Interlayer Registry to Determine the Sliding Potential of Layered Metal Dichalcogenides: The Case of 2H-MoS₂

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Supporting Information

ABSTRACT: We provide a simple and intuitive explanation for the interlayer sliding energy landscape of metal dichalcogenides. On the basis of the recently introduced registry index (RI) concept, we define a purely geometrical parameter that quantifies the degree of interlayer commensurability in the layered phase of molybdenum disulfide (2H-MoS₂). A direct relation between the sliding energy landscape and the corresponding interlayer registry surface of 2H-MoS₂ is discovered. A simple fit of the model parameters to capture the sliding energy landscape obtained at different external loads enables the identification and isolation of the prominent interlayer interactions dictating the interlayer sliding physics under different tribological scenarios. The success of our method in capturing the results of complex quantum mechanical calculations along with its high computational efficiency marks the RI as a promising tool for studying the tribology of complex nanoscale material interfaces in the wearless friction regime.

Nanotribology is the science of friction, wear, and lubrication occurring at nanoscale interfaces. Such interfaces often appear in nanoelectromechanical systems (NEMS), which present the ultimate miniaturization of electromechanical devices. One of the main known caveats of NEMS is their low mechanical durability resulting from severe effects of friction and wear on systems that are characterized by a high surface-to-volume ratio. While, in principle, lubrication should reduce such effects, traditional liquid-phase lubricants usually fail to perform under nanoscale-confined conditions as they become too viscous. Thus, one of the primary goals of nanotribology is the design of new materials that will present low friction at the atomic level.

Recent experiments on pristine solid-state layered materials have shown strong dependence of their interlayer sliding friction on the misfit angle where friction was found to nearly vanish when sliding occurred out of registry. This unique phenomenon, termed superlubricity, marks layered materials as promising candidates for serving as active components in NEMS as well as improved solid lubricants for macroscopic devices.

Among the various members of the family of layered materials, MoS₂ and WS₂ have been long known to serve as excellent solid lubricants, and MoS₂ has also recently emerged as a promising candidate for electronic components. Despite the widespread use of these materials as lubrication additives, the experimental and theoretical study of the nanoscopic origin of their tribological behavior remains a very active field of research. Theoretical studies often rely either on molecular dynamics simulations based on appropriately parametrized force fields or on first-principles calculations using advanced density functional theory approximations. While such calculations usually result in remarkable agreement with experimental measurements, their level of complexity may shadow the relation between atom-scale processes and collective tribological material properties. In the present Letter, we derive a simple and intuitive geometrical model that enables the characterization of the interlayer sliding energy landscape of 2H-MoS₂ and directly relates it to the detailed atomic structure and degree of commensurability of the interface.

To this end, we utilize the registry index (RI) concept, which has recently proven to be an efficient and reliable tool for quantifying the registry mismatch in bilayer systems and mimicking their corrugated sliding energy landscape. Within this approach, each atom in the unit cell is ascribed with a circle centered around its position, and the overlaps between the projections of circles assigned to atoms located on one layer with circles associated with atoms belonging to the other layer are calculated. The obtained overlaps are appropriately summed to produce a simple numerical measure of the overall registry mismatch. This numerical value is then normalized to the range [0:1], where 0 represents perfect interlayer registry and 1 stands for the worst stacking mode in terms of the total energy. In the case of graphene and h-BN, where the sliding between two perfect two-dimensional layers is considered, a single circle is ascribed to each atomic layer.
Here, the situation is somewhat more complex as each MoS$_2$ layer is composed of three parallel sublayers (see Figure 1). Therefore, the choice of circle radius has to reflect the distance between each pair of sublayers considered. To this end, we ascribe to each atomic position two radii representing different interactions between sublayers 2,3 and 1′,2′, as described in Figure 1. We mark these radii as $r^\alpha_\beta$ where $\alpha$ is the atom around which the circle is centered and $\beta$ is the corresponding atom on the other layer (see Figure 2). As will be shown below, in order to obtain optimal fitting with density functional theory (DFT) calculations, the following radii are chosen: $r^S_S = 0.9$ Å, $r^{S\text{Mo}}_S = 0.8$ Å, and $r^{M_0}_S = 0.3$ Å.

For the definition of the RI, the optimal and worst (in terms of energy) interlayer stacking modes have to be identified. The optimal (most energetically stable) interlayer configuration is known to be the AA′ stacking mode where S atoms of one layer reside atop Mo atoms of the other layer (see Figure 3a). Starting from this configuration, the worst (highest in energy) laterally shifted interlayer configuration is the AB$_2$ stacking mode, where the positions of S atoms from both layers are fully shifted.

**Figure 1.** Crystal structure of MoS$_2$. (a) Side view of two layers in the optimal AA′ stacking mode, emphasizing the structure of the three sublayers. (b) Top view of a single layer showing the hexagonal crystal symmetry.

