

Monolayer Transfer Layers During Sliding at the Atomic Scale

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Abstract One of the fundamental issues in friction is understanding the atomic details of how two materials slide against each other and start to wear. Whether this involves single-atom processes or the collective motion of atoms has been open to debate for some time. Here we report direct observations of this via in situ studies within a transmission electron microscope. We observed for both graphite and molybdenum disulfide that single atomic layers are transferred from the material to a sliding tip to form a transfer layer, and subsequent sliding takes place by sliding of single layers of graphite or molybdenum disulfide against each other. Despite the similarity of the end result, how the single layers are formed is quite different; with graphite, it involves buckling/wrinkling ~ 3 nm ahead of the tip, whereas with molybdenum disulfide it is via direct transfer of single sheets. Graphite is more like plastic wrap, molybdenum disulfide more like a pack of cards. This difference is attributed to the large difference in the bending modulus and strength of monolayers in the two cases. In both cases, collective processes are taking place.

Keywords Friction · Graphite · Monolayer · Lubrication · Wear · In situ · TEM

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1 Introduction

Friction is a pervasive problem, by some estimates consuming about 5 % of the GDP of the economies of the developed world, and a recent analysis has indicated that about one-third of the fuel energy in automobiles goes to overcoming frictional losses. While the importance of minimizing friction can be traced back at least as far as the tomb of Tehuti-Hetep, circa 1880 BC, where a man can be seen pouring a lubricant to assist moving a statue [1], there are still many unknowns in the field of tribology which encompasses friction as well as other critical processes such as wear and lubrication. With the introduction of the asperity model by Bowden and Tabor in the 1960s [2], it started to become clear that many of the fundamental processes taking place occurred at the micron to nanoscale, and perhaps even at the atomic scale. There have certainly been many advances since the 1950s both in the development of continuum-level models for plastic and elastic deformations [3–5], hydrodynamic models for lubrication [6], models for sliding processes taking place at the nanoscale involving dislocations [7, 8] as well as sophisticated atomistic simulations [9–12] and in the experiments such as those using atomic force microscopy [13].

It is generally accepted that solid on solid friction involves sliding processes taking place at the atomic and/or nanoscale. Often the triboactive region, that is the region where the sliding takes place, involves additional material such as wear particles (called third bodies) or layers of materials transferred from one material to another (called transfer layers). The importance of these was first recognized by Godet [14] and Singer et al. [15], and there are numerous forensic reports supporting their importance. Two notable observations are the formation of monolayers of crystalline MoS₂ following sliding by Dunn et al. [16]

and of somewhat thicker transfer layers in some elegant experiments by Hu et al. [17]. These results suggest that in many cases wear is a phenomenon which takes place at the fundamental atomic scale, although it is often more convenient to analyze it at a larger size scale ranging from nanometers to microns.

The issue of the fundamental size scale where frictional processes take place has been a topic of some debate for many years, due in large part to what has been called the buried interface problem. The triboactive layer is almost always hidden by the materials on both sides of it, so the exact details of what is occurring are often only accessible by post facto analyses and sometimes a matter for debate. While there have been several attempts to image the triboactive layer directly at the atomic scale dating from the original work by Gane and Bowden [18], progress has been slow; for a brief history see [19] and for some more recent work [20]. A range of processes have been inferred by

some authors to take place atom by atom [21–24]. For instance, there are indications of single-atom detachment due to adhesive forces in some scanning probe experiments [23], which can be contrasted with the well-known scotch-tape method of forming graphene films [25] which can only be a collective process.

2 Experimental

Sliding experiments were performed in a JEOL 2010F, equipped with a field emission gun and an ultrahigh-resolution pole piece, by utilizing an AFM-TEM holder from Nanofactory Instruments AB. The sample was prepared by cutting a 0.5-mm gold wire; then, a conductive epoxy was applied to the tip of the wire. Repeated peeling using scotch tape was used to obtain thin graphite in a similar way as to obtain graphene [25]. Finally, the tip of the gold

Fig. 1 Transfer of monolayer graphite to the AFM tip. The top monolayer was attached to the tip in the slide direction as arrowed in red (Color figure online)

