Single layer graphene induces load-bearing molecular layering at the hexadecane-steel interface

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Abstract

The influence of a single layer graphene on the interface between a polished steel surface and the model lubricant hexadecane is explored by high-resolution force microscopy. Nanometer-scale friction is reduced by a factor of three on graphene compared to the steel substrate, with an ordered layer of hexadecane adsorbed on the graphene. Graphene furthermore induces a molecular ordering in the confined lubricant with an average range of 4–5 layers and with a strongly increased load-bearing capacity compared to the lubricant on the bare steel substrate.

Keywords: atomic force microscopy, graphene, molecular layering, nanotribology

(Some figures may appear in colour only in the online journal)
is connected to an ordered layer of adsorbed hexadecane molecules and that the graphene induces an ordering in molecular layers in the confined liquid above graphene patches.

2. Experimental

Stainless steel samples (X5CrNi18-10) were polished using diamond paste and colloidal silica suspension to a roughness of 0.78 nm rms as determined by AFM. Graphene was transferred to the steel surface via a dry-transfer process using a 0.78 μm thick Cu foil through a CVD process. The graphene/Cu foil was laminated on the carrier film that consisted of thin polydimethylsiloxane (PDMS) layer on polyethylene terephthalate (PET) film. Then, Cu was etched with ammonium persulfate (APS) and the graphene on PDMS/PET was transferred to the steel surface. The successful transfer of graphene was proven by high-resolution friction force microscopy images exhibiting the periodicity of the honeycomb lattice (data not shown).

All AFM measurements were performed at room temperature using an Agilent AFM 5500 with a home-built fluid cell where the cantilever is fully immersed in hexadecane (Sigma-Aldrich). Molecular sieves with a pore diameter of 0.3 nm were added to the hexadecane in order to minimize the water content. Rectangular silicon cantilevers (PPP-CONTR, Nanosensors, Neuchâtel, Switzerland) with a backside reflective aluminum coating, a nominal spring constant of 0.2 N m⁻¹, and a nominal tip radius <10 nm were used. The individual spring constants were determined using Sader’s method [15]. To record force-distance curves, the cantilever was approached slowly (v < 2 nm s⁻¹) to the substrate surface until reaching a predefined maximum force and then retracted. The cantilever deflection was calibrated by determination of the slope of the force curve when the tip was in contact with the substrate. Lateral force were measured as the twist of the cantilever when scanning the tip in contact over the surface [16].

3. Results

Topography and friction contrast of the transition between a graphene flake and the steel substrate is shown in figure 1. The topography is dominated by the roughness of the steel substrate, to which the graphene layer adapts, and by folds in the graphene layer. While there is no particular contrast in the topographic features between graphene and steel substrate, the lateral force is significantly lower on graphene. We observe that in this boundary-lubrication regime, friction on steel in the model lubricant hexadecane is reduced by a factor of three on a single layer graphene. We will show in the following that the low-friction interface is an ordered layer of hexadecane on graphene.

Exemplary tip-approach curves for steel and graphene are compared in figure 2(a). The normal force is plotted as function of the tip-sample distance. The layering of hexadecane is revealed by a series of steps. A certain normal force is required to penetrate each molecular layer. In the example for graphene, the tip advances from the fourth to the third layer at a force of 0.15 nN, from the third to the second at 0.35 nN, from the second to the last remaining layer at 1.75 nN. The tip does not penetrate the last layer at the forces applied in these approach curves, as we will discuss below. We have limited the maximum normal force to protect the tip integrity. Experiments on graphite have also reported forces larger than 5 nN for the penetration of the last layer of hexadecane, which was confirmed by simultaneous measurements of the electrical resistance between tip and sample [17].

