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Thermally activated lubrication with alkanes: The effect of chain length

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Abstract. – Friction forces 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. This behaviour is described by a new approach: the formation and destruction of molecular bridges between confined alkane layers. These bridges which interdigitate between the layers exhibit a thermally activated resistance to shear. An analytical model involving activation barriers accounts for the overall behaviour of the speed dependence of the forces over four decades. 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.

Owing to its practical importance, tribology at a macroscopic or microscopic scale has been the subject of intense research in the past decade [1–3]. Because phenomenological approaches based only on adhesion, viscosity and other continuum properties are inadequate to achieve reliable prediction, any new friction system must be tested empirically to determine its performance under various conditions. In addition, simple questions as the speed dependence of friction are not easily obtained due to the difficulty of measuring over a satisfying speed range without modifying the surface geometry, usually by damage.

The tribological behaviour of confined liquids has been investigated by many groups [4–12]. The effective viscosities of several types of molecules (dodecane and OMCTS —octamethylcyclotetrasiloxane) have been shown to decay with shear rate, with an exponent ranging between $-2/3$ and -1 depending on the load [4]. These two molecules exhibited a very similar behaviour. At higher shear rates the viscosity attains the bulk value that has been independently observed in polymer melts [9]. Yoshizawa *et al.* [7] have pointed out that at low relative speed

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of the surfaces, chain molecules generally produce low friction forces because the molecules have time to disentangle spontaneously, in contrast to higher speeds, at which the friction forces are higher. This opens the way to an analysis based on the existence of activation barriers during friction [13]. Thermally activated processes under an imposed force have been investigated first by Bell [14] and then, by Evans [15] who described theoretically and experimentally the kinetics of rupture of single weak receptor/ligand bonds. Their approach offers a ready framework to analyse friction forces with entangled chain molecules. In general, the geometry of entanglements of chain molecules is too complicated to be modelled in a friction process, except for linear alkanes which, when confined between two smooth surfaces, adopt a layer structure over a few molecular diameters [16]. These layers have sometimes been suggested to be interdigitated [2, 6]. This has recently been confirmed using Grand Canonical Monte Carlo simulations of decane [17]. These bridge conformations for which a molecule has a few CH₂ in one layer, a few other ones in the adjacent layer and some in between, must contribute to the total friction force and may allow simple modelisations.

We have constructed a device [18] based on the surface force apparatus (SFA) technique [19] and capable of measuring the friction forces between two molecularly smooth curved surfaces separated by a few molecular layers of a lubricant. The principal characteristics of this apparatus are its high dynamic range (5 decades), the possibility of measuring in all directions, and its high mechanical impedance. 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.

Hexadecane and dodecane were chosen for their sufficient length to be considered as chain molecules. The device [18] measures the friction force, along with the force normal to the surfaces and their separation distance with an accuracy of ± 1 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 by changing the frequency of this waveform. The friction force is measured on an upper surface by a spring whose flexion is probed by capacitance plates, giving a sensitivity of 10 μN . The friction force traces are recorded when a steady-state value is obtained. These forces could be measured with sliding speeds ranging over nearly 5 orders of magnitude, from 3 nm/s to 150 m/s.

A droplet of alkane of ultra-high purity (chromatographic grade, Merck) was inserted between the two mica surfaces and the air in the box was dehydrated by P₂O₅ for 15 hours prior to all the measurements. The measured normal force *vs.* distance profile for hexadecane is given in fig. 1a. For the friction forces, the distance was chosen to be that of two molecular layers (9 Å) and the load was set to 100 ± 10 μN (which, with a contact area of 75 μm^2 , gives a pressure of 1.3 MPa). Two separate experiments were performed for dodecane and two for hexadecane. The process of bringing the surfaces together and the sequence of the sliding speeds were kept rigorously identical to ensure maximum reproducibility of the results. They were brought to 9 Å distance and 100 μN load by moving them quickly to a distance of 200 nm, and then by steps of 5 nm. The surfaces were left at rest for 20 minutes prior to the friction experiments. The sliding speeds were first varied from 350 nm/s up to 140000 nm/s. Then they were varied from 350 nm/s to 3.5 nm/s, and between each of these points, one measurement was done at 350 nm/s (the sequence of speeds was 175, 350, 70, 350, 35, 350, 17.5, 350, 7, 350, 3.5, 350 nm/s) to make sure that the friction force at this speed had not changed, and therefore that the load had not drifted. Figure 1b shows the friction force as a function of speed for hexadecane and dodecane. The error bars show the spanning between the two sets of data obtained for each alkane, which indicates an excellent reproducibility (this is probably due to the flatness of our surfaces that never suffered damage during our experiments—always monitored by an interferometry). The friction traces display transient friction forces

