Lubricants under high local pressure: Liquids act like solids

Schmierstoffe unter hohem lokalem Druck: Flüssigkeiten verhalten sich wie Feststoffe

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A lubricant layer solidifies when it is confined between two walls at large normal pressures. The atomic scale motion that occurs when the two confining surfaces slide past each other induces flow in the lubricant layer that is akin of plastic flow. This results in friction-velocity relationships similar to Coulomb's law of friction. Moreover, the lubricant layer does not necessarily melt, even when the two solids are in stick slip motion. In this paper, atomic-scale details of the plastic flow mechanism are investigated by means of molecular dynamics simulations.

Keywords: lubricant, pressure, plastic flow, friction law

Eine molekular dünne Schicht Schmierstoff verfestigt sich, wenn sie zwischen zwei Festkörpern großen Drücken ausgesetzt ist. Die atomaren Bewegungsmechanismen, die in dem Schmierstofffilm auftreten, wenn die Festkörper gegeneinander verschoben werden, können als plastisches Fliessen verstanden werden. Dieser Mechanismus führt zu einer Kraft-Geschwindigkeitsrelation, die dem Coulomb'schen Reibungsgesetz ähnlich ist. Selbst wenn die beiden Wände in Stick-Slip Bewegung sind, verflüssigt sich der Schmiermittelfilm nicht automatisch. In dieser Arbeit werden die Details des angesprochenen plastischen Fliessens anhand von Molekular-Dynamik Simulationen im Detail untersucht.

Schlüsselworte: Schmierstoff, Druck, plastisches Fliessen, Reibungsgesetz

1 Introduction

Many traditional theories of friction are based on the idea that solids are in plastic flow at the points of intimate mechanical contact. As argued by Bowden and Tabor [1], who put forth this idea, as well as by many other authors in their wake, the scenario is consistent with an essentially load-independent friction coefficient $\mu = \sigma_s / \sigma_Y$, where σ_s is the shear strength and σ_Y is the hardness of the less hard material in contact. The plastic flow model probably applies under certain circumstances. For instance, recent experiments indicate an almost perfect linear correlation between the friction coefficient and the shear strength of the surface coating [2]. However, Bowden and Tabor knew that their plastic flow scenario was not a universal explanation for solid friction. Already in the early 20'th century, Hardy had shown that applying a molecularly thin lubricant layer could change the friction force significantly. Since such a thin film cannot be expected to dramatically alter the contact mechanics and hence the plastic flow, different mechanisms must account equally or even more strongly for friction as well. This conclusion is supported by recent quantitative studies of the amount of plastic flow in macro [3] and nanotribological [4] experiments. They reveal that only a relatively small fraction of the energy loss should typically be converted into wear and plastic deformation. The estimates, which are in the order of 20%, might be seen as an upper bound, since the rubbed off material is most likely not fully dissociated (as partially assumed in the two studies) but – except for surfaces – in a quite favourable energetic state.

An appealing aspect of the plastic flow model nevertheless is that it is not only consistent with Amontons's law (μ is independent of the applied load L), but also with Coulomb's law of friction, which one may rephrase as follows [5]: The kinetic friction force varies (surprisingly) little with the sliding velocity v over a broad velocity range. Under non-extreme conditions (intermediate pressures and sufficiently small velocities) the kinetic friction force is essentially constant with corrections in the order of $\ln(v)$ or in the order of powers thereof, i.e., $\ln(v)^{2/3}$. The seminal paper by Prandtl [6] discusses very didactically how plastic flow leads to Coulombs's law of friction and the crucial aspects of his model will be repeated further below in this contribution. The logarithmic velocity corrections can increase or decrease kinetic friction depending on the detailed dynamics at the points of contact. Thermally-activated, adhesion-driven junction growth is consistent with positive corrections, while creep flow in lateral direction would release stress and hence reduce kinetic friction. Here, we will disregard both velocities sufficiently small for the system to be close to thermal equilibrium (leading to kinetic friction linear in velocity) and velocities sufficiently high to dynamically perturb the surfaces. Despite the appeal of the plastic flow picture, we may yet re-iterate objections against it: Tribological properties do usually not only depend on the less hard material but it depends on *both* surfaces *and* the lubricant. In most cases, it is not possible to reduce this dependence into simpler dependences such as it is possible for hydrodynamic lubrication, where the knowledge of the lubricant's viscosity and the slip boundary condition of the lubricant with each individual wall allows one to characterize the system reasonably well.

