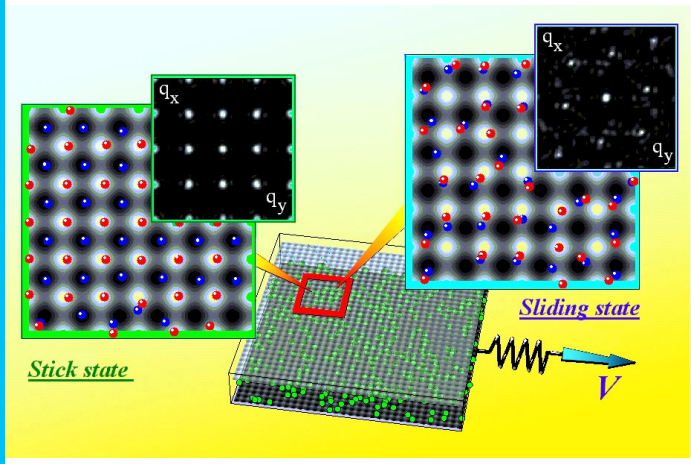
Nanotribology (NATRIBO)

An ESF scientific programme



The aim of the ESF NATRIBO programme is to improve the collaboration between experimentalists and theoreticians in the field of tribology on the nanometer scale.

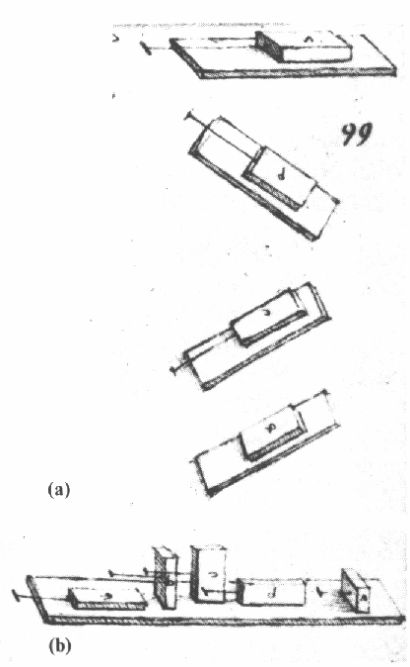
During recent years experimental and modelling tools have become available for the study of small contacts under pressure in relative motion. The understanding of friction, adhesion, fracture, and wear on the nanometer scale is the main issue. Atomic-scale stick-slip on solid surfaces, confinement of liquids between surfaces, electrical and mechanical properties of quantum contacts are subjects of this research. Since the processes in the tribocontact are highly complex, modelling is necessary. Atomistic simulations, preferably embedded in elastic continua, are dedicated to the study of small contacts. The comparison between experiments and modelling makes joint research between different groups and the formation of a network necessary.

Specific questions to be addressed by NATRIBO: Dissipation mechanism of contacts in relative motion, novel nano-materials for tribology, tribochemistry, triboluminescence, and mechanical properties of quantum contacts. One of the visions of NATRIBO is to achieve a sort of controlling of friction, in order to engineer tribological properties

The European Science Foundation acts as a catalyst for the development of science by bringing together leading scientists and funding agencies to debate, plan and implement pan-European initiatives.

Scientific background

Friction is an old subject of research. The empirical da Vinci-Amontons laws *(1. Friction is independent of apparent contact area, 2. Friction is proportional to the normal load, 3. Friction is independent of velocity)* are common knowledge. The school of Bowden and Tabor has performed systematic, macroscopic experiments and has related macroscopic friction to small asperities. In the1990s, experiments performed with atomic force microscopy, surface force apparatus, and quartz microbalance revealed interesting new physics on the nanometer scale (atomic-scale stick-slip, confinement of liquid films). During the same time, modelling of nanometre-sized contacts by molecular dynamics simulation have been performed and given insights into the processes in the buried interface (oscillation of forces due to size effects, wetting of contacts, confinement of liquids). So far, where and how energy is dissipated is poorly understood. The relative importance of electronic and phononic contributions is of interest. The observation of triboluminescence of nanometre-sized contact is an experimental goal. The effects of boundary lubricants is another central issue: Can we understand the relevant complex tribochemical processes with modern computer modelling and verify them with experiments (force microscopy and photon emission experiments on the wear track). The physics of quantum contacts is still a challenge for the next decade. In this programme, mechanical properties of nanometre-sized contacts will be determined and compared with electronic properties. The effect of quantum-size effects on properties, such as elasticity and plasticity, is of interest. All these phenomena are to be studied both by experiments and modelling.