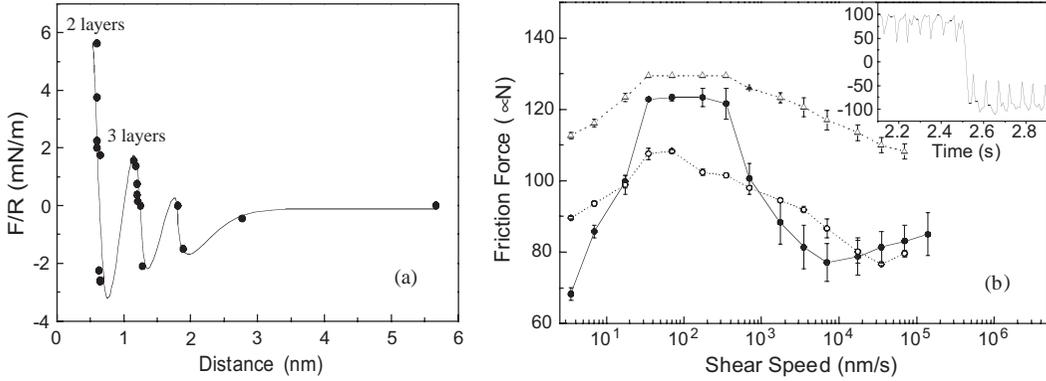


Fig. 1 – (a) Normal forces *vs.* distance between two mica surfaces across hexadecane. The solid line is a guide for the eye. (b) Friction force curves for hexadecane (closed circles) and dodecane (open circles) for a distance of 0.9 nm, and OMCTS (triangles) for a distance of 2.7 nm (3 layers). The load is $100 \pm 10 \mu\text{N}$ (applied pressure: 1.3 MPa). The inset shows a small part of a friction trace for hexadecane at $3.5 \mu\text{m/s}$ showing inverted stick-slip (the scale in μN is on the left).

that reach steady state within less than one cycle. The traces display stick-slip behaviour for speeds in the range $0.7\text{--}14 \mu\text{m/s}$ for hexadecane and $7\text{--}14 \mu\text{m/s}$ for dodecane. Unlike what is usually seen, this stick-slip (see inset of fig. 1b) displays a kinetic friction force that oscillates between two levels in a similar way to the one reported in ref. [20] with the difference that our second kinetic friction regime does not occur at an almost zero friction force. The forces reported in fig. 1b are mean values at steady state. At very low speeds, the friction force is the least, and over a small range it increases 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 micrometers per second, the force increases again. The longer (hexadecane) molecule appears to produce a friction force curve with larger variations than does that of dodecane. Changing the load to $60 \mu\text{N}$ (not shown) did only shift the forces to smaller values.