An alternative picture of the plastic flow model arises from a series of recent papers [7-14]: In many contacts the lubricant particles become immobilized under confinement and large local pressure. This immobilization makes the lubricant appear solidified or glassified. Under high-pressure conditions,

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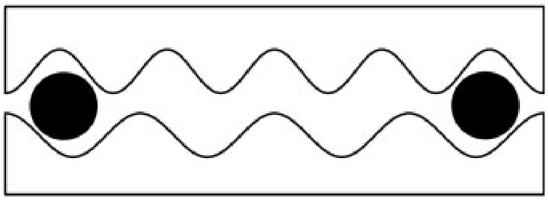

Figure 1. Sketch of two rigid, non-matching solids separated by lubricant particles represented by full circles. The confined layer is sufficiently compliant so that atoms can satisfy the interaction with both surfaces, thereby locking them together and increasing the kinetic friction force. From Ref. [9].

Abbildung 1. Schematische Abbildung von zwei geometrisch nicht ineinander passenden Festkörpern, die durch Schmiermittelteilchen (ausgefüllte Kreise) voneinander getrennt sind. Der in diese Geometrie eingeschränkte Film ist hinreichen elastisch, um die Wechselwirkungen mit beiden Wänden gleichzeitig zu befriedigen. Dadurch kann der Film die beiden Oberflächen verhaken, was zu einem Anwachsen der kinetischen Reibungskraft führt. Von Ref. [9].

lubricant particles behave similarly to hard-disks, which almost automatically would imply Amontons's law [7,9]. The generic mechanism is presented in Figure 1: Two non-identical solid surfaces, whose intrinsic corrugations (typically) do not match, can interlock geometrically if physi-sorbed atoms are present at the interface. During contact formation, these particles are mobile enough to find energetically favourable sites, i.e., sites where the gap between upper and lower surface is large. Once they are caught in favourable sites, it becomes ever more difficult to squeeze them out of the contact with increasing load. The reason is that the corrugation barriers, which suppress diffusion on the surface, will increase with increasing load. If we want to move the upper surface in Figure 1 to the right by applying a lateral force and a constant normal load, then the upper surface has to climb up an effective slope. An important conclusion from this consideration is that the friction coefficient depends on *both* surfaces *and* the lubricant. The friction force is likely to change when the size of the lubricant atoms in Figure 1 and/or the corrugation of either wall is altered. The arguments put forth in this paragraph are quite generic, i.e., they also hold if we consider more realistically polymers instead of spherical atoms or if the lubricant coverage is altered. Nevertheless, there will be corrections due to specific interactions. One may have to include adhesion and in some cases even pressure or sliding-induced chemical reactions, which our simple model cannot take into consideration.

For a general understanding of the dissipative processes, however, it may nevertheless be best to study the most simple model at hand that reproduce the well-established laws of friction. Such a model, which will be reviewed in section II, was suggested by Prandtl. While his model is very valuable from a didactic point of view, the friction mechanism put forth in his paper is probably irrelevant in most applications as it does not include the boundary lubricant. A simple model that includes the boundary lubricant and that is supposedly free of unintentionally built-in artifacts will be introduced in section III. The two subsequent sections IV and V then describe the flow of the lubricant in our model under two different conditions. First, we will assume two identical walls that are perfectly aligned in relative sliding motion. The lubricant will adopt the same periodicity when the confining surfaces are commensurate and hence become a crystal. This will allow us to study the dynamics of a crystalline boundary lubricant. Then, we will make the two walls incommensurate so that the lubricant cannot adopt the structure of both walls simultaneously, even when the normal pressure is large. This will allow us to study the dynamics of a glassified lubricant and to work out the similarities with plastic flow of confined crystalline lubricants. In section VI, we will conclude this contribution. It may be important to emphasize that many of the arguments discussed in this paper are meant to predict trends rather than exact laws. Amontons's and Coulomb's law of friction are phenomenological laws, which are not universal, although they describe many mechanical contacts surprisingly well.