Experimental Set-up. © L Da Vinci

Activities

The most recent information about the NATRIBO programme can be found at *www.nanotribo.org.* An electronic newsletter will be prepared on a regular basis. Information on conferences, workshops, courses and post-doc positions available in the field are disseminated through these media. Short articles and recent ideas and developments are also available. The programme will also be organising workshops during the five years from 2002 to 2006.

There is support for a number of short-term fellowships and scientific visits. The criteria for eligibility and application procedure for one of these grants can be found on the programme's web page: *www.esf.org/NATRIBO*

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Aims and objectives

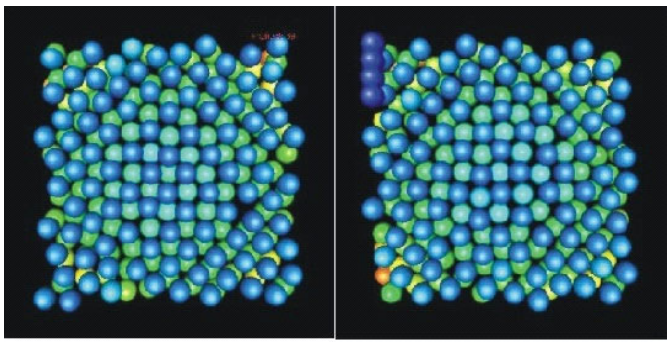
The research of NATRIBO will be dedicated to the following topics:

- *Fundamental dissipation mechanisms* are investigated by experiments with force microscopy, quartz microbalance, and surface force apparatus.

- *Soft matter*, such as polymers and bio- materials are studied by force microscopy.

- *Hard materials* are characterised by scratch tests, micro-hardness, roughness-dependence and indentation measurements.

- *Universal friction laws:* Under certain tribological conditions, friction is amenable to an essentially material-independent, i.e. universal phenomenological description. The chosen approach makes it possible to address problems at different scales: nm (junctions, meta-stable creep units), mm (load-bearing asperities), cm (macroscopic slider). It therefore contributes to *bridging the gap between nano- and macro-tribology*.



The squeezing of thin lubrication films between elastic solids with curved surfaces was studied. Well before the onset of squeeze out the lubricant bilayer form a hexagonal structure at the interface. Detailed analysis of the n=2—>1 transition reveals that the expulsion process is proceeded by a structural change (yield). Simulation snapshots show the formation of a more open structure during the yield, where the lubrication molecules in contact with the tip form a c(2x2) (approximately commensurate) structure and the second layer (in contact with the substrate) a similar structure, thus allowing the second layer to relax slightly towards the first layer, which relief elastic energy in the block. © B Persson

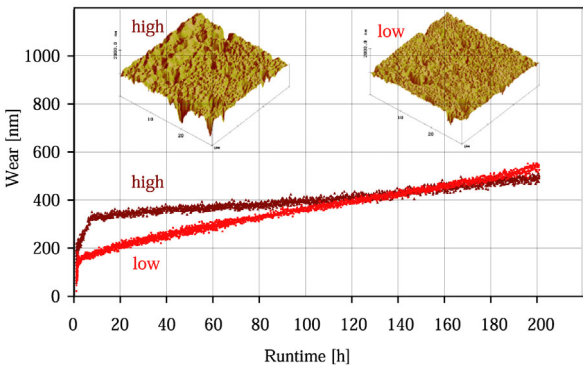
- *Confined liquids, adhesion, layering and friction:* For thin fluid layers, it is observed that the lubricant films form nearly commensurate structures. This is a thermally activated nucleation process that, with high probability, starts in the region where the pressure is maximal. This theoretical result explains the early experimental results of Tabor and Rabinowicz. The next application will be to study sliding friction at very low sliding velocities to investigate the very rapid processes that occur in the lubrication film.

- *The transition from boundary lubrication to hydrodynamic lubrication* with increasing sliding velocity will be considered.

- *The sliding of elastically very soft solids* will be addressed – in particular rubber – where it may be possible for elastic instability waves to propagate on the solid surfaces. Such waves (so called "Schallamach waves") have been observed for rubber on a macroscopic-length scale, but nobody knows if they also occur on much shorter (molecular-length) scales.

- *The transition from brittle to ductile fracture*, which has been observed for many materials with increasing temperature, and the properties of small particle systems will be studied.

