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Friction anisotropy and asymmetry in self assembled monolayers ☆

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ABSTRACT

Experiments with molecularly thin self assembled monolayers have suggested existence of friction force anisotropy and asymmetry. Here molecular dynamics simulations are used to study friction anisotropy and asymmetry between two self assembled monolayers (SAM) of n-alkanethiols [$CH_3(CH_2)_{n-1}S$, $n=14$] attached on Au (111) substrates. The simulations show the existence of friction anisotropy and asymmetry in agreement with some of the experimental works in literature. Friction shows dependence on the relative direction of sliding and monolayers tilt direction. The origin of this friction anisotropy is discussed. The friction asymmetry depends on the direction of sliding and is significant in the direction of the tilt. On this "molecular carpet" interestingly, it is easier to slide against the nap (tilt direction) than in the direction of the nap (tilt direction).

1. Introduction

Reports of friction anisotropy at macroscale go back several decades [1]. Rabinowicz reported that for some macroscopic contacts transverse friction force ($F_\perp$) can be as much as ~2–5% of the axial friction, $F_\parallel$ (friction force in the sliding direction). It has been demonstrated that non-zero transverse friction may arise from friction anisotropy [2]. Examples of friction anisotropy in mega/macro/micro/nano scale are ubiquitous in technological [3,4] and natural [5] contexts, such as between tectonic plates, in micro engineered surfaces [3], in carbon nanotube [4] and for quasicrystalline surfaces [6]. Frictional anisotropy refers to varying friction based on orientation, therefore it can be considered as directional friction (see Fig. 1a). Snakes crawl by effective utilization of friction anisotropy of their skin which is caused by preferred orientation of macroscale skin structures (scales). Understanding friction anisotropy is especially crucial in nanofabrication processes where determining preferred sliding and assembly pathways of interacting components is necessary. Although a transverse force due to friction anisotropy might be negligible for macroscopic contacts, at nanoscale it may become appreciable and of the same order of magnitude of the axial friction force. Molecular simulations have shown transverse motion due to friction anisotropy in sliding of hexagonal MoS_2 flakes [7]. At the molecular scale experimental works have also reported appreciable transverse component of friction force for molecularly thin lubricant films of linear alkanes confined between mica surfaces [2]. This experimental work conducted by a modified surface force apparatus (SFA) has shown that for free sliding (not constrained laterally) anisotropic friction can induce axial as well as transverse displacement of the slider which is then used to measure the axial and transverse components of the friction. Using molecular simulations, the author has recently reported the structural origin of such phenomena for linear and branched molecularly thin alkanes [8].

Self assembled monolayers (SAMs) are another class of important molecularly thin films which have emerged as potential means for lubrication and protective coatings in micro/nano scale devices. Therefore understanding friction anisotropy and asymmetry of surfaces covered by SAMs are very important to devise efficient assembly and operation pathways for device components. Park et al. have reported eight-fold friction anisotropy for the surface of decagonal AlNiCo quasicrystal when the direction of sliding of alkanethiol passivated atomic force microscope (AFM) probe is changed from periodic to aperiodic direction of the surface [6]. Molecular dynamics simulations have been used to study friction anisotropy for bare quasicrystalline surfaces [9]. Recent molecular dynamics simulation [10] works have suggested the observed frcition anisotropy in Park et al. experiments could be due to presense of SAM molecules on the AFM probe, and have demonstared that the actual anisothropy in their absense is very small. The friction anisothropy of quasicrystalline surfaces is an ongoing debate which is not the focus of the current work presented here. However it gives an example of areas where friction anisotropy due to presence of monolayers may play a role.

Friction asymmetry refers to cases where reversal of sliding direction (by 180°) causes a change in friction force (see Fig. 1b).

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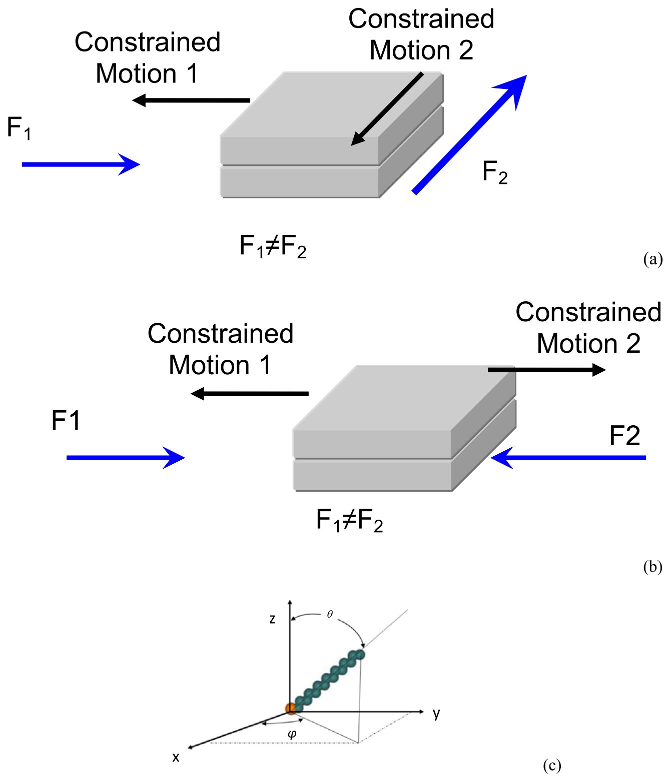

Fig. 1. (a) Friction anisotropy can be detected by observing variation in friction when the direction of a constrained sliding (or equivalently relative orientation of the two surface) is changed. The schematic shows change in the relative motion direction resulting in unequal friction forces ($F_1 \neq F_2$), a sign of friction anisotropy. (b) Friction asymmetry is seen by unequal friction force when the direction of sliding is reversed by 180°, (c) definition of the tilt (θ) and tilt orientation (ϕ) angles shown for a single SAM molecule.

