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# **RESEARCH ARTICLE**

# Rack-and-pinion effects in molecular rolling friction

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(...)

Rolling lubrication with spherical molecules working as "nanobearings" has failed experimentally so far, without a full understanding of the physics involved and of the reasons why. Past model simulations and common sense have shown that molecules can only roll when they are not too closely packed to jam. The same type of model simulations now shows in addition that molecular rolling friction can develop deep minima once the molecule's peripheral "pitch" can match the substrate periodicity, much as ordinary cogwheels do in a rack-and-pinion system. When the pinion-rack matching is bad, the driven molecular rolling becomes discontinuous and noisy, whence energy is dissipated and friction is large. This suggests experiments to be conducted by varying the rack-and-pinion matching. That could be pursued not only by changing molecules and substrates, but also by applying different sliding directions within the same system, or by applying pressure, to change the effective matching.

Keywords: nanotribology; rolling friction; fullerenes

#### Introduction 1.

The problem of designing nanomechanical devices, in particular, of reducing friction by means of nano- and micro-bearings [1, 2] is nowadays a hot one. The idea of using spherical molecules such as fullerene  $C_{60}$  as molecular nanobearings gave rise to experimental attempts [3–5] as well as Molecular Dynamics (MD) simulations [6–9]. Other potentially rolling molecules were considered as additives in oil lubricants, and predicted to provide interesting tribological properties [10]. The simulations indicated that ball-shaped molecules may either slide or rotate over a surface, depending on the substrate and the position of the molecule, and suggested that the rolling configuration should indeed attain extremely low friction [6, 8], with a predicted friction coefficient of the order  $\mu \sim 0.01 - 0.02$  [7] or smaller [8]. All experimental attempts however met with scarce success so far. A single  $C_{60}$  molecule confined between solid substrates should begin to roll under a torque of order  $10^{-19}$  Nm [11]. However, C<sub>60</sub> molecules generally condense to form close-packed islands, their two dimensional (2D) crystalline structure exhibiting order at low temperatures. Through a first-order orientational order-disorder transition [12] at  $T = T_m \approx 260$  K, the molecules actually unlock to attain seemingly free rotation at  $T > T_m$ . At  $T_m$  there is indeed an abrupt change in friction [4], but the lowest friction coefficient is still of order  $\mu \sim 0.15$  [3, 4], worse than with traditional oil-based

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lubricants. Coffey and Krim [5] undertook a quartz crystal microbalance study of one or two  $C_{60}$  monolayers adsorbed on Ag(111) or Cu(111). There are no rotations in a  $C_{60}$  layer on Cu(111), and only a slow change of molecular orientations for a  $C_{60}$  layer on Ag(111). In a bilayer,  $C_{60}$  molecules in the top layer rotate freely at 300 K, as expected. Nonetheless a molecularly thin methanol film deposited over the  $C_{60}$  bilayer failed to show either the expected low friction, or any essential difference between these systems. Altogether, these results apparently doom the idea to replicate the bearing concept at the nanoscale. The questions why, and how this could be overcome are still quite open.

First of all, even a small amount of charge transfer and/or bonding between  $C_{60}$ and the metal substrate may hinder the rolling; therefore, chemically inactive, insulating substrates should be preferred to metals. A second handicap lies in the close packing of molecules. Balls in bearings are arranged so as to prevent contact, but rolling molecules in a monolayer are in close contact, hindering, even in the apparently freely rotating phase, their mutual rolling and jamming the same way mutually ingrained rolling cogwheels would. As was found in earlier simulations [13], a way to avoid jamming is to lower dramatically the molecular coverage well below a monolayer – indicatively to coverages  $\leq 0.3$  – to approach the limiting rolling friction of a single molecule. A third element, not investigated so far, is a possible role of molecule-substrate matching. Using a single molecule model as our starting point, we now find that this element is unexpectedly important.

