specific alignment of ferroelectric polarizations in leading to distinct frictions of the present systems, we first analyze the energy band structure of 1QL In\(_2\)Se\(_3\) in Figure S7 in the Supporting Information, which exhibits semiconducting characteristic with an energy bandgap of 0.78 eV. Due to the out-of-plane polarization, there are positive and negative charges localized respectively on the top and bottom sides of a free standing 1QL In\(_2\)Se\(_3\), as defined in Figure 1a. Such a feature is also supported by the centrosymmetry breaking nature (along the z direction) of the electronic charge density of the valance band, which is mainly localized on the top surface, i.e., the starting side of the electric dipole, see Figure S8 in the Supporting Information. Correspondingly, the interfacial couplings of the three 2QL In\(_2\)Se\(_3\) commensurate contacts can be schematically simplified as models of two contacting surfaces carrying positive and/or negative polarization charges, as shown in the left panels in Figure 4a–c, for O-O(AP), I-O(P), and I-I(AP), respectively.

The contrast friction behaviors of the three systems can be readily understood from the distinct responses of these polarization charges at the \( E_{\text{max}} \) configurations under load. Specifically, for O-O(AP), due to the electrostatic repulsive interactions of the negative charge themselves and the experienced electric field force applied by the electric dipole of the opposite QL, part of the surface polarization negative charges are respectively repelled to the nearby Se atom sites, as demonstrated by the charge difference analysis in Figure 4d. Such a charge accumulation (in red) on Se atoms lowers the electrostatics energies of the two individual QL components and thus reduces the \( E_{\text{bar-ES}} \) via enhancing the Se-In ionic binding. Importantly, such a charge transfer is significantly enhanced subject to the load \( N \) increase. For example, the \( E_{\text{bar-ES}} \) increases from 0.129 to 0.159 eV, however the \( E_{\text{bar-ES}} \) decrease from –0.008 to –0.046 eV when \( N \) increases.

Figure 3. Calculated friction coefficient \( \mu (\mu = \Delta f / \Delta N) \), a) O-O(AP); b) I-O(P); c) I-I(AP).
Figure 4. a–c) Schematic shows of the interactions of the interfacial polarization charges of the \( E_{\text{max}} \) configurations. d–f) 2D charge difference counters in the (110) plane consisting of the [110] pathway are presented for all the three systems under \( N = 0, 1.1, 2.2, \) and 3.3 GPa. The black dashed lines represent the middle of the interfaces. a) and d): O-O(AP); b) and e): I-O(P); c) and f): I-I(AP).

from 0 to 2.2 GPa, and it is clear that the \( E_{\text{bar}-\text{ES}} \) decrease over- takes the \( E_{\text{bar}-\text{vdW}} \) increase by 0.006 eV. For I-O(P) shown in Figure 4e, in the load regime of \( \approx 0–1.1 \) GPa, the enhancement of In–Se ionic bonding induced by the charge transfer can only be observed in the bottom QL, however it is weakened in the top QL, which leads to quasizero friction coefficient. For I-I(AP) shown in Figure 4f, on the one hand, with the interlayer distance decreasing under load, the repulsive electrostatic interactions of the positive polarization charges on both sides of the interfaces increases, leading to the distortion of the interface. On the other hand, more electrons are attracted to the central regime of the interface from the two individual QL components under load which lowers the electrostatic potential barrier of the interface as illustrated in Figure S9 in the Supporting Information. In contrast to O-O(AP), such a reversed charge transfer in I-I(AP) from both the top and bottom QLS to the interface regime significantly lowers the intralayer binding of each QL component at \( E_{\text{max}} \). Collectively, such two factors result in enlarged potential corrugation and positive \( \mu \) in I-I(AP) contact.

2.2. Interlayer Sliding Energy Profile of 2QL-In\(_2\)Se\(_3\) Homojunctions Along [100]

Now, we briefly report that when the top QL In\(_2\)Se\(_3\) is displaced under external load along the [100] direction, though the X and Y coordinates of the top-two layers of atoms are fixed along the [100] direction, the six intermediate layers of atoms will be optimized to close the configuration as obtained that along the [110] pathway. Such a departure from the [100] to the [110] pathway of the intermediate atoms leads to instability of the contact, particularly at relatively large load regime shown in Figure S10 in the Supporting Information. These findings suggest that the interlayer sliding prefers to proceed along the present “guide rail,” i.e., [110] direction, probably due to the significantly anisotropic features of the potential surface, which facilitates in realizing superlubricity.[45]

2.3. Role of External Electric Field in Tuning the Friction

To the end, taking the most stable contact O-O(AP) as a typical example, we briefly highlight that the new strategy established here in modulation of the friction by ferroelectric polarization can be further convincingly demonstrated by applying external electric field which can modify the out-of-plane polarization and/or by changing the in-plane polarization arrangement of the two QLs as well. As shown in Figure 5a, for the case of O-O(AP), under positive electric fields, along the [110] direction, the \( E_{\text{bar}}(f) \) can be further lowered and the negative friction coefficient feature becomes more significant in the relatively low load regime \( (N < 2.2 \) GPa), which can be also rationalized by the interfacial polarization charges changes under the external electric field, as detailed in Figure S11 (Supporting Information). Moreover, as shown in Figure 5b, the sliding \( E_{\text{bar}}(f) \) in O-O(AP) can be significantly lowered via reversing the in-plane dipole alignment to parallel arrangement, i.e., O-(P), however leading to positive \( \mu \) in the whole present load regime. These findings suggest that In\(_2\)Se\(_3\) with controllable friction is highly desirable in design of functional nanodevices wherein tunable friction is demanded.

3. Conclusion

In conclusion, the present study predicts that negative sliding friction coefficient can be realized in electrically polarized
2D material commensurate contacts. By selecting appropriate dipole–dipole alignments between the individual components of the contact, the raise of the sliding energy barrier contributed by vdW interactions can be thoroughly compensated by the electrostatic energy reduction, which is a spontaneous polarization charge redistribution process under appropriate load regime. As a consequence, negative friction coefficient can be obtained in the commensurate contact, and incommensurate condition is broken. Also importantly, the new strategy established here in reversion of the sliding friction coefficient by electric-dipole is also demonstrated by applying out-of-plane electric field and/or by changing the in-plane ferroelectric polarization alignments. Due to the fundamental importance, the present central findings are also expected to play an instrumental role in developing functional lubrications, nanosensors, and related mechanical-electronic nanodevices based on ferroelectric materials.

4. Experimental Section

The calculations were carried out using the density functional theory (DFT)[58] as implemented in the VASP code.[59] The interaction of valence electrons with atomic cores is described by the projector-augmented wave (PAW) method,[60] as parameterized by the Perdew-Burke-Ernzerhof (PBE) functional.[61] It is demonstrated that, relative to other vdW correction schemes (such as many-body dispersion which is powerful in describing other systems[34,62]), semiempirical DFT-D3 method[63] can more accurately describe the $\alpha$ configuration of the ground state of 1QL-In$_2$Se$_3$.[54] More calculation parameters and testing computational details are provided in Figures S1 and S6 in the Supporting Information. For 2D systems, the out-of-plane electric polarization is well-defined following the classical electrodynamics and calculated by the integration of local charge density times the coordinate in the out-of-plane axis over the whole supercell.[54]

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.