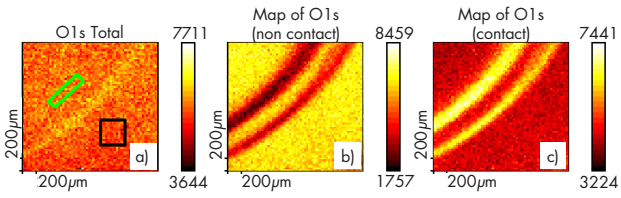
- *Relation between friction and adhesion in polymeric systems:* The study of molecular energy dissipation mechanisms at polymer-polymer interfaces is performed. Parameters such as the grafting density or crosslink density can be systematically varied. The rate dependence of both adhesion and friction will be studied in parallel. The objective is to correlate these velocity effects to the intrinsic visco-elastic parameters. A special focus will be on the transition between the static and the dynamic friction in relation to the extrapolated adhesive energy.



By means of the radionuclide technique wear of metals was measured continuously with a resolution in the nanometre range. The figure shows two wear curves of identical materials. Both tribosystems experienced a running-in, however with different loads. While the system that was subjected to a high load shows increased initial wear, the other system showed moderate wear after a low running-in. The insets depict the surface of the metal after high and low running-in. The system with the high load exhibits a significantly lower wear velocity than the system that experienced a low load running-in. © M Scherge

- *Nanostructuring and nano-hydrodynamics:* Experiments carried out with automotive parts revealed that the tribological performance is determined by the material properties of the first one hundred nanometers. This involves chemical and structural changes induced by the mechanical interaction of both solids. In addition, topography changes accordingly. Therefore, force microscopy can provide a good tool to study atomic mechanisms of lubricant spreading, lubricant reflow after impact, and lubricant behaviour under confinement. Not only the attachment of the molecules to the solid surface but also ordering phenomena inside the lubricant are of main interest. Another interesting field is the nanostructure of the material. Are there any structures that prevent wetting (lotus effect) or allow better wetting of the solid by hydrocarbons? Can nanostructuring boost micro- or nano-hydrodynamics? How mechanically stable are adsorbed oil layers?

- *Tribochemistry studied by surface-analytical tools:* The study of reactions that are induced by tribological conditions is of ever-increasing importance in a world that is energy conscious, environmentally conscious and generally searching for a more sustainable overall materials balance during use cycles. Current major challenges for the field include the replacement of the many existing, highly effective lubricant additives with alternatives that are equally (or more) effective, but more environmentally benign. To achieve this end, the mechanisms by which the current additives function must be better understood, and this is one of the goals of our tribochemistry efforts. One of our approaches has been to employ a combination of imaging surface-analytical techniques with classical tribometry under very carefully controlled conditions.



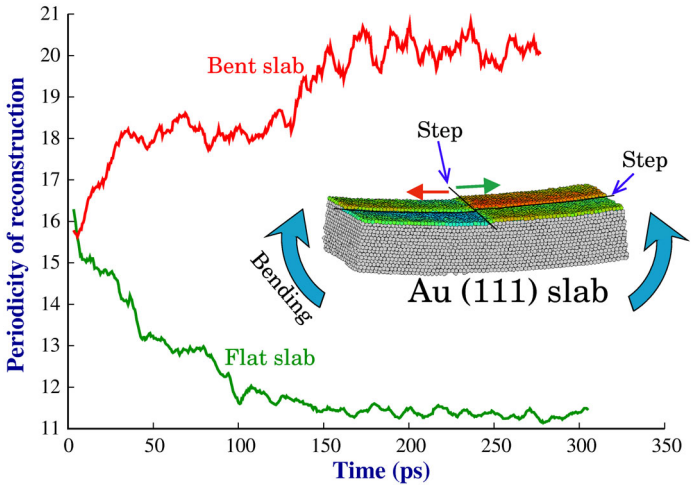
XPS chemical state map of the O(1s) signal. Two wear scars are visible produced at 1 N and 10 N load in ZnDTP containing lubricant. Map b) shows areas with typical oxide type O(1s) spectra, map c) shows the wear scars with a phosphate type O(1s) spectra. © M Eglin, A Rossi and N Spencer

- *Contact charging:* The charge transfer on the atomic scale and the charging observed macroscopically in contact charging, tribocharging and erosion are strongly related to the mechanisms of friction. Tribocharging is influenced by the speed of the relative motion of surfaces. One important concept, which is related to this effect and is often ignored, is the *extent to which equilibrium is achieved* in contact. Even in contact charging, rate-limiting steps (such as tunnelling to defects, or transport in one or more of the media in contact) can be so slow that the normal Fermi-level descriptions are insufficient. Yet another important issue is whether or not behaviour is determined by the *average* properties of the interface, or whether impurities, adsorbents or special sites are particularly important.