In our ordinary, macroscopic world, the main source of rolling friction is deformation, since both substrate and roller elastically or plastically deform at the contact. The deformation energy is partly released and lost in the form of bulk frictional heat when the roller moves on [14]. By designing the bulk so that dissipation is poor in the right frequency range, rolling friction can be made  $10^2$  to  $10^3$ times lower than sliding friction, since the latter implies breaking and re-forming of slider-substrate bonds. As the roller size is decreased however, adhesion grows in importance, eventually becoming the main source of friction. To rotate a molecule, one has to break the molecule-substrate bonds one side of the molecule and create new bonds on the opposite side; hence, molecular rolling friction might not be much lower than sliding friction.

Our goal is to understand what physics may yield the lowest friction coefficient attainable for molecular rolling and which system parameters might provide it. In the end, we find that nanobearings might indeed work as well as macroscopic ones, but one has to choose properly the macroscopic counterpart, which here turns out to be a perfect rack-and-pinion matching as in cogwheels. Because we are interested in general trends, we presently explore a minimal 2D model, which allows us to span a large number of parameters, and also provides an easier visualization of all processes.

# 2. Model

Consider two substrates with lubricant molecules in between, all elements made up of classical point particles (atoms). Atoms can generally move in the (x, y)plane, where x is the sliding direction and y is perpendicular to the substrates. The substrates, pressed together by a load force  $F_l = N_s f_l$ , consist of rigid atomic chains of length  $N_s$  and lattice constant  $R_s$ , so that the system size in the sliding direction is  $L_x = N_s R_s$  and the total mass of the substrate is  $N_s m_s$  (we use periodic boundary condition along x). The bottom rigid substrate is fixed at x = y = 0, the top one is free to move in both x and y, while driven along x through a spring of elastic constant  $k_s$  moving with speed  $v_s$ . The spring force

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F, whose maximum value before the onset of sliding measures the static friction force  $F_s$ , and whose average during smooth motion  $F_k = \langle F \rangle$  is the kinetic friction force, is monitored during simulation (throughout the paper we will normalize forces per substrate atom  $f = F/N_s$ ). Thus, our model is a 2D variant of a typical experimental setup in tribology [14, 15]. Between the substrates we place circular ("spherical") lubricant molecules. As in Ref. [13], each molecule consists of one central atom and of L atoms on circle of radius  $R_m = R_{ll}/2\sin(\pi/L)$  so that their chord distance is  $R_{ll}$ . All atoms interact via a 12-6 Lennard-Jones (LJ) potential  $V_{\rm LJ}(r) = V_{\alpha\alpha'} \left[ (R_{\alpha\alpha'}/r)^{12} - 2 (R_{\alpha\alpha'}/r)^6 \right]$ , where  $\alpha, \alpha' = s$  or l for the substrate or molecular atoms respectively. The latter are additionally coupled to the central atom by stiff springs of the elastic constant  $K_m$ ,  $V_{\text{stab}}(r) = \frac{1}{2}K_m(r - R_{\text{stab}})^2$ , where the distance  $R_{\text{stab}} = R_m + (12 V_{ll}/K_m R_m) \left[ (R_{ll}/R_m)^6 - (\bar{R}_{ll}/R_m)^{12} \right]$  is chosen so that the total potential  $V_{\rm LJ}(r) + V_{\rm stab}(r)$  is minimum at  $r = R_m$ . With  $K_m = 100$  the resulting stiff molecular shape resisted destruction during the simulations. Thus, the lubricant-lubricant interaction is described by the parameters  $V_{ll}$  and  $R_{ll}$ , while the lubricant-substrate interaction, by  $V_{sl}$  and  $R_{sl}$  (direct interaction between the top and bottom substrates is omitted). We use dimensionless units, where  $m_s = m_l = 1$ ,  $R_{ll} = 1$ , and the energy parameters  $V_{\alpha\alpha'}$  takes values around  $V_{\alpha\alpha'} \sim 1$ . Because a 2D model cannot reproduce even qualitatively the phonon spectrum of a 3D system, and because frictional kinetics is generally diffusional rather than inertial, we use Langevin equations of motion with Gaussian random forces corresponding to temperature T, and a damping force  $f_{\eta,x} = -m \eta(y) \dot{x} - m \eta(Y-y) (\dot{x} - \dot{X})$ , where x, y are the atomic coordinates and X, Y are the coordinates of the top substrate (the force  $f_{\eta,y}$  is defined in the same way). The viscous damping coefficient is assumed to decrease with the distance from the corresponding substrate,  $\eta(y) = \eta_0 \left[1 - \tanh(y/y_d)\right]$ , where typically  $\eta_0 = 1$  and  $y_d \sim 1$ .

