The origins of friction and the growth of graphene, investigated at the atomic scale

Baarle, D.W. van

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Summary

On the origins of friction

The friction behaviour of an interface between two macroscopic bodies that are pressed against each other, is determined by the collective behaviour of all the individual micro- and nanocontacts that together define the physical contact between the two bodies. A popular method to study the friction of such a nanocontact experimentally, is the use of a Friction Force Microscope (FFM). The conventional interpretation of the FFM-data relies on a sophisticated version of the Prandtl-Tomlinson model. This classical model is very successful in reproducing many features of atomic-scale friction experiments. However, the one thing that it cannot do is to provide a true physical understanding of the origin of the friction force as it simply assumes instantaneous loss of the excess potential energy in every slip event. More sophisticated models, based on a Langevin equation, introduce an energy dissipation rate, but this quantity is usually employed as a mere fitting parameter, again revealing nothing about the microscopic energy loss mechanisms at play.

In the work described in this PhD thesis, an atomistic approach was taken, starting from an estimate of the dissipation rate that should be expected from a single atom. This estimate, in combination with reasonable assumptions concerning the scaling of dissipation at the nanoscale, allowed us to calculate the friction force experienced by a tip that is moving over a substrate at a certain velocity. Our estimates showed that typical dissipation rates are in the order of 10^{-12} kg/sec. Comparison with values in literature that are obtained by taking the dissipation rate as a fitting parameter in the Langevin equations, yielded a discrepancy as large as six orders of magnitude. The origin of this discrepancy was found to hide in the choice for the mass of the tip apex that is deformed significantly during the stick phase of the characteristic stick-slip motion that results in a friction force. We argued that this mass corresponds to a very modest number of atoms that is associated with the very end of the tip apex, twelve orders of magnitude smaller than the mass of the entire tip plus cantilever that may follow the motion of the apex, but always with a significant delay. The experimentally found value for the effective spring constant agrees with our picture of a very small, flexible and dynamic mass. Due to this small mass, the tip apex acquires extremely high velocities, which enables the tip apex to dissipate the released slip energies with extreme efficiency. Our findings are in agreement with the observed atomic-scale stick-slip behaviour in many experiments, that can only be described by an approximately critically damped motion.

In order to test the validity of our arguments, we constructed a two-mass-two-spring model as a more refined description of the FFM experiment with a flexible tip, dragged over an atomically corrugated surface. In accordance with the ideas summarized above, we associated a very small dynamic mass with the tip apex. The numerical calculations resulted in friction force maps that showed a surprisingly limited regime of tip configurations for which atomic periodicities were observed clearly. This regime was characterised by a specific ratio between the number of atoms present in the tip-surface contact and the number of atoms in the dynamic mass. Based on this ratio, the situations of critically damped, underdamped and overdamped motion could be coupled directly to the tip apex geometry. Additionally, the numerical model allowed us to study various aspects of the experiments done with the FFM. Typical observations of the lateral deflection of the cantilever and determined Q-factors could be reproduced and explained, which should be regarded as new insight into the origin of friction, introduced by our approach.

Based on our theoretical model of a friction contact and on the calculation results, a friction ‘phase’ diagram was constructed. We conclude that most tips used in AFM- and FFM-experiments have geometries that make the tip apex naturally critically damped, which explains why regular stick-slip motion is readily observed. Deliberate construction of asperities with a geometry that would lead to low-friction contacts, may provide a way to even tune the friction of macroscopic surfaces.

Graphene growth on Ir(111)

To improve the quality of synthesized graphene, and to improve our understanding of nanolayer growth, the growth of graphene on Ir(111) was studied in real time by a Scanning Tunneling Microscope (STM). As the synthesis of graphene on Ir(111) requires a substrate temperature of more than 950 K, a variable temperature STM (VT-STM) was used. With this apparatus, the nucleation, ripening and growth of graphene could be studied while the temperature was being changed deliberately.

First, the evolution of the Ir(111) surface was studied after exposure to ethylene. While the temperature was increased from room temperature up to approximately 1000 K, the substrate was followed by the STM. Several structural rearrangements were observed, after which the adsorbate layer finally converted into graphene at a temperature of 967 K. Further annealing to approximately 1000 K led to an iridium surface only decorated with structures containing moiré-patterns. The moiré patterns indicated that, at 1000 K, most graphene islands were perfectly aligned with the substrate, and that half moiré units of graphene were the smallest stable configuration of graphene at a temperature close to its nucleation temperature.

In addition, the growth of graphene at a temperature of 1180 K was studied at sub-moiré-unit level by the STM. The observations showed that the growth of graphene islands on iridium is characterised by a two-step process: first, the graphene edge is decorated with finger-like structures with the length of an entire moiré unit cell. Second, the space between the fingers is filled up with graphene, at which point the edge has acquired an extra row of moiré unit cells. This growth behaviour showed that the local interaction between graphene and the iridium surface atoms plays a decisive role in the graphene growth process. As a consequence, the two edge types of graphene islands on Ir(111) evolve non-equivalently.

We have also addressed the ripening process of graphene on Ir(111), a subject that had not been reported before in the literature. For this, we have studied the evolution of small graphene islands during a slow temperature ramp between 1000 and 1036 K. Although the average size of the graphene islands increased and the total graphene coverage was constant, no mobility of entire graphene islands was observed. The spatial distribution of graphene islands, in combination with the island size distributions showed that graphene on iridium ripens via the attachment-limited Ostwald ripening mechanism.

When individual islands in the graphene overlayer merge, the risk of the formation of defects at the resulting domain boundaries is very high, especially when islands are misaligned. To investigate this effect for the graphene-Ir(111) system, we studied the closure of the graphene film on iridium at temperatures between 1067 and 1107 K while the surface was exposed to an ethylene partial pressure of 7×10^{-8} mbar. At the point where graphene domains grew together, graphene was found to avoid the formation of boundary defects by the introduction of long-range strain inside the graphene domains. We expect that the introduction of strain has much less impact on the physical and chemical properties of the graphene layer than series of point defects, such as dangling bonds, 5-rings or 7-rings. Hence, this effect should be regarded as beneficial to the quality of synthesized graphene.

Finally, the behaviour of iridium underneath graphene was studied, again at high temperature. In this context, we observed the growth of graphene over iridium step edges, typically climbing upwards from the lower to the higher terrace. No loss of quality of the graphene layer was observed. We also studied the fluctuations of the iridium steps underneath a graphene overlayer. Advancement of iridium steps buried by graphene was observed, in a way that suggested that iridium atoms can easily slip under the graphene at specific locations. The shape of the mobile iridium steps was strongly dominated by the moiré lattice, as macro-kinks with a width of the full moiré unit cell were observed. In case the iridium was not aligned with the moiré lattice, strong fluctuations of the iridium steps were observed, which involved the relocation of hundreds of iridium atoms over several nanometers within milliseconds.