- *Triboluminescence* is a well-known macroscopic observation: Visible and ultra violet light is emitted when surfaces of a variety of substances are scratched. The effect is closely related to contact charging, since the light emission is often initiated by an electric discharge in the breaking contact. The microscopic processes causing triboluminescence are poorly understood. Questions to be answered are: What materials show triboluminescence? Is triboluminescence a collective phenomenon, or can the breaking of single contacts or even single bonds produce light emission? Is there triboluminescence without charge separation?

- *Electronic and phononic contributions to friction:* The electronic contributions to friction remain a poorly understood aspect of nanotribology. Much insight can be gained by studying the properties of several generic "quantum" contacts by experiments and ab initio calculations.

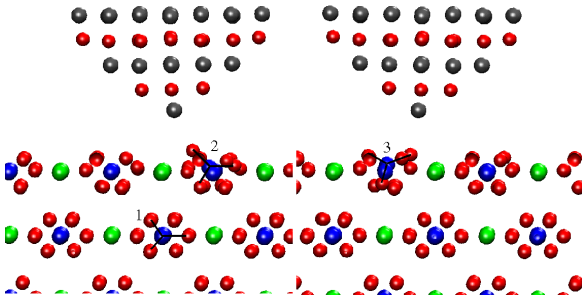
- *Atomic-scale friction and energy dissipation:* Theoretical studies on the atomic scale friction and quantum contacts revealed that the friction between two solid surfaces in relative motion is a complex and non-equilibrium process and involves a number of physical events, such as concerted bond exchange, bond breaking and bond forming, adhesion, atomic scale reconstruction and structural transformation, complex electronic and phononic energy dissipation involving tunnelling and ballistic energy transfer with novel quantum effects. The asperities, molecules and lubricants (or simply *nanostructures*) between the surfaces in relative motion are crucial for the friction and energy transfer. First-principles calculations have shown that the atomic and electronic structure, vibration spectrum and frequency level spacing of a nanostructure are strongly size dependent. The following questions are addressed: What is the optimal composition and size of the nanostructure that yields the smallest friction and wear? How can the atomic



Surface reconstruction and sliding friction: A Molecular Dynamics study: The Au(111) surface reconstructs with a periodicity (l x sqrt(3)), lower l's meaning higher densities. Bending the gold slab give rise to a change of periodicity l, due to strain. The step shown in the inset slides accordingly, letting the top layer change its density. Red line: the concave surface of a bent slab increases its periodicity, the density decrease and the step move forward. Green line: an originally bent slab is suddenly brought back to zero curvature, l decreases (density increases) and the step withdraws. An oscillating lamella with steps should show sliding friction, while a lamella with no steps should not.

structure of the surface and nanostructure be modified to achieve optimal friction conditions? What should the character of the nanostructure be in order to provide for the fastest transfer of energy from the place where heat is generated?

- *Superlubricity:* Friction is recently receiving renewed interest thanks to the availability of atomic force microscopes (AFM) and friction force microscopes (FFM). At the same time, enormous advances in computer power have stimulated the development of new strategies for large-scale ab initio simulations, which can be nowadays directly applied to study the interaction of two materials in local contact at the same (nanometric) scale investigated by the experiments.

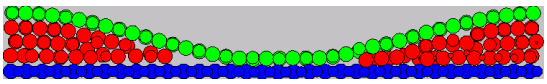


Snapshots from atomistic simulations of AFM scanning of the molecular solid calcite ($CaCO_3$) at about 0.2 nm tip-surface separation with a positive potential ionic tip. The simulations show that the original (1) configuration of the carbonate group is strongly influenced by the tip's position. Initially as the tip passes from the left side, the whole carbonate group spins to the right and displaces up (2). However, the strong repulsion between the tip apex and the highest O atom at very close range forces the group back into the surface, and it eventually spins to the left as the tip moves over the in plane O atom (3). © A Foster