Within the new context offered by the existence of bridges between the layers [17], a relatively precise explanation of the friction behaviour can be developed. First, because they bind the layers together, the bridges are expected to offer a substantial resistance to shear in contrast to the non-interdigitated parts of these layers. This is true only if there is negligible slip at the alkane/mica interface. The good wetting properties of the alkanes on mica [21] indicate that these molecules have stronger interactions with mica than between themselves. It is therefore reasonable to assume that the layers move with the adjacent surface [22]. An analysis of the data can therefore be conducted by considering that the bridges are the main contribution to friction. The small value of the friction force F_f at very low speeds indicates that the bridges have time to adjust to the shear by diffusion because the rate of increase of the forces applied to them is smaller than the rate of spontaneous conformational changes towards the non-bridge state. At higher speeds, they have less time and their changes of conformation will occur at increasing forces. If the friction force mainly results from the intramolecular tensions, it should then increase, and it indeed increases linearly with $\ln(v)$. As the speed further increases, the lifetime of the bridges is shorter and their population decreases so much that the friction force reaches a maximum and then decreases as shown in fig. 1b. Above 10^4 nm/s , the friction force increases again. This last final increase has been seen before and is generally associated to a regime in which the viscous drag is the dominant contribution to the shearing forces.

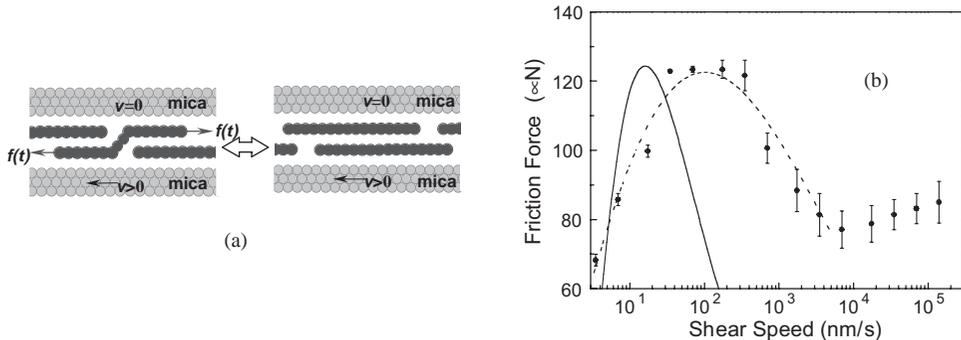


Fig. 2 – (a) One molecular bridge across two alkane layers confined between two mica surfaces. During sliding at speed v , the chain molecules undergo a time-dependent ramp force $f(t) = kv t$ until, at a critical force, they go entirely in one of the two layers. (b) Hexadecane friction data *vs.* speed. The solid line is a fit with eq. (5) with $v_0 = 2$ nm/s and $x_\beta = 0.4$ nm, and $N = 1.5 \times 10^8$. The dashed line is a fit obtained from the alternative model using a Boltzmann distribution to calculate the bridge population, as described in the text ($v_0 = 0.6$ nm/s and $x_\beta = 1.4$ nm, and $N = 0.8 \times 10^8$).

The following discussion focuses on the physics of forced changes of conformation of the alkane molecules and on the orders of magnitude of the significant parameters. We will assume that one quarter of the alkane chains form bridges between the two layers, as estimated from simulations for decane [17]. During sliding, the bridges suffer a force that tends to stretch them: as the part of the molecule that is in one layer is pulled in a direction opposite to the one in the other layer, there is a tendency to draw the whole molecule completely into one layer or the other (see fig. 2a). To go thus from the bridge configuration to the non-bridge one, the molecule must pass an activation barrier because a few CH_2 groups leave one layer (and one surface). When stretched, chain molecules exhibit an elastic restoring force with a spring constant k [23]. As a consequence, the sliding of one layer relative to the other one at the speed ν will result in a time-dependent ramp force $f(t) = kv t$. Theory [14, 15] predicts that when a ramp force $f(t) = r_f t$, with a loading rate r_f , is applied to one molecule, the most probable value f^* of the force at which it will pass an activation barrier increases linearly with the logarithm of r_f , *i.e.* with the logarithm of kv [14, 15]:

$$f^* = \frac{k_B T}{x_\beta} \ln(v/v_0), \quad (1)$$

where x_β is the escape distance from the potential well, *i.e.* 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) because of their finite lifetime. The time-averaged force suffered by each bridge during its lifetime is equal to $f^*/2$. The friction force F_f results from the contributions of all the stressed bridges:

$$F_f = N_b(v) f^*/2, \quad (2)$$

where $N_b(v)$ is the number of bridges. Under zero shear, the number of bridges created per unit time is equal to the number of those which disappear. As the sliding speed v is increased, the rate of disappearance of bridges and that of the creation of new bridges change until a new steady state value of $N_b(v)$ is reached. When the molecules are stretched faster than the time between two significant fluctuations, one expects a substantial decrease of $N_b(v)$. This gives rise to a maximum of the friction force followed by its decrease at high speeds.

