Tribological Behavior of Very Thin Confined Films

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ABSTRACT

The tribological properties of two smooth surfaces in the presence of a thin confined film are investigated with a generic model for the interaction between two surfaces and with computer simulations. It is shown that at large normal contact pressures, an ultra thin film automatically leads to static friction between two flat surfaces - even if the surfaces are incommensurate. Commensurability is nevertheless the key quantity to understand the tribological behavior of the contact. Qualitative differences between commensurate and incommensurate contacts remain even in the presence of a thin film. The differences mainly concern the thermal diffusion of the contact and the transition between smooth sliding and stick-slip.

INTRODUCTION

Understanding the dynamics of a system under shear containing a confined fluid is intimately connected with understanding the effects that are invoked through the corrugation of the confining walls. In the case of bare, flat surfaces, not only the degree of corrugation is relevant, but more importantly, the correlation of the corrugation in the upper wall and in the lower wall, i.e., commensurate systems exhibit wearless static friction while incommensurate systems do not [1-3]. This situation is dramatically changed if small amounts of “fluid” are injected into the interface and the fluid atoms do not form covalent bonds with neither surface [4]. Independent of the type of commensurability, static friction can be expected to occur. Here we will discuss why such mobile atoms in the interface lead to friction and address the question whether the differences between commensurate and incommensurate systems are remedied in the presence of a fluid layer.

The studies discussed here address fundamental issues rather than questions of direct, practical use. How does a tiny amount of fluid/contamination between two perfectly flat, crystalline surfaces alter the tribological behavior of the contact and what are the implications of commensurability in the presence of a thin film? Experimentally, it might be impossible to study these effects satisfactorily, because clean surfaces are hard to obtain even in UHV, e.g., the contaminant may reside within the bulk and diffuse to the surfaces only after sliding has been initiated.

THEORY AND COMPUTER SIMULATION MODEL

A simple, idealized model to treat interactions between two flat walls with only atomistic roughness allows a large number of predictions [5]. The main feature of the model is that two surfaces pay a local energy penalty that increases exponentially fast as the distance between the surfaces is decreased or the overlap is increased. The consequences of this model are among others: (i) Commensurate systems show a static friction coefficient \( \mu_s \) that is independent of the area of contact \( A_c \), (ii) for amorphous crystalline contacts \( \mu_s \propto 1/\sqrt{A_c} \) is found, and (iii) for incommensurate
contacts $\mu_s = 0$. In this case, sliding is only opposed by a viscous drag force. These predictions are based on the analysis of the Fourier transform of the surface modulation. $\mu_s$ can only be independent of $A_c$ if the upper and the lower wall’s corrugation is systematically correlated. Atoms that are injected into the interface can easily accommodate the surface modulation of both surfaces simultaneously: The “fluid” atoms sit at positions where the spacing between both walls is maximum. Once the normal pressure becomes large, the atoms are caught in these position and they can only escape via thermal activation, which one can assume to take place on long time scales only. If one tries to initiate relative sliding of the walls, the available free volume of the atoms will decrease. Thus the total energy of the system increases, which results in a force opposing the initiated motion.

However, there is an important difference between commensurate and incommensurate walls if thermal activation and diffusion of the fluid atoms is taken into account. Consider a system that is only subject to thermal noise. In the commensurate case, fluid atoms jump into (more or less) equivalent positions. Therefore, the relative lateral equilibrium position of the top wall does not change even if the fluid atoms undergo diffusion. In other words, there is a well-defined free energy profile of the contact that has the periodicity of the system. Therefore, static friction is an equilibrium phenomenon. In the incommensurate case, the expected situation is strikingly different. The fluid atoms jump into inequivalent positions as they undergo thermally activated diffusion. With each such jump, the lateral, relative equilibrium position of the walls shifts slightly. If we allow the fluid to explore the whole phase space, all relative, lateral positions of the two walls are identical. Therefore the free energy is not a function of the relative, lateral displacement of the two walls unlike the commensurate case. For incommensurate systems, static friction is a non-equilibrium phenomenon. From this discussion, one would expect an exponential slowing down of thermal diffusion with contact area of the whole contact in the commensurate case (at fixed normal pressure), while creep motion would be expected for incommensurate surfaces.

A generic model is employed in order to analyze the thermal motion of a mechanical contact including a thin confined layer of atoms. It consists of two (111) surfaces whose atoms are harmonically pinned to their ideal lattice sites. Periodic boundary conditions are employed in the plane of the two walls. The fluid atoms, which are confined between the walls, interact with Lennard Jones potentials among each other and with the walls. For further details of the model, we refer to Refs. [3-5].