2 Adiabatic versus non-adiabatic friction

Coulomb's law of friction for solids is strikingly different from Stokes's law of friction which applies to a colloidal particle immersed in fluids, to name an example. Why can the friction force be almost independent of sliding velocity v in one case while it is proportional to v in many another cases? There is a rather general answer to this question as reviewed in Ref. [5]. If a system is (locally) close to thermal equilibrium, i.e., it is driven adiabatically, then the friction force will be linear in v, which follows rigorously from linear response theory – unless one is in the vicinity of a phase transition point. For example, consider the case where a 'ghost particle' is moved laterally at constant v over a substrate at a distance of a few Angstroms. The particle will induce sound waves in the solid that will ultimately propagate away from the surface and their energy will be lost as heat. The faster we move the test particle, the more violent the oscillations in the solid will be and the larger is the energy dissipation. However, if we move the test particle very slowly, barely any energy will be dissipated. The proportionality between the friction and the instantaneous velocity of the particle is often referred to as the drag coefficient. In fluids, such drag coefficients would be related to the viscosity, and they are an equilibrium property of the system.

The Prandtl model illustrates very nicely how falling out of thermal equilibrium leads to non-adiabatic friction. Consider a particle coupled elastically to its ideal lattice site, which moves laterally over a substrate at constant velocity v, see Figure 2. Suppose furthermore that the particle's coupling to its lattice site is relatively weak and that we can disregard thermal fluctuations for a moment. If the particle sits in a stable equilibrium site at time t=0 and the lattice moves to the right as shown in Figure 2, the position of the equilibrium site will move as well. However, the (local) minimum of the potential energy will become more and more shallow with time until the position becomes unstable at some given point. The particle will then pop forward to the next available equilibrium site. After a relatively short period in time, the atom will settle in the minimum of the new equilibrium, since during the jump and thereafter energy can be lost due to interactions with the phonon bath. The interesting aspect of this process is that at small v and in the absence of thermal noise, the energy dissipated is always the same amount ΔE per lattice constant moved, irrespective of the precise value of v, which implies that the friction force is independent of velocity. This behaviour is reminiscent of Coulomb friction. Once the particle has jumped and the sliding direction is inverted, we would not expect the particle to jump back immediately. Thus, there would be a hysteresis no matter how small v. One may con-

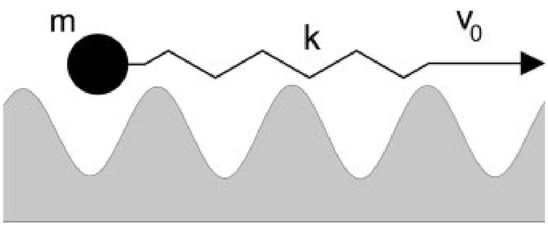

Figure 2. Sketch of the Prandtl model. A surface atom is coupled to its ideal lattice site with a spring of stiffness *k*. The ideal lattice site is supposed to move at constant velocity v_0. If *k* is greater than the curvature of the substrate potential (indicated by the sinusoidal line), then the atom has a well defined equilibrium position at all times and hence moves with a velocity in the order of v_0. This leads to simple Stokes friction. If *k* is less than the maximum curvature of the substrate potential, there will be more than on stable position at times and some of the position that were initially stable become unstable as the spring moves further to the right. The atom then 'pops' forward to the next available energy minimum, thereby dissipating the energy difference between the metastable site and the new equilibrium site. This leads to Coulomb like friction.

Abbildung 2. Schematische Abbildung des Prandtl'schen Modells. Ein Oberflächenatom ist durch eine Feder mit Federkonstante *k* an seine ideale Gitterposition gebunden. Diese bewegt sich mit einer konstanten Geschwindigkeit v_0 fort. Wenn *k* größer ist als die maximale Krümmung des Substrat-Potenzials (das durch die wellenförmige Kurve angedeutet ist), dann hat das Atom immer genau eine wohl definierte Gleichgewichtsposition und bewegt sich daher immer mit einer Geschwindigkeit in der Größenordung von v_0 weiter. Solch eine Bewegung führt zu Stoke'scher Reibung, die linear mit v_0 anwächst. Wenn *k* kleiner ist als die maximale Krümmung des Substrat-Potenzials, dann wird es zu gewissen Zeiten mehr als eine mechanisch (meta) stabile Lage für das Oberflächenatom geben. Eine ursprünglich stabile Lage kann mit der Zeit instabil werden und das Atom springt in das nächste Energieminimum. Bei jedem Sprung wird die Energiedifferenz zwischen der alten metastabilen Lage und der neuen Gleichgewichtslage dissipiert. Dies führt zu Coulomb'scher Reibung.

clude that instabilities invoke plucking motion, mechanical hysteresis and ultimately friction laws akin of Coulomb's law of friction.