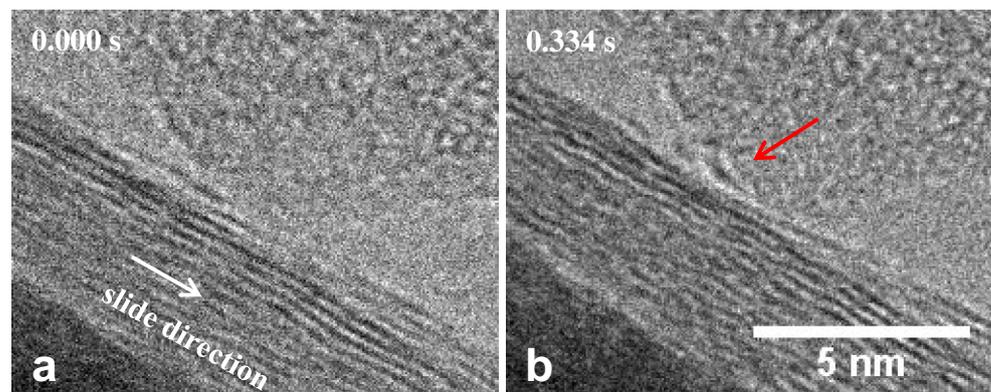
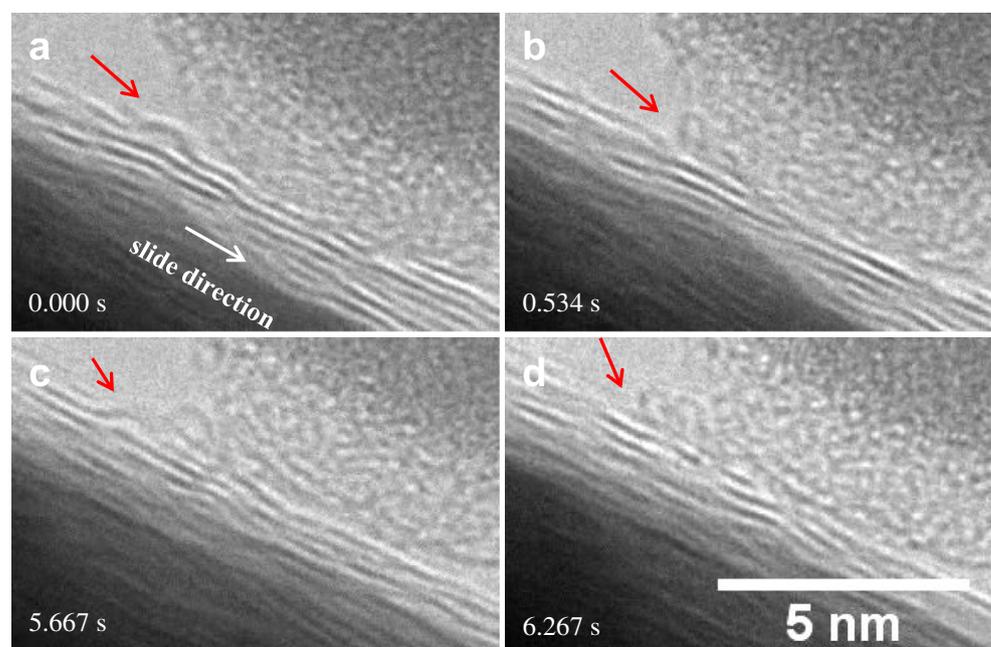


Fig. 2 Buckling of the top sheet in the slide direction as arrowed in red (Color figure online)