## 3. Results



Figure 1. Activation energy  $E_a$  as a function of the substrate lattice constant  $R_s$  for the rigid L = 6 molecule, for  $f_l = 0.5$ ,  $V_{sl} = 1/9$ , and  $R_{sl} = R_{ll}$ . Open symbols correspond to sliding, solid symbols to rolling.

Simulation results for single molecule friction were obtained from L = 5 (the simplest circular molecule) up to L = 13 and 14, which may be considered as a 2D version of fullerene. In fact in the 3D case, the surface area of the spherical molecule is  $s = 4\pi R_m^2$ . With  $L_3 = 60$  atoms on the surface, this gives  $s \approx L_3 R_{ll}^2$ , or  $R_m/R_{ll} \approx 2.18$ . In 2D, the length of the circle is  $2\pi R_m \approx LR_{ll}$ , or  $L \approx 2\pi R_m/R_{ll}$ , which leads

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Figure 2. (color online): Sliding adiabatic motion of the rigid L = 6 molecule for  $R_s/R_{ll} = 0.66$ ( $\Delta \phi < \phi_0$ , left panel) and rolling for  $R_s/R_{ll} = 1.29$  ( $\Delta \phi > \phi_0$ , right panel). Other parameters as in Fig. 1. Lower panels: X-dependence of the potential energy V(X), and the angle  $\phi(X)/\phi_0$ . Top panel: configurations as the molecule moves from one minimum of V(X) to the next.



Figure 3. (color online): Rigid molecule activation energy  $E_a$  versus  $R_s/R_{ll}$  for  $f_l = 0.5$  and  $V_{sl} = 1/9$ . Unlike Fig. 1, here  $R_{sl} = R_s$ . Panel (a): even L = 6, 8, 10, 12, 14; panel (b), odd L = 5, 7, 9, 11, 13. Empty triangles in L=6 indicate sliding friction intervals.

to  $L \approx 13.7$  for the same ratio  $R_m/R_{ll}$  as for 3D fullerenes. We first consider a rigid molecule,  $V_{ll} = \infty$  and  $K_m = \infty$ , fix X of the top substrate and seek the potential energy minimum V by varying its y-coordinate Y, the molecular center  $(x_c, y_c)$  and the rotation angle  $\phi$ . The X dependence of V,  $(x_c, y_c)$ , and  $\phi$  defines the adiabatic trajectory, which describes the joint substrate and lubricant motion when infinitely slow. We extract the activation energy  $E_a = \max[V(X)] - \min[V(X)]$ , and the static friction force magnitude, approximated as  $f_s = \max[dV(X)/dX]$  ( $f_s \sim E_a$ in our units).

Figures 1 and 2 show results for the L = 6 molecule when, to simplify further,  $R_{sl}$  is fixed to  $R_{sl} = R_{ll}$ . The energy V(X) is periodic with  $R_s$  (or a multiplier of  $R_s$ ). The molecular angle  $\phi$  varies by  $\Delta \phi$  as the potential energy V(X) changes from minimum to maximum. Because  $\phi(X)$  must be continuous, the motion corresponds to sliding if  $\Delta \phi < \phi_0 \equiv 2\pi/L$ , while if  $\Delta \phi > \phi_0$  the molecule must rotate when it moves. As Fig. 1 shows, for  $R_s < R_{ll}$  the motion corresponds to sliding, i.e.,



Figure 4. (color online): Position  $R_s^{(1)}$  of the main minimum of  $E_a(R_s)$ , extracted from Fig. 3, for increasing molecular size *L*. Curves are fits to the cogwheel model Eq. (1). The asymptotic limit of 1 is still relatively far for reasonable molecular radii.