**Figure 2.** Projected circle overlaps used in the definition of the RI. (a) $S_{\text{MoS}}$-projected overlap between a circle of radius $r^\text{Mo}_S$ centered on a Mo atom of one layer and a circle of radius $r^S_{\text{Mo}}$ centered on a S atom of the adjacent layer. (b) $S_{\text{SS}}$-projected overlap between two circles of radii $r^S_S$ centered on two S atoms belonging to adjacent layers.
eclipsed and the Mo atoms reside above the centers of the hexagons of the adjacent layers (see Figure 3c). We note that the S−S overlap (SSS; see Figure 2) is maximal at the worst stacking mode, whereas the Mo−S overlap (SMoS; see Figure 2) is maximal at the optimal stacking mode. Since we would like the RI to be maximal at the worst stacking mode and minimal at the optimal stacking mode, we set it to be proportional to the difference between the S−S and Mo−S overlaps, $\text{RI} \propto (S_{SS} - S_{MoS})$. Finally, normalizing this expression to the range $[0:1]$ yields

$$\text{RI} = \frac{(S_{SS} - S_{SS}^{AA'}) - (S_{MoS} - S_{MoS}^{AA'})}{(S_{SS}^{AB_1} - S_{SS}^{AA'}) - (S_{MoS}^{AB_1} - S_{MoS}^{AA'})}$$

where $S_{SS}^{AA'}$ and $S_{MoS}^{AA'}$ are the S−S and Mo−S overlaps at the AA' stacking mode, respectively, and $S_{SS}^{AB_1}$ and $S_{MoS}^{AB_1}$ are the S−S and Mo−S overlaps at the AB_1 stacking mode, respectively.

Once we have a closed expression for the RI, we can calculate it for various interlayer configurations and compare the resulting RI surface to the sliding energy landscape obtained from DFT calculations. To this end, we construct a unit cell of bilayer 2H-MoS$_2$ using the lattice parameters of the bulk crystal (see Supporting Information). The unit cell of the lower layer is multiplied to form a sufficiently large finite sheet, and a single unit cell of the upper layer is then shifted with respect to the finite sheet to represent different relative interlayer positions. At each interlayer position, the RI is recalculated resulting in a full RI sliding surface.

In Figure 4, we present the main result of this study, where the sliding energy landscape obtained under an external pressure of 500 MPa using DFT calculations at the local density approximation level of theory$^{29}$ is compared with the predictions of the RI model. First, we consider the total RI landscape (Figure 4a) as compared to the full sliding energy surface obtained via the DFT calculations (Figure 4b). As can be seen, remarkable agreement between the two surfaces is achieved. The simple RI model is able to fully capture all important physical features appearing in the sliding energy landscape, including all stationary points that occur at high-symmetry interlayer configurations. By construction, the RI model correctly predicts the AA' stacking mode to be the lowest-energy interlayer configuration and the AB_1 mode to be the highest-energy stacking mode. Furthermore, the AB_1 stacking mode, where the positions of Mo atoms from both layers are fully eclipsed and the S atoms reside at the centers of the hexagons of the adjacent layers (see Figure 3b), is found to be a local minimum on the RI landscape, in accordance with its metastable nature obtained via the DFT results. To better appreciate the agreement between the two calculations, we
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ASSOCIATED CONTENT

Supporting Information
Partial coordinates representation of the natural 2H-MoS2 unit cell and Cartesian coordinates of some of its high-symmetry interlayer stacking modes. This material is available free of charge via the Internet at http://pubs.acs.org.

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Figure 5. 2H-MoS2 interlayer RI surface (a) tuned to match the DFT sliding energy landscape at an external pressure of 15 GPa (b). The overall corrugation of the DFT sliding energy landscape is ~1 eV. DFT results were reproduced with the kind permission and help of Prof. S. Ciraci and his co-workers from ref 31. Copyright (2012) by the American Physical Society.

The notable agreement obtained between the RI results and more sophisticated first-principles calculations for 2H-MoS2 further enhances our confidence that sliding energy landscapes of layered materials, however complex they may be, can be well-captured by simple models based on geometrical considerations. These, in turn, may provide an intuitive description of the physical processes underlying wearless friction in complex layered structures as well as an efficient means for modeling the tribological behavior of complex nanoscale material interfaces under various external conditions.

To summarize, in this work, we have defined the RI for layered metal dichalcogenides, focusing on the layered phase of MoS2. Unlike the case of few layered graphene and hexagonal boron nitride,32,33 where each layer is composed of a single flat sheet of atoms, 2H-MoS2 has an intricate sublayer structure that reflects on its tribological properties. Despite the involved network of interlayer interactions between different sublayers, the RI is able to provide an accurate description of the interlayer sliding physics in 2H-MoS2 at a fraction of the computational cost of first-principles calculations. On the basis of these results and the experience accumulated with the RI thus far, we believe that our suggested model can be applied for other members of the family of metal dichalcogenides, such as the layered phase of WS2, and may also be expanded to describe their tubular counterparts.32 The conclusions of the present work further affirm the robustness of the RI concept as an intuitive, flexible, and computationally efficient tool for studying nanoscale tribological characteristics of complex layered structures at the wearless friction regime.
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**REFERENCES**


(35) The interactions with sublayers 1 and 3 are neglected due to their relatively large distance and the expected screening effects induced by the inner layers.

(36) We find that the sliding friction is captured well without considering Mo–Mo overlap contributions; we therefore choose \(r_{\text{MO}}^\text{MO} = 0\).

(37) We note that here we are comparing higher-pressure PBE results to lower-pressure LDA results. Nevertheless, the corrugation of the sliding energy landscape can be mainly attributed to Pauli repulsions between overlapping electron clouds of atoms belonging to two adjacent layers as they cross each other during the sliding process. These repulsions are well-captured by both functional approximations in the short–middle range regime, and therefore, the overall effect of the choice of functional approximation for the study of the sliding friction at such high external pressures is expected to be small.