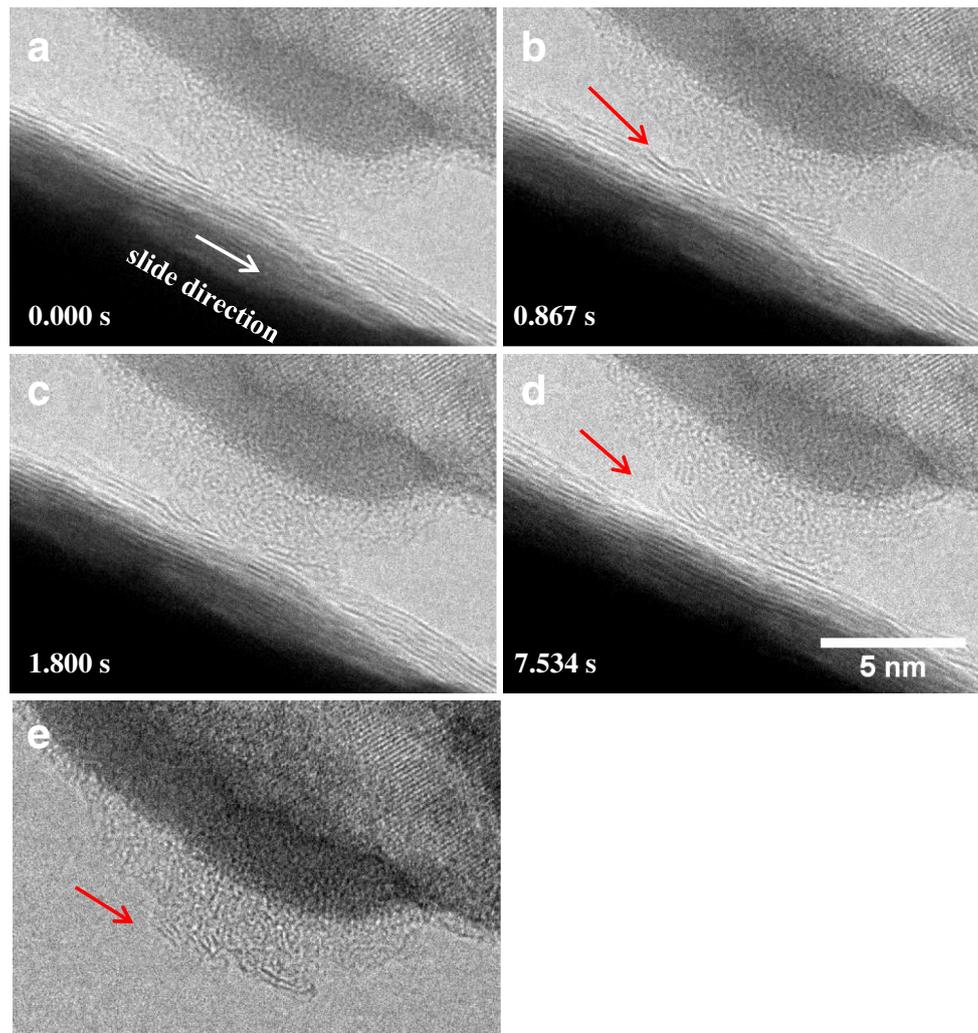


Fig. 3 In one occasion, three layers were transferred to the tip. Again, the transfer was initiated by buckling of the top monolayer at $t = 0.867$ s

wire with the epoxy was gently pressed on to the scotch tape, leaving behind flakes of graphite. The gold wire then was mounted onto the gold hat which subsequently is positioned in the AFM-TEM holder. The electron dose was kept to a minimum in order to avoid damage to the graphite. A silicon tip with a spring constant $k = 2.3$ N/m was used for these experiments. This holder enables the manipulation of the sample by means of piezo elements. Its piezo resolution is 0.2 \AA in the XY and 0.025 \AA in Z. Images were recorded using an AMT CCD camera with an exposure time of 0.067 s per frame.

3 Results and Discussion

This note reports direct in situ observation of atomic sliding of a silicon tip on graphite and molybdenum disulfide (MoS_2). We are able to directly verify a commonly

postulated process during sliding on these layered materials, namely the formation of a single atomic transfer layer on the tip, followed by interfacial shear between the transfer layer and the remaining graphite or MoS_2 on the substrate. This is not an atom-by-atom process, but instead involves collective motion. However, how the monolayer forms is very different. With graphite, the transfer process involves buckling of the material ahead of a sliding tip following by adhesion of single or in some cases a few layers to the silicon tip, whereas with MoS_2 it involves direct transfer of monolayers.

All the experimental results we will show used a typical AFM tip made out of silicon with a protrusion of diameter ~ 5.6 nm; the surface had been oxidized as can be seen in the static high-resolution TEM image shown in Figs. 1, 2, and 3. The normal pressure was determined to be 150–500 MPa based on the displacement of the tip from its rest position (Fig. 4).

The steady-state sliding for both materials is similar, and by carefully tracking single frames from the videos, it occurred by interfacial shear between a single layer attached to the tip and material adhered to the substrate as shown in Fig. 1, with videos of representative time sequences in Video 1a (graphite) and 1b (MoS_2). The monolayer transfer layers were observed for both materials in five experiments so appears to be a general phenomenon. However, since the materials are quite inhomogeneous with defects, transfer of two or several layers was occasionally observed.