RESULTS

We first want to report results for the thermal diffusion of the contact. Commensurate surfaces show the expected exponentially slowing down with increasing area of contact $A_c$ for a given normal pressure $p_\perp$ and temperature $T$. Of course, a similar slowing down of the diffusion is achieved by either decreasing $T$ at fixed $(A_c, p_\perp)$ or by increasing $p_\perp$ at fixed $(A_c, T)$ [3]. Surprisingly, dramatic size effects are also found for incommensurate surfaces as shown in figure 1.

At small temperatures, the system appears to be pinned elastically during a time window of $10^6$ molecular dynamics (MD) time steps. The effective lateral stiffness increases linearly with the area of contact $A_c$ similar to the net friction force in Amontons law, which is proportional to $p_\perp \times A_c$. This generalized Amontons law for elastic pinning has also been observed experimentally [6]. It can be extracted from the small magnitude of the MSD and the decrease of the MSD with the number of atoms $N$ per surface layer (in Lennard Jones units $N$ and $A_c$ are related by a factor
close to unity). At large temperatures, the contact can be considered “diffusive”. In this regime the same scaling factor, namely $N$, collapses the data for the two system sizes. However, in between these two regimes, a non-trivial size dependence is observed, where the increase of the system size by a factor of four decreases the MSD of the top wall by more than a factor of hundred. It is important to note that the diffusion of individual fluid atoms is not affected by the size of the upper wall. In all cases, the MSD of individual atoms is larger than $N$ times the MSD of the top wall.

This observation goes beyond the theoretical considerations from the last section. The pinning mechanism seems to be even more effective than anticipated. The large wall still appears to be pinned even when individual fluid atoms have typically diffused over significantly more than hundred lattice constants. We speculate that the indirect long-range interactions between monomers mediated through the top wall’s center-of-mass may be the reason for the unexpected slowing down of the equilibration of the top wall. (Remember that all lateral position of an incommensurate top wall are equivalent provided that the fluid is in thermal equilibrium.) Long-range interactions have been shown to frequently slow down equilibration [7].

There is nevertheless a significant difference at what system size commensurate or incommensurate systems appear to be pinned at fixed $(T, p_\perp)$. Other parameters like coverage of the fluid, the strength of the repulsive interactions, etc. play a much less crucial role. In our model, commensurate systems always pin at smaller system sizes as compared to incommensurate systems. This is also reflected in the static friction, which is shown in figure 2. The default system in figure 2 consists of a quarter layer lubricant composed by simple Lennard Jones atoms that interact with $V(r) = 4\epsilon[(\sigma/r)^{12}-(\sigma/r)^6]$ with the default values for $\sigma$ and $\epsilon$ being unity. Potentials are cut-off such that interactions are purely repulsive. In the absence of free surfaces, the main effect of the long-range adhesive part can be absorbed into the load. We note in passing that the net interaction between two fluid atoms is nevertheless attractive due to their elastic interactions with the confining walls. As long as the two confining walls are incommensurate, the static friction coefficient $\mu_\text{s}$, which can be defined as the slope of the curves in figure 2, is relatively independent of the model: The inequality $0.0022 < \mu_\text{s} < 0.0035$ holds for the default system, and systems for which one parameter is changed, namely, a half layer lubrication instead of a quarter lubrication, $\epsilon = 10$, and

Figure 1. Mean square displacement of incommensurate top wall times number of atoms $N$ per surface layer after $10^6$ MD steps for two system sizes, $N = 31 \times 36$ and $N = 62 \times 72$, as function of temperature.
Figure 2. Shear pressure $p_s = F_s/A$ versus normal pressure $p_\perp = L/A$ for different model systems. The default system consists of two flat incommensurate walls with a quarter layer of fluid confined in between them. The default Lennard-Jones interaction parameters are $\sigma = 1$ and $\epsilon = 1$.

$\sigma = 0.9$. Rotating the walls to make them orientationally perfectly aligned, however, increases $\mu_s$ by nearly a factor of five to $\mu_s \approx 0.17$.

While these differences in $\mu_s$ are merely quantitative, there is a qualitative difference in the transition from stick-slip to smooth sliding. Here, we calculate the (average) kinetic friction coefficient $\mu_k = F_k/L$ for a system that is pulled with a spring of stiffness $k$. For small values of $k$ the system shows stick-slip for large values of $k$ smooth sliding at constant velocity is found. The average friction force is shown in figure 3. The commensurate surfaces show similar behavior as dry commensurate surfaces. For a weak spring, the frictional forces are large. In this regime, the top wall shows large scale stick-slip motion. In an intermediate regime, in which atomic scale ratcheting is found, the frictional forces decrease dramatically upon increasing $k$.

