How linear molecules resist to shear: the origin of nanoscale friction

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Abstract Friction force measurements between smooth surfaces across two layers of linear alkanes over five decades of speeds are presented. A maximum friction dissipation is observed at a characteristic speed. The behaviour is described by a new approach: the formation and destruction of molecular bridges between confined alkane layers. The bridges interdigitated between the layers exhibit a thermally activated resistance to shear. An analytical model involving activation barriers accounts for the overall behaviour of the forces over four decades of speed. This first simple semi-quantitative description sheds new light on the subtle mechanisms of friction at the nanoscale level and shows how the molecular length influences the tribological properties of the liquid.

Keywords: nanotribology, friction, surface force apparatus, interface molecular films, linear alkanes.

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Although studied since the 17th century because of their practical importance, the origin of friction forces is not well understood[1, 2]. In the past decades, many groups[3−6] investigated the tribological behaviour of confined liquids and reported different regimes of friction behaviour over various ranges of sliding speeds. Granick[3] showed that the effective viscosities of several types of molecules decayed with shear rate, with an exponent ranging between −2/3 and −1 depending on the load. At higher shear rates the viscosity attained the bulk value that was independently observed in polymer melts[4]. Yoshizawa et al.[5] pointed out that at low relative speed of the surfaces, chain molecules generally produced low friction forces because the molecules had time to disentangle spontaneously, whereas, at higher speeds, they had less time, so friction forces were higher. This opens the way to make analysis on the basis of the existence of activation barriers during friction[6,7].

The theory of thermally activated processes under an imposed force has been thoroughly investigated first by Bell[8] and then, by Evans[9] who described theoretically and experimentally the kinetics of rupture of single weak receptor/ligand bonds. Their approach offered a ready framework to analyze friction forces with entangled chain molecules. When confined between two smooth surfaces, many liquids adopt a layer structure over a few molecular diameters[10]. In the case of linear alkanes, such layers have sometimes been suggested to be interdigitated[2, 5]. These bridges, as entanglements, must contribute to the total friction force. Therefore, with the simple geometry of their entanglements, linear alkanes are easier to be modelled in a friction process. In this case, the bridging molecules, although without real bonds, may easily be described in a similar way as the weak bonds used in Bell and Evans' theories[8, 9].

The new description of confined alkane layers, the theory describing the kinetics of thermally activated processes subject to an imposed force and a new measuring device create together an opportunity to shed new light on friction forces. It is shown here, how in the case of these simple molecules, this theory is able to explain friction behaviour, and why bridge formation and rupture is an important mechanism in the shearing of thin layers of liquids made of linear chains.

1 Experiments and results

We have constructed a friction force apparatus[12] based on the surface force apparatus (SFA) technique[13]. The device is able to measure the friction force between two curved surfaces, along with the force normal to the surfaces and their separation distance with an accuracy of ±1-2 Å. To produce the shear, a lower mica surface is driven horizontally by a piezoelectric bimorph. The displacement waveform is a triangle with an amplitude of 35 μm, and the sliding speed is varied from 3 nm/s to 150 μm/s. The friction force is measured by a spring whose flexion is probed by capacitance plates, giving a sensitivity of ±2 μN.

Hexadecane and dodecane were chosen because they have relative simple structure and their sufficient length can be considered as chain molecules. To have a high level of confinement, the distance was chosen to be that of two molecular layers (9 Å) and the load was 100 μN. Fig. 1 shows the friction force as a function of speed. At very low speeds, the friction force is the least, and over a small range it increases approximately linearly with the logarithm of speed. At higher values, it reaches a maximum and then decreases as speed is further increased. Above a few tens of μm/s, the force increases again. It can be noticed that the hexadecane friction force curve has larger variations than that of dodecane.