In contrast, how the monolayer forms on the tip was quite different. For the MoS_2 in all cases we observed a relatively long (5–20 nm) and flat monolayer became adhered to the tip and then detached from the substrate as shown in Fig. 2 and video V2. While there was some slight bending of the monolayer, it was minor. Due to the slow rate of the video (15 frames/second), we were not able to observe any of the single-atom or collective fracture processes associated with the detachment. These can be expected to occur fast, some reasonable fraction of the speed of sound which translates to less than a microsecond.

The monolayer formation process with graphite was smaller in size. In all cases, graphite sheets ~ 3 nm (20

atoms) ahead of the sliding tip either buckled or became trapped in front of the sliding tip and then compressed in the region between the tip and substrate as shown in the series of single frames of Fig. 3 and video V3.

Of a total of five sliding experiments, four showed a single monolayer transfer. However, since graphite is often an inhomogeneous material, it should not be surprising that the other experiment was slightly different; for instance, three transfer layers were observed as shown in Fig. 3 (taken from video V3). The tip sliding direction is arrowed in white. One layer of graphite was buckled at $t = 0.867$ s. In ~ 7 s, a fragment of 3–4 graphite layers were piled up ahead the tip in the sliding direction ($t = 7.534$ s). When the tip was retracted from the graphite, a ~ 1.4 -nm-long segment consisting of three graphite layer was transferred to the tip.

The end result for the two materials is exceedingly similar, predominantly a single monolayer transfer layer with the important triboactive region being just one layer away from the surface of the tip. Of course this is for the experimental conditions we used. Almost all sliding experiments are inhomogeneous with the results at the macroscale appearing to be somewhat reproducible, but do not have to be fully reproducible at the atomic scale. Hence, if the load and contact areas were varied by orders of magnitude, the exact details may easily change, but we see no reason to believe that the fundamental nature of the sliding would.

Why then is the formation mechanism so different? We will argue that the bending modulus and strength of the two materials are associated with the deformation. Single MoS_2 sheets contain three layers, Mo in the center and bridging S on either side. This makes it harder to bend (high bending modulus), and beyond some angle, it will fracture. By comparison, single sheets of graphite (i.e., graphene) can be relatively easily bent and indeed crumpled, rather like sheets of paper [26]. The formation of a flat transfer layer is associated with crumpled regions being trapped in front of the advancing tip.

The results we have presented here verify some of the fundamental processes taking place that have been inferred from less direct experiments and clearly point to collective processes being critical rather than isolated single-atom phenomena. Our results also point to the atomistic processes with real asperities being somewhat complicated. For instance, the presence of atomic steps, second phases, dislocations, and boundaries in real materials will add additional layers of complexity that will require substantially more work to unravel.

In summary, sliding in layered systems such as graphite or molybdenum disulfide takes place at the single atomic layer level, and the direct imaging data demonstrate that single layer transfer is effective during sliding, which can

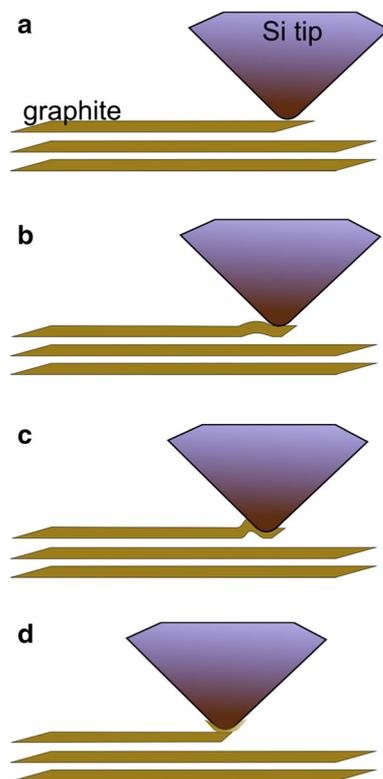


Fig. 4 Schematics showing buckling and graphite sheet transfer. The tip slides from the right to the left. **a** The buckling tends to nucleate ahead a defect formed in previous slide passes. **b, c** Buckling of the topmost layer. **d** Buckle fracture and film transfer to the silicon tip

be the origin of excellent lubricity. The processes involved require the cooperative motion of multiple atoms at the nanoscale, not single atoms, and it is these nanoscale processes which lead to the macroscopic behavior of materials during sliding and wear at the macroscale. The precise details of the collective processes will vary from system to system, here the formation process being quite different.

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