Figure 3. Average kinetic friction force per load as a function of the stiffness $k$ of the spring that drives the system for commensurate and incommensurate surfaces separated by a quarter layer of fluid atoms.
At large $k$, the upper wall goes up and down the free energy surface adiabatically, resulting in small frictional forces. Of course, in the smooth sliding regime, $F$ vanishes all together in the limit $k \to \infty$ and driving velocity $v \to 0$. The incommensurate surfaces, however, can not be driven adiabatically resulting in considerably larger friction at large values of $k$. We want to note in passing that commensurate surfaces show periodic stick-slip events while the incommensurate surfaces with boundary lubrication show much more erratic stick-slip events.

So far, we have only studied the friction between flat surfaces. However, boundary lubrication also affects the friction between curved surfaces. In order to study effects related to the curvature of surfaces, we have studied a Hertzian contact of a curved tip on a flat surface as a function of commensurability and boundary lubrication [8]. Due to the finiteness of the contact, even incommensurate contacts show friction, although it can certainly be considered insignificantly small - as long as the friction remains wear free. The situation changes when a thin layer with mobile atoms is present on at least one of the two surfaces. In the study of such systems, the interaction of the tip with the lower wall and with the mobile atoms is purely repulsive. This choice eliminates adhesive effects such as the so called offset load. All other interactions are chosen to be attractive. Some representative results are shown in figure 4.

Non-adhesive commensurate tips show the expected linear relationship between friction force and load, e.g., $F_s = L^\alpha$ with $\alpha = 1$. A dry amorphous tip on a crystalline substrate shows sublinear behavior with $\alpha = 2/3$, which agrees well with friction force microscopy experiments [9]. Dry incommensurate surfaces show the smallest friction forces with an insignificant increase in $F_s$ force with increasing $L$. As soon as a thin film is present in the interface, the wearless friction increases dramatically. However, unlike for the friction between flat surfaces, sublinear behavior is found. In the present study, the exponent $\alpha = 0.85$ is found, which we do not believe to be universal. Details of the friction-load dependences will depend among other on the wetting properties of the fluid.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{friction_load.png}
\caption{Static friction force $F_s$ vs load $L$ for different curved tips on a crystalline substrate.}
\end{figure}
CONCLUSIONS

We have shown that the commensurability of two walls confining a thin fluid film has systematic implications for the tribological properties despite the presence of the confined film. The differences are both quantitative and qualitative. Static friction is considerably larger between two flat commensurate surfaces than between incommensurate surfaces. In the case of a Hertzian contact, the friction-force load dependence can even be qualitatively different, e.g., incommensurate contacts may have a sublinear dependence on the load. The most striking difference, however, is the transition from stick-slip to smooth sliding. In our studies, commensurate surfaces show a dramatic decrease in kinetic friction from stick-slip to smooth sliding. A rather abrupt decrease in kinetic friction is seen as the slipped distances become small. This abrupt decrease in kinetic friction, which was achieved by increasing the stiffness of the driving device, is absent for incommensurate surfaces. It would be an interesting question, how friction control mechanisms such as proposed in Ref. [10] would be effected by the incommensurability of the surfaces in the presence of a thin confined film.

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Some additional results are presented on the cond-mat server, which will not be published in the MRS proceedings Dynamics in Confining Systems VI. The figures presented here serve to shed further light on the discussions related to figure 3 and figure 4 in the main manuscript.

The time dependence of the frictional force leading to figure 3 are shown in figure 5. It is interesting to note the difference in the friction forces in the commensurate case between atomic ratcheting, where $F$ is nearly always positive and smooth sliding where the friction force oscillates. In the incommensurate case, the fluctuations of the friction force is much smaller for small values of $k$ than for commensurate surfaces.

![Figure 5](image)

**Figure 5.** Time evolution of friction force for different stiffnesses of pulling spring. **Left.** Commensurate surfaces. **Right.** Incommensurate surfaces.

In order to understand the sublinear behavior of the friction load law shown in figure 4, it is instructive to analyze the normal and lateral forces acting on individual tip atoms. This is done in figure 6. The center of the tip is in direct contact with the substrate. It carries a considerable amount of load, but the lateral forces are small and in addition of random sign. At positions where one fluid layer is found, tip atoms also carry load. This region contributes the largest fraction to the net friction force, in particular at the entrance of the tip. The friction mechanism of the confined fluid is similar to the one found between flat surfaces. The net friction force of the tip results from the wetting and squeezing out properties of the lubricant.

![Figure 6](image)

**Figure 6.** Force on individual tip atoms. **Left.** Normal force. **Right.** Lateral force. Light atoms represent “friction” while dark atoms represent “antifriction.”