2 Discussion

When two surfaces are separated by a layer of alkane molecules whose thickness is twice the molecular chain diameter, one quarter of the alkane chains form bridges between the two layers[11]. Because the first layer of molecules is practically adsorbed on the mica surfaces, it is reasonable to assume that the layers move with the adjacent surface. As a consequence, during sliding, the bridges suffer a force that tends to stretch them and therefore to reduce their number (fig. 2). Thus from the bridge configuration to the non-bridge one, the molecule must pass an activation barrier for a few CH2 groups leaving one layer (and one surface) to the interlayer region.

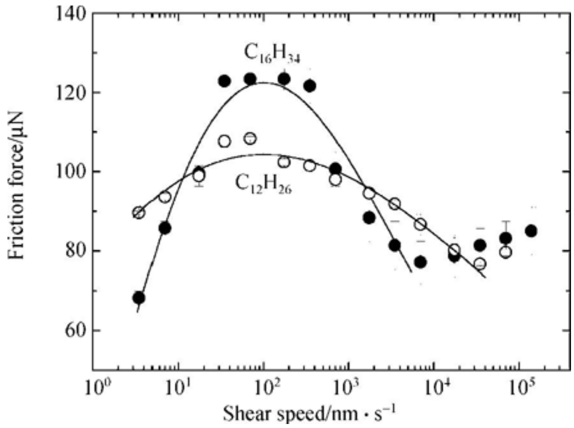

Fig. 1. Friction force curves for hexadecane and dodecane for a load of 100 μN and for a distance between the surfaces of 0.9 nm. The apparatus measures the friction forces between two molecularly smooth surfaces separated by two alkane layers. The solid lines are fits to eq. (2).

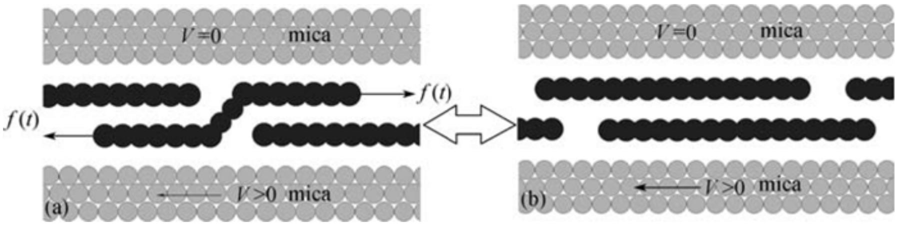

Fig. 2. (a) The confined alkane chains form bridges between two mica surfaces. During sliding, chain molecules are elastically stretched and exhibit a time-dependent ramp force $f(t)$=kvt. (b) The ramp force $f(t)$ applied to the bridges increases their energy level, until, at a force ft , they undergo transition and the molecules go entirely in one of the two layers.

When stretched, chain molecules exhibit an elastic restoring force with a spring constant k[14]. As a consequence, the sliding of one layer relative to the other at the speed v will result in a time-dependent ramp force $f(t)=kvt$. T. Theory [8, 9] predicts that when a ramp force $f(t)$ is applied to one molecule to help it overcome an activation bar- rier, the most probable value $f^*$of the force ft at which it will pass it, varies linearly with the logarithm of the loading rate r_f, here, $f^* \propto \ln kv$. The time-averaged force suf- fered by each bridge during its lifetime is equal to $f^*/2$, and its time-averaged energy level is $f_t^2/6k+1.1k_BT$ . . The friction force F_f results from the contributions of all the stressed bridges:

$$F_f = \frac{n(v)f^*}{2} \tag{1}$$

where $n(v)$ is the number of bridges. Under zero shear, the rate of creation of bridges is equal to their rate of disappearance. As the sliding speed v is increased, the rate of dis-appearance of bridges exceeds that of the creation of new bridges until a new steady state population of bridges $n(v)$ is reached, depending on the sliding speed. If all the bridges had their transition at the most probable value${}^{v}f^{*}$, the steady state population of bridges would be $n(v)$ $n(v) \approx Ne^{-1.1-f^{*2}/6kk_BT}$, where N is the number of molecules in the contact area. Because of thermal fluctuations, the transition forces f_t taken separately from each molecule follow a Gauss distribution. As f^{*} is linear inln, the friction force is expected to be of the form:

$$F_f = a(\ln v + b)e^{-c(\ln v+b)^2}, \tag{2}$$

with

$$a = \frac{N}{3}\sqrt{ckk_BT}, \quad b = -\ln, v_0 \quad \text{and} \quad c = \frac{2k_B{}^2T^2}{x_\beta{}^2\left(12kk_BT + \sigma^2\right)},$$

where x_β is the escape distance from the potential well, which is the distance the molecule has to travel in order to pass the activation barrier, v_0 is the speed at which the bridges disappear spontaneously (under zero force) due to thermal fluctuations, and $\sigma \approx \frac{k_BT}{2x_\beta}$ is the half standard deviation of the distribution of the actual forces f_t at which the bridges disappear[9].

This description predicts a linear rise of F_f at ultra-low speeds and a decrease at high speeds. The amplitude of the rise and decrease should be higher for more bridges, i.e. with longer chains, and smaller for shorter chains because they are closer to spheres. This relatively simple description is in quantitative agreement with the experimental results, as can be seen from the fits to eq. (2) in fig. 1 (solid curves). The fit parameters are displayed in table 1.

Table 1 Values of the fit parameters *a*, *b*, *c*, corresponding to the molecular bridging model for hexadecane and dodecane. The escape distance *x*β, the number *N* of molecules in the contact area and the speed v0 at which the bridges disappear under zero force are also given

	a/μN	b	c	N	x_β /nm	v_0 /nm · s^{-1}
$C_{16}H_{34}$	39.1	0.55	0.019	0.82×10^8	1.37	0.577
$C_{12}H_{26}$	18.4	4.75	0.006	0.95×10^8	2.08	0.009

The number of molecules N in the contact area (table 1) is close to the one expected (~1.3×10^8) from the geometry of the system (two surfaces with a radius of curvature of 2 cm separated by two 0.45 nm thick alkane layers). The energy barrier considered here is mainly the work of removing a few CH_2 groups from one surface and to make some room in the other surface in order to adsorb them. The large value of the escape dis-tance x_β can be explained as follows: the alkane molecules are not pulled in a direction normal to the surfaces, but parallel to them. This model does not require the knowledge of the rate of creation of bridges. However, the use of a Boltzmann distribution has some limitations for a system of molecules in an out-of-equilibrium situation. An alternative model based on the lifetime of the bridges under a force can be easily derived and pre-dict to a similar behavior[15].

Several regimes with an increase or decrease in friction forces have already been reported separately in a limited range of speeds[4, 5]. Here, the measurements are made over a wide range of speeds and a unified theory is established that explains the whole behavior. At ultra-low speeds, the molecules have enough time to rearrange by diffusion and thermal fluctuations, hence the friction force is low (fig. 2). At higher speeds, the molecules have less time to adjust and the rearrangements are increasingly forced. Consequently, there is an increase in the friction force. When the speed is increased even further, the bridges are reduced considerably in number because their rate of disappearance exceeds their rate of formation by an increasing amount: the force therefore reaches a maximum and then declines at higher speeds. Finally, when the speed exceeds tens of μm/s or more, the friction force increases again. We have reached a hydrodynamic regime in which viscous drag is the dominant contribution to the shearing forces. Comparison of the curves of dodecane and hexadecane shows that a shorter chain fluid gives a flatter curve.

3 Conclusion

When confined to a few molecular layers between two surfaces, long chain molecules can form layer interdigitations, which can be one of the main sources of friction as we have shown. Molecules that interdigitate the layers resist to the “ironing” due to sliding and this generates friction. Their simple geometry will lead to the establishment of an analytical model which can account for the force over 4 decades of speed. This model could be extended in future to other types of molecules and to systems with more sophisticated entanglements.

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