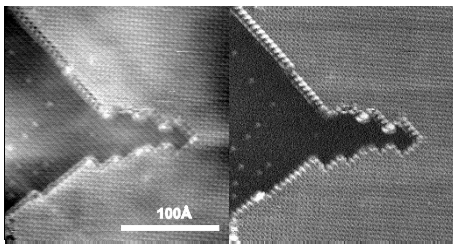
One of the key issues is the connection between forces and energy dissipation mechanisms active in small (e.g. single-atom or few-atom) contacts, and the forces and dissipation channels at work in more realistic contacts, with e.g. millions of atoms in the contact area. Scaling up the single-atom results to a larger area is indeed not a simple matter. A length-scale that plays a crucial role in atomically resolved friction is defined by the crystal lattice over which the tip is sheared. This length-scale is independent of the dimensions of the contact, leading to the prediction of a peculiar effect called "superlubricity". Namely, if the lattice spacing or the mutual orientation of the lattices in contact are not identical, the local frictional forces should exhibit a two-dimensional periodicity, with a high degree of mutual cancellation. The total friction force should therefore not increase monotonically with the contact area, and for certain combinations of contact area and orientation, it should even, in principle, vanish.

- *Mechanical properties of nanoscale contacts:* Direct information on the mechanical properties important in friction can be found by molecular dynamics and statistical simulations of such processes as nanoindentation and sliding friction. For example, molecular dynamics simulations of nanoindentation provide details of the changes in the tip shape, the size of the tip-sample contact area as a function of the indenting force, as well as information on the phononic processes at the surface during contact. Even with some understanding of the mechanisms of nanoscale friction, it is still difficult to link experimental FFM data with those mechanisms. Lack of information about the probing tip in friction experiments is especially limiting for clear interpretation. By directly modelling contacts at the atomistic level we can establish how the tip is affected structurally and chemically during scanning, and how the interaction forces are dependent on these properties. This should point to methods for reliably controlling the tip properties, and greatly improve the link between the mechanisms of friction and experimental results. The transition from wearless friction to plastic deformation (nanoindentation) will be investigated.

- *Extreme nanotribology*, where only several atoms can be involved in initial stages of energy dissipation, is achieved in dynamic force microscopy. To consider dissipation mechanisms on this scale one should establish their relation



The picture represents a tip (green atoms) that is modelled in a way such that long-range elasticity is included; not simply by harmonic springs but with anharmonic springs such that the proper pressure distribution in the contact area is obtained) There is some lubricant confined between tip and surface (red atoms), which is responsible for most of the shear forces. Of course, tip and substrate are incommensurate. © M Müser



Individual molecules are resolved in non-contact force microscopy in ultrahigh-vacuum conditions. The interaction at step sites and kink sites is different from the terraces. The topography on the left side is due to constant conservative force. The variation of the excitation amplitude on the right side is due to non-conservative, dissipative interactions.
© R Bennewitz

to local vibrational surface properties. This requires extremely sensitive experimental methods and a theory based on non-equilibrium statistical consideration of the interaction of the tip with vibrating surface atoms. As has been demonstrated in recent studies, this effect is crucial as surface atoms never establish complete equilibrium with the moving tip. Two dissipation mechanisms associated with surface vibrations are currently considered: (i) a friction force acting on the tip is determined by the response of the phonons associated with the surface atoms; (ii) surface atoms may experience instabilities at the closest approach of the tip which may lead to formation of local soft vibrational modes at the surface interacting strongly with the tip and resulting in a adhesion hysteresis phenomenon. Soft vibrational modes associated with a molecule at the end of a functionalised tip's tip can also be formed.

- *Biological systems:* In addition to the more traditional additives alluded to above, we have also begun looking at aqueous, protein-lubricated systems. These function highly effectively in biological environments, although their mechanisms are not well understood. Using a combination of surface functionalisation and in situ protein-binding analysis techniques, we are trying to explore protein-mediated lubrication, with the ultimate goal of application of biologically inspired lubrication in non-biological systems.

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For the latest information on this programme consult the *NATRIBO* home page:
www.esf.org/natribo

Cover picture:
Control of Friction: Macroscopic friction is modified through shear induced phase transitions in a mixed lubricant monolayer of a base solvent and an additive. The solvent-additive intermolecular interaction and relative concentration play a major role in determining the friction force magnitude and the nature of the response; namely, if it is stick-slip or sliding. © O K Dudko, A E Filippov, J Klafter and M Urbakh

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