Experimental evidence of friction anisotropy and asymmetry has been reported for self assembled monolayers (SAM) [11–14]. The structure of saturated self assembled monolayers at temperatures below their melting point is often characterized by their tilt angle (θ) and collective direction of this tilt (ϕ) (see Fig. 1c). Therefore it is essential to understand the relationship between friction and the sliding direction with respect to this structural parameter namely the tilt angle direction (ϕ).

Some works in the literature have reported anisotropy and lack of asymmetry for polydiacetylene monolayers [11]. Whereas both friction anisotropy and asymmetry [12] are reported for alkanethiol self assembled monolayers. For polydiacetylene monolayers 300% friction anisotropy is reported however no friction asymmetry was observed [11]. In contrast for alkyl lipid monolayers, experiments by Liley et al. showed both friction anisotropy and friction asymmetry [12]. In the work conducted by Liley and coworkers bare AFM tip was moved against the monolayer and it was shown that friction was larger for sliding perpendicular to the direction of the tilt than that for sliding parallel to the tilt. Dependence of friction on the sliding direction relative to the monolayers tilt direction is also reported for monolayers of oligothiophene (C14-5TBA) on mica [13]. Molecular dynamics simulations conducted by Ohzono et al. for friction between an AFM-like tip and a single alkanethiol monolayer found friction anisotropy only at very low temperature of 50 K, and anisotropy vanished at higher temperature of 200 K. [15].

For most practical tribological applications relevant to micro/nano device assembly one would expect to have both surfaces covered by SAMs. Therefore, understanding friction anisotropy and asymmetry between two surfaces coated by SAMs is very important from both practical and fundamental tribological point of view. In this article anisotropy and asymmetry between two surfaces coated by alkanethiol self assembled monolayers will be studied at room temperature using molecular dynamics simulations. The results here show that both friction anisotropy and asymmetry are present for SAM on SAM sliding configuration; however the direction at which the friction is maximum differs from that obtained for AFM on SAM configuration reported in experiments. In agreement with experiments [12,14] the friction asymmetry depends on the relative direction of sliding and tilt orientation angle. It is found that asymmetry is significant when the sliding direction is almost parallel to the monolayer tilt direction, and friction is lower when sliding is against this tilt direction.

2. The model and methodology

2.1. Molecular models

Self assembled monolayers (SAM) of thiol based alkanethiol (CH_3 $(CH_2)_{n-1}S$) [n=number of carbon atoms], were simulated using a united atom model, whose interaction potential details are given elsewhere [16]. In this model groups of CH_2 and CH_3 and S are treated as single interaction sites. The flexible molecular model also includes intramolecular interaction potentials of bond stretching, angle bending, and torsional potentials [17]. In the simulations performed here the two gold surfaces in contact were covered at saturation density by tetradecanethiol ($CH_3(CH_2)_{13}S$), which will be referred by its number of carbon atoms, C14 for brevity. Details about the method of preparation and simulation protocols can be found in previous works [16,18–22].

A 6–12 Lennard-Jones (LJ) potential is used to model the interactions of united atoms on different molecules and also between those on the same molecule that are not interacting via intramolecular potentials mentioned before. This LJ potential is shifted and cut off at a distance of $r=2.5\sigma$ (0.983 nm) in the simulations. Lorentz-Berthelot's combining rules [$\varepsilon_{ij}=(\varepsilon_i\ \varepsilon_j)^{1/2}$ and $\sigma_{ij}=(\sigma_i+\sigma_j)/2$] are used for interactions of unlike united atoms.

2.2. Modelling the gold substrate

The SAM monolayers are constructed on crystalline gold Au (111) substrates. Each crystalline gold substrate has four layers of (111) faces of fcc (face centred cubic) lattice structure with a lattice constant of 0.408 nm and the nearest neighbor distance of 0.288 nm. Dimensions of this gold substrate were 7.790 × 7.495 nm in the lateral (x–y) directions. Density and atomic weight of gold are respectively 19.32 g/cm^3 and 196.97 amu. Both Au(111) surfaces were coated by a C14 monolayer at the same saturated coverage density.

The interaction of the gold atoms and alkanethiol united atoms is also governed by the 6–12 Lennard-Jones potential described before. The LJ interaction parameters for gold atoms are ($\varepsilon_{Au}/k_B=$ 990 K) and $\sigma_{Au}=0.2655$ nm, which yield energy and length parameters for the interaction of CH_2 and Au of $\varepsilon_{Au\text{-}CH2}=1.795$ kJ/mol and $\sigma_{Au\text{–}CH2}=0.328$ nm. These values which were obtained by fitting the calculated and experimental desorption data of alkanes from metal surfaces, were adopted from ref [23]. In all simulations gold atoms were kept fixed with respect to their lattice position.

2.3. Simulations of SAMs in sliding contact under constant loading

The self assembled monolayers (SAMs) are initially equilibrated on each gold substrate before bringing the two substrates into contact under constant normal load conditions at $P=300$ MPa.

Constant load simulations were conducted using a Nose