TABLE I – Estimated values of v_0 and x_β , from linear extrapolation of the friction forces to zero at very low speeds, and E_b from eq. (3).

	v_0 (nm/s)	x_β (nm)	E_b ($k_B T$)
Dodecane	0.003	6.5	7.5
Hexadecane	0.8	2.3	3.5

Assuming for simplicity that $N_b(v)$ is constant at low speeds, it is possible to estimate v_0 and x_β by extrapolating the linear part of the friction force to zero and scaling it to one bridge using eqs. (1) and (2). The number of bridges N_b at ultra-low speeds can be estimated from the geometry of the system (the flattened area with two alkane layers can be determined [7]: for a load of $100 \mu\text{N}$, it is equal to $75 \mu\text{m}^2$ which will contain about 1.5×10^8 molecules; if one fourth of the molecules forms a bridge, there will be 3.75×10^7 bridges). This yields the estimates for v_0 and x_β given in table I. The relationship between v_0 and the activation barrier E_b is [15]

$$\ln(kv_0) = \ln(k_B T/x_\beta t_D) - E_b/k_B T, \quad (3)$$

where t_D^{-1} is the attempt frequency, equal to $k_B T/\gamma l_c l_{ts}$; γ is the viscosity and l_c and l_{ts} are two lengths related to the shape of the potential well. t_D^{-1} is about 10^9 s^{-1} in water [15]. The effective viscosities of the confined alkanes, as deduced from fig. 1b, are higher than that of water by a factor $\simeq 3 \times 10^6$, yielding t_D of the order of 10^{-2} – 10^{-3} s . Injecting the values for N , x_β , and v_0 in eq. (3) yields the values for E_b reported in table I. Here, E_b is the work for removing a few CH_2 groups from one surface and for making some room for them in the other surface. It can be noticed that the value ($3.5k_B T$) obtained for hexadecane is realistic (refs. [17,24] use $0.72k_B T$ for the interaction between one CH_2 and mica). The one for dodecane ($7.5k_B T$) is not because it is much higher than that of hexadecane in contrast to what can be expected from a shorter molecule. The van der Waals potential energy well is known to have a width of the order of the \AA in a direction normal to the surfaces [25] and one should expect the escape distance x_β to be of the same order. However, the alkane molecules are not pulled in a direction normal to the surfaces but parallel to them. Along this trajectory which will be almost parallel to the surface, the potential energy profile will display variations over a larger distance. This can explain some widening of the potential barrier and the large value obtained for x_β for hexadecane. For dodecane, the x_β value is much larger (6.5 nm) and unrealistic. In contrast to dodecane, the realistic parameter values for hexadecane show that the bridges dominate the friction process in the range of speeds where the increase and then decrease of F_f is observed. For dodecane, the contributions of non-interdigitated parts of the layers are not negligible.

The analysis of the hexadecane behaviour can be improved to describe the maximum of the friction force. As the force acting on the molecules is a ramp force kvt , the lifetime t^* of the bridge under force is $t^* = f^*/kv$ with f^* as defined in eq. (1). At zero speed, the sum of the number of bridges N_b^0 and of non-bridges N_{nb}^0 is equal to the total number of molecules N . At any speed, the bridge population is governed by k_{on} and k_{off} , the rates of creation and of disappearance of bridges with a steady state ($t \rightarrow \infty$) form:

$$N_b(v) = N k_{\text{on}} / (k_{\text{on}} + k_{\text{off}}). \quad (4)$$

At steady state, we have $N_{nb} k_{\text{on}} = N_b k_{\text{off}}$. In a first approximation, we can assume that the probability of bridge creation does not depend on the speed, and assuming [17] that at zero speed, one quarter of the molecules forms a bridge, k_{on} is set equal to $k_{\text{on}} = k_{\text{off}}(v = 0)/3$. The k_{off} value at zero speed ($1/t_0$) is given by [15] $k_{\text{off}}(v = 0) = \exp[-E_b/k_B T]/t_D$ which

becomes, with eq. (3), $k_{\text{off}}(v = 0) = kv_0x_\beta/k_B T$. The k_{off} value ($1/t^*$) at speed v is $k_{\text{off}}(v) = kvx_\beta/(k_B T \ln(v/v_0))$ (note that this equality does not hold for $v = v_0$). From eqs. (1), (2), (3) and (4) and from the expressions for k_{off} , we get the friction force

$$F_f = \frac{Nk_b T}{2x_\beta} \frac{v_0 \ln(v/v_0)}{v_0 + \frac{3v}{\ln(v/v_0)}} \quad (5)$$

in which the adjustable parameters are v_0 and x_β . Equation (5) predicts a rise of F_f at ultra-low speeds followed by a maximum and then by a decrease at high speeds close to the hexadecane data. This is shown as a solid line in fig. 2b for $v_0 = 2$ nm/s, $x_\beta = 0.4$ nm, and $N = 1.5 \times 10^8$ molecules. The model is compatible with the right orders of magnitude for the main parameters, but a close quantitative agreement is not yet possible as shown in fig. 2b. It is instructive to list the main approximations made in this model: i) the friction from the non-interdigitated parts of the layers is neglected; ii) k_{on} is assumed to be independent of v ; iii) the bridges are assumed to be pulled by their ends; iv) the most probable force f^* is used instead of the mean force. Point ii) is the main approximation because the fit is very sensitive to the k_{on} parameter which, in a more elaborate model, should depend on v . An alternative approach to calculate the friction force would be to average the energy of a stretched bridge over its lifetime and assume a Boltzmann distribution for the bridge population. Strictly speaking, this is not valid because the molecules undergoing a ramp force are not at equilibrium, but it has the advantage of not assuming a particular form of k_{on} . If N is also used as an adjustable parameter, it would give the dashed line in fig. 2b with $N = 0.8 \times 10^8$, $x_\beta = 1.4$ nm, and $v_0 = 0.6$ nm/s.

The measured forces at low speeds are consistent with the forced passage of activation barriers by individual molecules. When confined to a few molecular layers between two surfaces, the layer interdigitations formed by long chain molecules can be one of the main sources of friction at low speed because the molecules resist to the “ironing” due to sliding. Because thermally activation processes also occur with globular molecules, the model also predicts for them a bell-shaped $F_f(v)$, though with rising and decreasing parts less steep than for chains of globules with the same diameter. We have performed measurements with OMCTS at a distance of 2.7 nm (3 layers) and the same load. The friction force level is higher than for the alkanes (fig. 1b) but it indeed displays a curve with a maximum which is flatter than the ones of hexadecane and dodecane. This difference gives qualitative information on the friction from the non-interdigitated parts of the layers. Altogether, the results show that the longer the molecules, the more bridges there are, and the larger the amplitude of the variation of the friction force as a function of $\ln(v)$. The curves of fig. 1b show a clear effect of the length of the molecules on their tribological properties. The length of the chain will also affect the elastic modulus of the molecules, and through this, the loading rate and the lifetime of the bridges. In eq. (5), k seems to play no role, but this is due to the approximations made on k_{on} . Several regimes with an increase or decrease of friction forces have already been reported separately in a limited range of speeds [4, 5, 7]. Here, the measurements are made over four decades of speeds. This model, which shares concepts akin to those used in refs. [26, 27], gives a unified description of the dynamics of confined alkanes molecules using an extremely simple geometry and mathematics that do not go beyond rules of three. This model could be refined and, we believe, could be extended in the future to other types of molecules and to systems with more complicated entanglements like polymers.

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