Figure 5. (color online): Static friction force  $f_s$  as a function of the substrate lattice constant  $R_s/R_{ll}$  for (a) L = 14 and (b) L = 13 for different system parameters: (i)  $f_l = 0.5$  and  $V_{sl} = 1/9$  (solid curve and circles and stars), (ii)  $f_l = 0.5$  and  $V_{sl} = 1/3$  (down triangles and red dotted curve and stars), and (iii)  $f_l = 0.1$  and  $V_{sl} = 1/9$  (up triangles and blue dotted curve). Other parameters are:  $R_{sl} = R_s$ ,  $K_m = 100$  and  $V_{ll} = 1$ .

the molecule is shifted as a whole, slightly oscillating during motion (see Fig. 2, left panel). The sliding activation energy has maxima at  $R_{ll} = nR_s$  (where n is an integer) and minima at  $R_{ll} = (n - 1/2)R_s$ . On the other hand, for  $R_{ll} < R_s$  the motion corresponds to rolling (Fig. 2, right panel). Here  $E_a(R_s)$  has sharp minima at unanticipated values of  $R_s/R_{ll}$  (e.g., for  $R_s/R_{ll} \approx 1.29$  in Fig. 1).

Varying  $R_s$  in Fig. 1 at fixed value of  $R_{sl}$  for the lubricant-substrate interaction, we find that for  $R_s < R_{ll}$  rolling replaces sliding already around  $R_s/R_{ll} = 2/3$ . Preference for rolling over sliding increases for increasing load  $f_l$  and for decreasing interaction strength  $V_{sl}$  [16] (choosing alternatively  $R_{sl} = R_s$  rolling is even more prevalent than for fixed  $R_{sl}$ ). When sliding wins over rolling, it generally provides a lower activation energy. Recalling that  $\phi_0 = 2\pi/L$ , the region of parameters for rolling should increase with L — a rounder wheel rolls better! The  $R_s$  dependence of  $E_a(R_s)$  for increasing size L (Fig. 3) shows rolling for all  $R_s$  and for all  $L \geq 5$ , except for L = 6 which shows both rolling and sliding (see open symbols in Fig. 3a). As  $R_s$  varies, the value of  $E_a$  oscillates by more than two orders of magnitude for even L and more than three for odd L, with deep sharp minima separated by broad maxima. Clearly, by suitably choosing  $R_s/R_{ll}$  a very strong decrease of rolling friction is attainable.

The unexpected minima of  $E_a(R_s)$  can be explained by simple engineering — a

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"rack-and-pinion" model. Consider the molecule as a cogwheel (the pinion) with L cogs, primitive radius  $R_m$  and external radius  $R^* = R_m + h$ , where  $h \propto R_{sl}$ . The chord distance between nearest cogs is  $R_{ll}^* = 2R^* \sin(\pi/L)$ . Best rolling conditions are expected when  $R_{ll}^*$  matches the substrate potential period  $R_s$ , i.e., for  $R_s^{(1)} = R_{ll}^*$  and its fractions,  $R_s^{(2)} = R_{ll}^*/2$ ,  $R_s^{(3)} = R_{ll}^*/3$ , etc. The main minimum of  $E_a(R_s)$  is expected at

$$R_s^{(1)}/R_{ll} = 1 + (2h/R_{ll})\sin(\pi/L).$$
(1)

As shown in Fig. 4, the cogwheel model (1) with  $h = \beta R_{sl}$ , where  $\beta$  is a parameter, fits extremely well the shift of minimum position with molecular size L. Moreover, it can explain its variation with load (the radius  $R^*$  and therefore h decreases as the load grows) as well as with the lubricant-substrate interaction  $V_{sl}$  ( $R^*$  and hdecreases with  $V_{sl}$ ) [16]. It also accounts for the even-odd effect since odd L involves perfect ingraining for one substrate at a time, justifying why roughly double values of  $\beta$  are needed for even relative to odd L.