Including thermal fluctuations can alter the picture if temperature is sufficiently high. Atoms can jump prematurely before the true instability point is reached. This will obviously reduce the friction in the present model. In the extreme limit of sliding velocity sufficiently small for the system to reach full thermal equilibrium at every instant of time, i.e., at v=0, the average friction force will be zero and then increase linearly with v. In an intermediate velocity regime, the velocity corrections can be shown to vary only slowly with velocity, i.e., friction is constant with corrections in the order of $\ln(v)^{2/3}$ [15]. While the atomic-scale interpretation of this particular type of instability is not necessarily relevant to tribological systems, it is useful to describe atomic force microscope data. Most importantly, the Prandtl-Tomlinson model makes it easy to introduce the concept of instabilities and their crucial importance for the explanation of typical friction laws.

It is important to mention that non-adiabatic driving does not necessarily imply Coulomb's law, but it can take any nonlinear dependence in principle. In the extreme case, friction can decrease with increasing velocity. This can even be the case at relatively small velocities, for instance when two polymer brushes in good solvent conditions slide past each other [16,17].

3 Model

Our model contains two parallel [111] surfaces of an fcc solid. Atoms in the surfaces are coupled elastically such that the bulk modulus of the surfaces is in the order of 20 GPa. Sometimes, the atoms are also pinned to their lattice site. In the present study, this constraint does not affect the results. The surface atoms are spaced at a distance of about 3 A and the linear length of the surfaces is in the order of 6 to 10 nm. Periodic boundary conditions are applied normal to the interface in the the *xy* plane. The position of the lower surface is fixed, while the upper surface is driven under constant load. Laterally, the upper wall will be moved at constant velocity or – when stick slip motion is studied – pulled with a complaint spring. Two different relative orientations of the confining walls will be studied. They can be perfectly aligned forming a commensurate interface or they can be rotated by 90 degrees. In the latter case, the two surfaces are essentially incommensurate, i.e., the smallest common length scale is that of the periodically repeated cell. Moreover, the walls are compressed in one direction so that they become perfectly quadratic. In either case, the walls are pressed against each other with a local pressure of 0.2 GPa and the temperature is set to about 300 K.

In between the two surfaces, additional, weakly interacting atoms are included. These atoms will be called the lubricant. The number of atoms is chosen to be close to that in one of the two outermost surface layers of the confining solids. Again, changing the number of atoms in the interface does not affect qualitatively the model's frictional properties. The choice for this number is motivated by the expectation that all but the last layer of lubricant is suspected to be squeezed out under contact formation. The lubricant atoms interact with one another and with atoms from the confining wall through a Lennard Jones potential

$$V = 4\varepsilon\left[\left(\frac{\sigma}{r)}\right)^{12} - \left(\frac{\sigma}{r)}\right)^{6}\right] \tag{1}$$

where ε is chosen to be 30 meV and σ =3.4 A. These are typical values for the interaction between closed electron shell units such as an argon atom or a CH_2–like unit in a polymer and other chemically passivated units of similar size. The unit of time in the simulations presented below can be roughly associated with pico seconds. In most cases, the interactions are cutoff at $r = 2^{1/6}\sigma$ and the potential is shifted above so that no discontinuity occurs at the cutoff. Such a small cutoff value might yield qualitatively wrong results at small external pressures, but given the large pressures in the intimate points of contacts, no artefacts are produced in most cases. The advantage of choosing small cut-off radii is that the simulations become less CPU time demanding. In previous simulations, we also imposed chemical bonds [7, 10, 13] between the monomers forming short hydrocarbon like chains and found that – in our model - most results showed strong similarities with those obtained by the more simple spherical lubricant atoms.

Of course, tribological properties would depend dramatically on the chemical connectivity between the monomers in real systems. Polymers are much less easily squeezed out of a contact than monomers and hence prevent contact of the two opposing surfaces more efficiently than monomers. However, once the lubricant is forced to stay in the contact, i.e., via periodic boundary conditions, or if one considers an area away from the contact line, this important difference between polymers and monomers becomes almost irrelevant.

