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Summary

The phenomenon of friction forms one of the oldest subjects in the history of science and engineering. Even now, many intriguing questions remain to be answered about the contact dynamics of solid interfaces and their behavior at different geometrical scales and under different atmospheric and lubrication conditions. With ever more demanding requirements to efficiency and lifetime of nano- and microelectromechanical systems and to other high-tech devices, the importance of understanding and control of friction and wear increases too. Growing technological requirements for ultra-low friction and wear-rate coefficients as well as precise motion control open new horizons for research into new, revolutionary concepts in lubrication.

In this PhD thesis, I described our work towards reduction and control of dry friction with solutions that promise to meet some of the challenges set by modern technology. In particular, I demonstrated three attempts to make unique nanoscale lubrication phenomena active on the macroscopic scale. In **Chapter 2**, I introduced first experiments to reduce friction in macroscopic contacts, employing the atomic-scale effect of thermolubricity. We used arrays of silicon nanopillars (NPs) that were dimensioned such that each would mimic the mechanical behavior of the apex of a single tip in a Friction Force Microscope (FFM): namely combining a high lateral vibration frequency with a relatively large thermal vibration amplitude, of a significant fraction of an interatomic distance, at room temperature. In **Chapter 3**, I demonstrated how to apply conventional cleanroom techniques to produce large, highly reproducible and well-ordered arrays of such NPs. The philosophy behind the NP approach was to introduce a multitude of thermally activated mechanical contacts on a macroscopic area and translate them all by the low-friction scenario due to thermal vibrations known for a single FFM tip apex. In practice, along with the high mechanical strength and surprising flexibility of the NPs, the first friction experiments demonstrated that the contact area between a slider and the NP array plays a crucial role and that this area should be made as large as possible. Experiments with an Atomic Force Microscope (AFM), using a ball-shape probe as the sliding body, showed that even for a large radius, the ball had sufficient freedom to 'sink' in significantly between the NPs. The NPs were

found to bend sideways, which we expect to lead to severe damping of the thermal fluctuations of the NPs. We proposed a larger NP array of several square centimeters as the next step towards realization of thermolubricity on the macroscopic scale. This should allow one to use larger slider surfaces and minimize alignment difficulties.

The second effect that I explored to lower friction and that is also rooted in subtle effects on the nanoscopic scale, is lubrication with graphite. In contrast with thermolubricity, this lubrication mechanism is well known on the practical, macroscopic scale, that we make use of in everyday life. Materials with a structure like graphite, i.e., with strong atomic layers that weakly interact with each other, enable low friction due to the ease of sliding of these layers over each other. In **Chapter 4** of this thesis, I also associate this graphitic behavior with the ultralow friction of another solid material that doesn't have intrinsic graphite-like properties, namely Diamond-Like Carbon (DLC). Essential in my approach to unravel the lubrication mechanism of DLC was micropatterning of the studied contacts. This enabled us to strongly limit the apparent area of contact and directly observe the origin and the build-up of an ensemble of third-body elements during sliding. By imaging the contacting surfaces at various stages in the sliding process, we found that the sliding quickly leads to the formation of DLC microparticles that break up into nanoparticles and to subtle transformations of the highest asperities of the DLC surface, both of which we attribute to the high local shear stress levels. Friction on these nanoparticles and modified asperities was found to be much lower than on the rest of the DLC surface. Local Raman spectroscopy showed an increased proportion of sp^2 -bonding on the particles and the high regions, which is indicative of local graphitization. We concluded that the first sliding on a DLC surface leads to mechanical and chemical changes towards a more graphitic form of amorphous carbon, which naturally introduces the scenario of graphite lubrication.

In **Chapter 5**, I showed that the friction properties of the investigated, hydrogenated DLC coating in dry and humid environments are surprisingly different from common tribological behavior of this type of coatings. We ascribed this difference largely to the unusual geometry of our experiment: in our measurements, most microcontacts do not leave the actual sliding interface, which is due to the combination of the micropatterned DLC substrate and the ultraflat,

silicon counter-surface, that we used as the slider. This geometry accelerated the formation of the third-body elements and their graphitization. We further showed that water adsorbed from a mildly humid environment can play a lubricating role for the graphitized DLC clusters at low sliding velocities, which we ascribe to capillary condensation of water between them and their DLC substrate. At high humidities, friction is lowered even further, suggesting a hydrodynamic contribution, i.e., water acting directly as a lubricant, for example due to the formation of capillary bridges at the sliding interface between the graphitized DLC particles and DLC asperities and the silicon wafer.

On the atomic scale, the phenomenon underlying graphite lubrication is probably structural lubricity, also known as superlubricity. It is the effect that two perfectly smooth and stiff lattice planes that are incommensurate with each other and only weakly interact can slide over each other with nearly zero friction. Even though this effect has been identified experimentally only on the nanometer scale, graphene, graphite and structurally similar materials should be expected to all exhibit this self-lubricating behavior, also on larger scales. In **Chapter 6**, I reported the results of an experiment to demonstrate structural lubricity on the macroscopic scale. Large-area copper surfaces, completely covered with a high-quality monolayer of graphene, were chosen as the best candidates for this study. We demonstrated that covering copper surfaces with a single monolayer of graphene reduces the sliding friction force between them in ambient by approximately a factor 3, in comparison with bare copper surfaces. We also found a great impact of the graphene on the static friction behavior. The graphene introduces low surface free energies, minimizes the interaction between contacting asperities, enhances the load capacity and, presumably, only locally causes structural lubricity. Unfortunately, even on these low-defect-density surfaces we have not been able to acquire direct proof of the lattice-mismatch mechanism of this friction lowering, by distinguishing a signature of 60° rotational symmetry in angle-dependent friction measurements. The sharp maxima in the friction force, expected every 60° , were simply washed out by the residual width of the distribution of domain orientations in the graphene layers.

Finally, we demonstrated a significant additional lowering of the friction coefficient measured with FFM on graphene on top of a locally oxidized copper substrate. We ascribe this to a reduction of the so-called “puckering effect” that

otherwise makes the graphene bulge strongly in front of the sliding tip. The increased volume of the copper oxide resulted in tensile strain in the graphene. We propose that in addition to this tensile strain, also the increased adhesion between the graphene and the oxidized substrate and the reduced interaction of the tip with the rougher landscape of the graphene-covered oxide made the puckering effect smaller.

The observations presented in this thesis provide new fundamental insights that are of potential relevance to several technological processes. They carry the promise to contribute to future developments towards tunable interaction and tunable friction between surfaces on various length scales.