These insights for rigid molecules are confirmed by the static friction force obtained from simulation with deformable molecules (Fig. 5). The friction coefficient  $\mu_s = f_s/f_l$  ranges from  $\mu_s \sim 0.1$  at  $R_s/R_{ll} \approx 0.7$  to  $\mu_s \sim 0.01$  or even  $\mu_s \sim 0.001$  at  $R_s/R_{ll} \approx 1.1$ . The results are also robust to changes of model parameters. For example, Fig. 5 compares the dependences  $f_s(R_s)$  for two values of the amplitude of lubricant-substrate interaction,  $V_{sl} = 1/9$  and 1/3, and for two values of the load,  $f_l = 0.5$  and 0.1. We found both static  $f_s$  and kinetic friction  $f_k$  to increase approximately linearly with load,  $f_{s,k} \approx f_{0s,0k} + \mu_{s,k}f_l$ . Visualization of MD trajectories shows that for  $R_s/R_{ll} = 0.7$ , where friction is high, rolling rotation is in fact discontinuous, and accompanied by a molecular shift/sliding — much as cogwheels with excessive clearance would do — which dissipates mechanical energy into vibrations, whereas for  $R_s/R_{ll} = 1.1$ , where friction is low, the motion is a smooth rotation, corresponding to optimal rack-and-pinion coupling.

Simulations further showed that this scenario remains valid at nonzero temperature T. As T increases, both static and kinetic friction forces are found to decrease, the stick-slip changing to creep and finally to smooth motion at high temperatures. We also found transitions from stick-slip to smooth rolling for increasing velocity. The cogwheel effect remains, and for example calculated static friction for  $R_s/R_{ll} = 0.7$  and  $R_s/R_{ll} = 1.1$  still differ by a factor of ten or more. The critical velocity  $v_c$  of the transition from stick-slip to smooth rolling also differs by a factor of about four in the two cases. In all cases we find  $f_k \ll f_s$  [16].

The present approach to the single rolling molecule can be extended to a finite coverage of lubricant molecules. For M molecules the individual molecular load is  $f_{l1} = f_l/M$  so that the friction per molecule  $f_{s1,k1}$  also decreases. However, the total friction force  $f_{s,k} = M f_{s1,k1}$  increases, so that the combined effect is a slow increase of the total friction with M. In a real situation, coalescence may lead to jamming, with molecules blocking their mutual rotation. In our model, jamming starts already at  $\theta_M \approx 0.1$  and completely destroys rolling at  $\theta_M > 0.3$  [13, 16] (here  $\theta_M = M/M_1$  is the coverage, with  $M_1$  the number of molecules in a monolayer).

# 4. Conclusion

Our 2D modeling leads to overall conclusions of considerable novelty. Rolling spherical lubricant molecules can indeed provide better tribological parameters than sliding atomic lubricants. The effect may be as large as in macroscopic friction,

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where rolling reduces friction by a factor of  $10^2 - 10^3$ , however only for low concentration of lubricant molecules, and for specially chosen values of the ratio  $R_s/R_{ll}$ , e.g., for  $R_s/R_{ll} \sim 1.1$ , corresponding to perfect rack-and-pinion matching.

While of course the matching condition will be more delicate and difficult to realize in 3D than in 2D, the concept can surely be pursued experimentally, for different spherical molecules, different substrates, and different coverages. Inert nonmetal surface (such as perhaps self-assembled monolayers) could represent a better choice of substrate than metals for fullerene deposition; and lower coverages should be preferred to complete monolayers. Because 3D rolling has an azimuthal degree of freedom, the novel cogwheel effect found here will be direction dependent, and rolling friction will exhibit anisotropy depending on direction. At fixed rolling direction, increasing load could offer the simplest tool to change the rack-andpinion matching through a pressure-induced decrease of  $h = \beta R_{sl}$ . In this case, the effect would show up as a strikingly nonmonotonic (non-Amontons) behavior of friction with load.

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- Due to space limitations we defer this and other details to a successive extensive paper, O.M. Braun [16] and E. Tosatti, to be published.