In our simulations, the confining walls are allowed to deform elastically. For flat surfaces and interfaces, the effect of elastic deformation is however rather small, as the elastic modulus of solids is typically much larger than that of the lubricant. Hence to understand the energy dissipation mechanism at the nanoscale one may as well neglect elastic deformation. Only curved surfaces need a separate treatment as discussed in reference [18].

4 Crystalline Boundary Lubricants

While it may not be realistic to consider two commensurate (perfectly matching and oriented) walls in contact, it is instructive to consider such configurations. If lubricant atoms are confined between the two walls and if the wall atoms' and lubricant atoms' size are not too different from one another, then the confined layer will adopt the same periodicity as the walls, i.e., it will be in a crystalline state, albeit possibly one with defects. When the two commensurate confining walls are in relative lateral motion, the position of the ideal lattice sites becomes a function of the relative displacement passing through 'ideal' configuration in which the confined layer is able to form an ABC sequence such as they occur in face centred cubic solids or an ABA sequence as in hexagonal closed packed structures.

Figure 3 shows snapshots of the lubricant configuration while the two confining walls are sheared past each other. (Movies can be downloaded under the author's home page following links to research and friction. The homepage can currently be found at http://publish.uwo.ca/~mmuser/.) The left colon represents driving under constant velocity while the right-hand side shows driving with a weak spring in the stick-slip regime. The time evolution of the potential energy of the embedded system (interaction among lubricant atoms plus interactions with the walls) and the friction force on the top wall is included as well. Both sets of simulations were started from the same initial configuration, which – while having defects – were in metastable equilibrium at a zero shear stress condition at time *t*=0. The (outer) circles represent the positions of atoms. Information on normal and lateral forces with the top wall is included as well, i.e., the one that is coupled to the driving device. The radius of the inner circle is proportional to the load an atom carries, while the shade and orientation of the semicircles indicate the magnitude and direction of the lateral force exerted on the top wall.

Under both driving conditions, constant velocity and stick slip, one can note that he defect structure remains rather stable, even after the top wall has been moved by one or more than one lattice constant. There is some reshuffling of the defects, but even under stick slip there is no melting of the layer under the high-pressure conditions imposed in the simulations. In the case of commensurate surfaces and extreme boundary lubrication (i.e. one monolayer or less), one may argue that the system moves along easy sliding planes. Slip occurs between film and substrate and/or film and upper wall. Shearing along easy sliding planes implies that instabilities can be avoided in principle, which can be understood as follows: The energy needed to move a plane to the top of the energy barrier can be regained by having the system slide downhill to the next available potential energy minimum. This scenario is clearly borne out in the upper left graph of