The force steps are result of a tip-sample interaction potential which oscillates as function of the distance. This potential arises from molecular density fluctuations in the confinement. The resulting solvation forces acting on confining asperities have been predicted for linear alkanes by molecular dynamics simulations [18]. The distance jumps can be predicted by comparing the slopes of an exponentially decaying oscillatory solvation force with the cantilever stiffness [19]. The equilibrium character of the layering is revealed by the observation of jumps back and forth between the third and the fourth layer in figure 2(a) at a force around 0.25 nN. The average distance between the force jumps of 0.45 nm agrees with the expected width of the hexadecane molecule and reveals that the molecules arrange parallel to the confining surfaces. The histogram of tip-sample distances in the background of figure 2(a) visualizes the position of the layer. A small peak at a distance of 2.2 nm indicates even a fifth layer of hexadecane.
On steel, only two layers are distinguished in the force curve, where the transition from the second to the last occurs below 0.05 \( \text{nN} \) and from the last to the substrate at about 0.1 \( \text{nN} \).

Molecular layering was observed in 95% of the approach curves recorded on graphene and in 80% of the ones recorded on the steel substrate. A statistical evaluation of the range of tip-sample distances in which layering can be distinguished is provided in figure 2(a). The parameter \( n \) counts the number of hexadecane layer between tip and sample. (b) Histograms of the layering range, i.e. the distance from the sample up to which molecular layering was observed. These histograms represent the results of many approach curves.

![Figure 2](image)

Figure 2. Summary of molecular layering of hexadecane on graphene and stainless steel. (a) Exemplary force-distance curves on graphene (black) and steel (blue). The shaded histograms in the background indicate the probability to find the tip at a certain distance from the sample during approach. The parameter \( n \) counts the number of hexadecane layer between tip and sample. (b) Histograms of the layering range, i.e. the distance from the sample up to which molecular layering was observed. These histograms represent the results of many approach curves.

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We will now discuss the last layer of hexadecane on graphene, which is not displaced by the tip at forces up to 5 \( \text{nN} \). Evidence for its stability and its structure is given by high-resolution friction force microscopy results in figure 3(a). The lateral force map reveals an arrangement of the hexadecane molecules in form of lamellae. The width of each lamella is 2.1 nm, close to the expected length of hexadecane. A cross-section of the lateral force indicates eight molecular-scale features across the lamella, from a structural point of view one for each ethylene group of the hexadecane molecule. The lamellae have been observed before by force microscopy [17, 20] and structural details have been resolved by scanning tunneling microscopy [21]. They have also been predicted in atomistic modeling of the adsorption [22]. In contrast, no comparable molecular order is observed in lateral force maps recorded in hexadecane on the steel substrate. We conclude that the lamellar order is induced by specific interaction of hexadecane with graphene, while the irregular stick-slip pattern in the lateral force originates in direct interaction of tip and amorphous oxidized steel surface.

![Figure 3](image)

Figure 3. High-resolution lateral force maps recorded in hexadecane with a normal force of 3 \( \text{nN} \). (a) On graphene, the adsorbed hexadecane molecules arrange in form of lamellae with a width of 2.1 nm. The cross-section was taken along the line indicated. The schematic depiction of the orientation of one hexadecane molecule is informed by the results in [21]. (b) On the steel substrate, an irregular stick-slip pattern with a characteristic slip length of about 1 nm is observed. The two cross-sections are taken the along the lines indicated in the respective color.

4. Conclusion

A single layer of graphene on steel surfaces causes a change in the near-surface structure of the model lubricant hexadecane. Hexadecane adsors in an ordered layer aligned straight molecules, and this layer is stable under scanning in contact with the tip of an atomic force microscope, while no such layer is observed on the steel substrate. Graphene and hexadecane layer reduce friction at the nanoscale by a factor of three compared to the bare steel in hexadecane. Furthermore, graphene introduces a pronounced structuring into four to five layers of hexadecane aligned parallel to the surface. Only two such layers are observed on the bare steel substrate. The normal load that can be borne by the last two layers in
this quasi-static boundary lubrication increases by a factor of at least 50 on graphene. These effects can be observed despite the fact the roughness of the substrate is replicated by the graphene topography. We conclude that specific interactions between the alkane chains and graphene lead to the dramatic increase in order and load-bearing capacity of the solvation forces. The enhancement of molecular layering by graphene due to specific molecular interaction has previously been reported for an ionic liquid, where the cations adsorb preferentially on graphene [23]. An enhanced layering has been observed for various liquid lubricants on graphite compared to other substrates [24], so that the effects of graphene on hexadecane can be expected to contribute also in formulated oils.

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