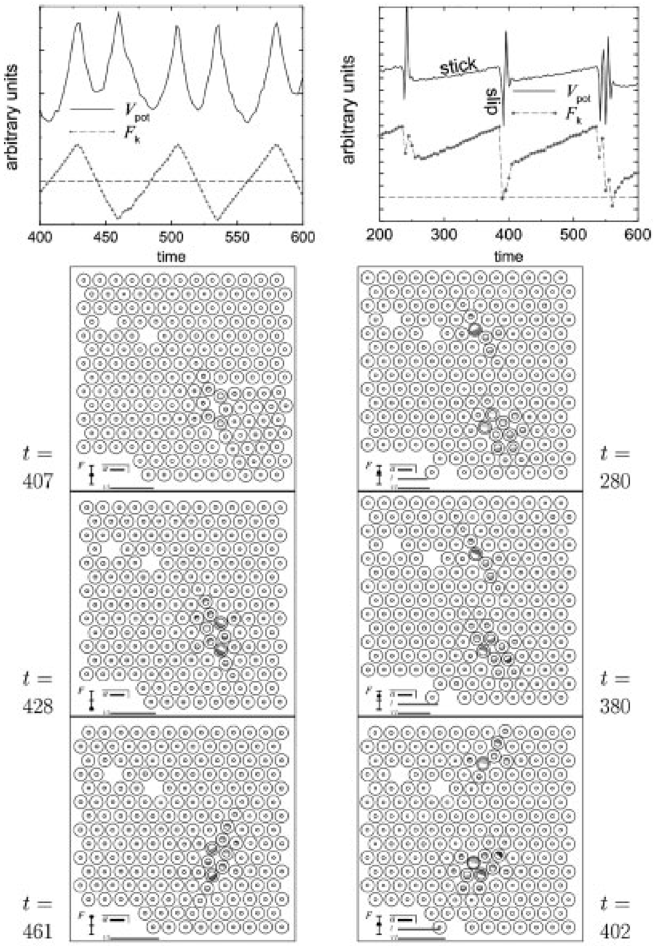

Figure 3. Representation of a boundary lubricant. Left colon: Upper wall is driven at constant velocity. Right colon: Upper wall is pulled with a weak spring leading to stick slip motion. In both cases, the two confining walls (not shown explicitly) are identical and perfectly aligned. Top row: Potential energy and kinetic friction as a function of time. The straight dashed lines indicate zero. Bottom three rows: In-plane view of boundary lubricant at various instances of time. The bar labelled *a* shows the lattice constant of the confining walls, the bottom bar *vt* indicates the distance moved by the top wall. The middle bar labelled *t* shows the position of the spring with which the upper wall is pulled (only in stick slip mode). The coding of load and lateral force is described in the text. Periodic boundary conditions are employed in the plane.

Abbildung 3. Darstellung der Grenzflächenschmierung. Linke Spalte: Die obere Wand bewegt sich mit konstanter Geschwindigkeit. Rechte Spalte: Die obere Wand wird mit einer weichen Feder gezogen, so dass der Kontakt sich im Stick-Slip Modus befindet. In beiden Spalten sind die nicht explizit dargestellten Wände identisch und perfekt orientiert. Oberste Reihe: Potenzielle Energie und kinetische Reibung als Funktion der Zeit. Die gestrichelte Linie entspricht dem Wert null. Untere drei Reihen: Aufsicht auf die Schmiermittelschicht zu verschiedenen Zeitpunkten. Der mit *a* gekennzeichnete Balken zeigt die Gitterkonstante der begrenzenden Festkörper an, der Balken *vt* zeigt die von der oberen Wand zurück gelegte Strecke an. Der mittlere mit *t* markierte Balken zeigt die Position der Feder an, mit der die obere Wand gezogen wird (nur im Stick-Slip Modus). Die Kodierung von normaler und lateraler Kraft ist im Text erklärt. Periodische Randbedingungen werden innerhalb der gezeigten Ebene angewendet.

figure 3, where one can see a mainly oscillatory behaviour of the lateral force around zero. This oscillatory behaviour gets lost when more layers are included between the two surfaces. The yield or creep mechanism then crosses over from easy-plane sliding to a plucking dislocation motion, the latter of which includes instabilities and hence larger kinetic friction.

We return to the discussion of single or sub-monolayer lubrication of commensurate surfaces. As argued above, constant velocity sliding leads to oscillatory later forces, resulting in almost zero kinetic friction. Conversely, when the upper wall is pulled with a weak spring, the lateral force essentially always opposes sliding. The lubricant only changes its configuration significantly during the short slip phases. The defect structure changes surprisingly little during each slip, at least as long as the slip is of atomic dimension. For instance, it can be seen on the right-hand side of figure 3 that the vacancies only move about one lattice constant to the right during the slip event and also the interstitial defect barely moves during the slip event.

Finally, without showing explicit proof of the following statement here, I wish to comment that also 2-dimensional commensurate interfaces are critical points similar to their one-dimensional counterparts, which were discussed in Ref. 12. That is to say that the properties of the contact can change *qualitatively* if one parameter in the system is altered slightly. For instance, I analysed the trajectories of a commensurate, confined layer in the absence of interstitial defects and found that the collective dynamics (and hence the friction force) depends crucially upon whether adhesive interactions between the lubricant atoms are switched on or switched off. In the latter case, self-healing cracks appear in the lubricating film, which are not present in adhesive films. One might not have expected such a dramatic effect, as the normal pressures are relatively large and a Lennard Jones type adhesive interaction could have simply been a small local perturbation.

5 Glassified Boundary Lubricants

In the last section, we considered commensurate confining walls, which can be considered atypical. Even chemically and physically identical surfaces will usually have random orientation. Therefore it is more common to have effectively incommensurate interfaces, which means that the periodicities in the both confining walls do not match along a given direction. (Strictly speaking, the ratio of the lattice constants along a direction must be irrational to be called incommensurate. However, it can be shown in a simple model that the strength of geometric interlocking vanishes exponentially fast with the common period so that most non-identical surfaces can be considered effectively incommensurate.)

For non-matching walls, the lubricant cannot satisfy the periodicity of both walls simultaneously. Therefore the structure cannot be long-range ordered. The lubricant can nevertheless get trapped into mechanically favourable sites as shown schematically in figure 1. The top view of the boundary lubricant is shown in *figure 4*. Unlike the previous case, there is no long-range periodicity in the confined layer and as a consequence the mechanical behaviour of the system is strikingly different.

While the commensurate layer showed oscillating forces averaging almost to zero, the incommensurate layer always opposes the externally imposed motion of the upper wall. However, the lubricant maintains many of its characteristics with time, for instance there are only few atoms changing neighbours separating the two graphs at times t = 250 and t = 350. During this time span, corresponding approximately to 100ps or 10^4 molecular dynamics steps, a fluid layer would have reconstructed significantly. While the plastic flow behaviour is borne out more clearly in movies than in static figures, one can certainly notice that the patches of high density (bottom right of the simulation cell) and the patches of low density (centre to left in the simulation cell) have moved only insignificantly during the said time period. If we simulate the same system under different conditions, i.e., at room temperature and under its own adhesive load using a large value for the cut-off radius, then density fluctuations will relax within less than 1 ps if no external load is applied.

The solid character of the contact is exhibited more strongly under stick-slip driving. The structure of the lubricant barely changes during the stick phase $360 < t < 480$. The analysis of atomic trajectory shows that the lubricant atoms only move by

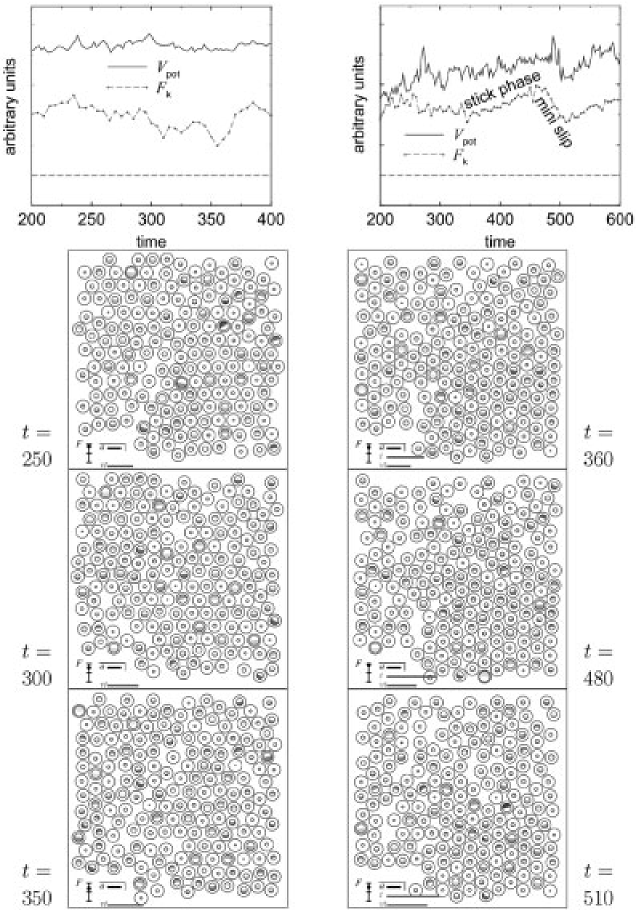

Figure 4. Same as previous figure, however, the two confining walls are incommensurate. The atomic configurations barely change during the stick phase (see t = 360 and t = 480 configurations). Even during steady sliding and after slip occurs, there is a strong memory of zones of high and small lubricant density.

Abbildung 4. Gleiche Anordnung wie in voriger Abbildung. Jedoch sind diesmal die begrenzenden Oberflächen inkommensurabel. Die atomaren Konfigurationen verändern sich kaum während der Stick-Phase (siehe die Konfigurationen zu den Zeitpunkten t = 360 und t = 480). Selbst wenn die Wände mit konstanter Geschwindigkeit gezogen werden und auch nach einer Slip Phase gibt es starke Gedächtniseffekte bzgl. der Zonen mit hoher und kleiner Schmiermitteldichte.

typically less than half a lattice constant during the slip phase. It is therefore erroneous to think that the lubricant layer necessarily melts when the contact is in stick-slip motion. Of course, as the slip length increases, the reshuffling of the atoms will be more violent and hence the topology of the lubricant will be significantly before and after slip.

It is interesting to note that the kinetic friction under stick-slip sliding is barely greater than under constant velocity sliding. In the present simulations, the main dissipation thus occurs due to micro slips within the lubricant rather than to the instabilities of the confining wall. These mini instabilities have also been discussed in Refs. [12-14]. Another interesting observation is that the characteristics of the motion does not change when the load and/or the top wall's sliding velocity is altered.

The main effect of increasing the load is to increase the lateral forces by approximately the same factor as the normal load. This means that the trajectory of mechanically stable sites is not affected very strongly when we change the load. (This last statement is only valid if a contact can be locally approximated as flat, which is a reasonable approximation for *most* of the contact. Exceptions are contact lines and changes in the lubricant thickness due to surface curvature from monolayer to double layer, etc.) Since the motion of the atoms is centred around the motion of the current equilibrium position, trajectories become surprisingly independent of load L and Amontons's law follows quite naturally. If we increase velocity, we also obtain similar atomic trajectories except that things now occur in fast motion. Yet, per distance slid, the same instabilities are invoked leading almost automatically to Coulomb's law of friction. In the simulations discussed in this paper, the typical persistence time of a trajectory is in the order of 100 ps, which means that if we change normal load or velocity by a factor of two, the trajectories of particles are typically very close to one another up to 100 ps. After this time period, some details of the trajectories start to deteriorate and owing to non-linearities in the interaction potentials, the detailed dynamics are starting to differ from one another even more as the sliding distance increases. Yet, the *average* kinetic friction does obey Amontons and Coulomb reasonably well for quite a broad parameter range in load and sliding velocity.

It is important to mention that the characteristic dynamics of the lubricant film and the velocity-dependence of friction small changes in the parameter space is barely affected by small changes in the parameter space of incommensurate surfaces. This behaviour is akin of experimental results but in stark contrast to the previous section, in which commensurate systems were considered.

6 Conclusions

In this paper, the motion of a boundary lubricant was analyzed in terms of molecular dynamics simulations. It was shown in agreement to previous studies [7-13] that the lubricant structure and the dynamics depend very strongly on the symmetry of the confining walls. Identical and perfectly aligned crystalline walls lead to a lubricant layer that has the same periodicity as the confining walls, i.e., it forms a crystal. Conversely, if the walls are non-matching, the intermediate layer forms a disordered structure similar to that of a glass with short-range order but with a lack of long-range order. These statements are valid at zero and non-zero shear rates.

The (topological) structure of the lubricant changes with time only slowly at sufficiently high normal pressure, even when the two confining walls are slid past each other. This means that neighbouring atoms remain neighbouring atoms for much longer times than in fluids. This observation also holds for stick-slip motion, provided the slip distance is not too large, irrespective of whether the layer is in a crystalline or in a disordered state. The degree with which defects in the lubricant film remain stable as a function of time has not been noted hitherto. The vacancy structure in commensurate layers and the area of low-density patches in disordered layers both turned out surprisingly robust. The detailed dynamical features, however, do depend dramatically on the degree of order. If the two confining walls are commensurate and all the lubricant is squeezed out but the last layer (or less), then most atoms move rather smoothly most of the time. (The movies eluded to in the main text show more details than what one can present with a few graphs.) Except for interstitial defects no significant instabilities or 'pops' (sudden, seemingly erratic jumps of certain degrees of freedom) remain absent under constant sliding conditions. Only when the upper wall is pulled with a sufficiently compliant spring does the system show stick slip motion and a kinetic friction force in the same order of magnitude as the static friction force. (This point is discussed in detail elsewhere [12,13].) In a disordered layer, friction is dominated by the sub Angstrom slips of lubricant atoms and the tribological characteristics are relative insensitive to changes in the parameters describing this model (relative orientation of the two surfaces, sliding velocity, degree of contamination, etc.).

Of course, the simulations discussed here and in papers on which this discussion is based upon does not allow a quantitative prediction for a specific system of interest. However, it probably gives a quite detailed and generic description of the processes that occur in boundary lubricant layers, irrespective of their chemical nature. It shows that Amontons's and Coulomb's laws can be valid at the nanometre scale, provided the lubricant is not completely squeezed out. Moreover, the validity of the statements made here is limited to moderate sliding velocities, say in the range of 0.01 mm/s to 10 m/s and local normal pressure below the yield of the softer solid in contact.

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