Direct Measurement of the Adhesion and Friction of **Smooth C₆₀ Surfaces**

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Using a surface forces apparatus, measurements were made of the static adhesion and dynamic friction forces between two smooth solid crystalline surfaces of C₆₀ deposited as uniform layers on mica substrates. Between molecularly smooth surfaces, the surface energy (adhesion energy per unit area) was unusually low, whereas the static friction force was very high. However, the kinetic friction force between both smooth and rough C60 surfaces was "normal", and the same as previously measured between rough surfaces. Some of these unusual properties can be rationalized in terms of the large size and nearly perfect spherical shape of the C_{60} molecule. The results and analysis suggest that C_{60} and other large spherical molecules with diameters greater than 5-10 Å interact more as macroscopic particles than as conventional molecules.

Introduction

Buckminsterfullerene, C₆₀, and its derivatives has drawn wide attention due to its unique molecular structure and the unusual physical, chemical, and electronic properties. 1-5 C₆₀ molecules are near-perfect spheres, and in the solid crystal each molecule rotates at a high frequency while remaining within its lattice position. Much speculation has centered around this property as being conducive for good lubrication because the molecules could mimic ball bearings, but this has not been borne out by experiments. 6-9 Other unusual physical properties of C_{60} are its high sublimation temperature (460–600 °C) 10 and heat of sublimation (40 kcal/mol),11 the absence of a liquid phase, and low volume compressibility of the solid (7 \times 10⁻¹² cm²/dyn, which makes solid C₆₀ the softest solid carbon struc-

An important distinguishing feature of the C₆₀ molecule is its large diameter, about 10 Å, which is large

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enough that one may expect continuum or macroscopic theories to describe some of its intermolecular interactions. 13 The results reported here arose from direct experimental measurements of the interaction forces of solid crystalline surfaces of C₆₀ using the surface forces apparatus technique, which has previously been used to investigate the fundamental static and dynamic forces between various surfaces both in air (or vacuum) and in different liquids. 14,15

Materials and Methods

A surface forces apparatus (SFA)16 was used for the first time to measure the interactions between molecularly smooth and optically transparent sheets of mica substrates coated with solid C₆₀ layers, in air. Normal forces were measured from the deflection of a horizontal spring supporting one of the two curved surfaces (radius $R \sim 1$ cm) using an optical technique, based upon fringes of equal chromatic order (FECO) interferometry. This multiple beam interference technique allows measurement of surface separations and spring deflections (which give the normal force) with a resolution of about 1 Å.¹⁶ Friction forces were measured with an attachment to the SFA that measures lateral or shear forces using strain gauges attached to a vertical friction-force measuring spring. 15,18

Solid C₆₀, 99.5% pure, was obtained from Bucky USA, Houston. Solid surface films of C_{60} on mica were produced by sublimation under vacuum, as described in ref 19. The approximate thickness of each deposited film (~500 Å) was measured during the deposition by absorption spectroscopy. The exact thickness and smoothness of each film was mea-

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sured by FECO interferometry¹⁷ after the deposition. The films produced were also characterized by atomic force microscopy (AFM) as previously described20 and found to have a molecularly smooth (crystalline FCC²¹) surface lattice with a mean square roughness of <5 Å over at least a micron in distance. In addition, from the flattened shapes of the FECO fringes for two surfaces in contact, 17,20 one could further ascertain that the outermost surface layers were smooth and step-free over lateral distances of at least 100 μ m.

Results and Discussion

Measurements were made on surfaces having contact diameters in the range 33-41 μ m, corresponding to contact areas in the range A = $850-1300 \mu m^2$. Loads were varied from L = 0-60 mN, corresponding to applied pressures of P = L/A = 0-45 MPa. Sliding velocities were varied from V = 0.2 to 4 μ m/s. All measurements were conducted at room temperature, T= 23 °C, in an atmosphere of air, or in dry or humid clean nitrogen gas. All the data shown were recorded in an atmosphere of dry, clean nitrogen gas (the SFA apparatus chamber is sealed from the atmosphere and its internal atmosphere can be rigorously controlled 16). Some measurements were also conducted in humid atmospheres, but the effects of humidity were not studied in detail.

Adhesion Experiments. From the measured adhesion force, F_a , required to separate two molecularly smooth crystalline surfaces of radius R from adhesive contact, which is related to the surface energy by²² $\gamma =$ $F_a/3\pi R$, a value of $\gamma = 2.0 \pm 0.5 \text{ mJ/m}^2$ was obtained. This is a very low value for a van der Waals solid at room temperature—about an order of magnitude lower than typical surface energies of van der Waals, such as hydrocarbon, solids, and liquids.²³

Friction Experiments. Figure 1 shows typical friction traces obtained in these experiments and the corresponding fringe patterns and surface profiles. When two molecularly smooth surfaces were brought into molecular contact and sheared, the starting (or static) friction force, F_s , which is the shear force needed to initiate sliding, was very high. In terms of the shear stress (shear stress = friction force/contact area, or S= F/A) the static shear stress needed to initiate sliding was $S_s = F_s/A = 42$ MPa even in the absence of any externally applied load on the surfaces. On yielding, sliding proceeded smoothly (without stick-slip) at a kinetic shear stress value of $S_k = F_k/A = 0.43$ MPa, which is fully 2 orders of magnitude below the static value-an unusually large difference. These values are comparable to some of the highest and lowest values measured between van der Waals surfaces or across molecularly thin hydrocarbon films, which range from >20 MPa across frozen surfaces or solidlike films to <1 MPa across fluidlike films. 18,24

Figure 1A also shows the shapes of two self-adhering (self-flattened) surfaces under zero load. During the buildup to the yield point, F_s , there was no discernible

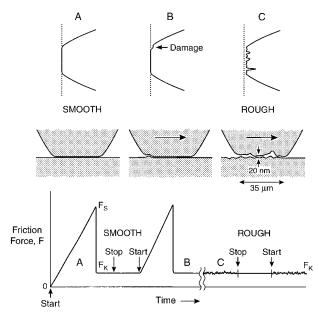


Figure 1. Schematic illustrations of typical friction traces, FECO fringe patterns (top), and corresponding surface profiles (middle) for (A) static conditions, (B) "smooth sliding" of initially smooth, undamaged surfaces at the point where damage just begins to occur, and (C) "rough sliding" of fully damaged surfaces.

change in the contact area, which also remained unchanged during sliding. The kinetic sliding was very smooth, with less than 1% rms variation in F_k . However, after continuous sliding for some time, the surfaces became rough or "damaged" (Figure 1B). This was ascertained from the changing shapes of the FECO fringes inside the contact zone which became rippled (after being extremely flat at the start) with an rms variation corresponding to a roughness of about 15 nm. During the transition from smooth to rough sliding (Figure 1, $B \rightarrow C$), the friction force became less steady and the rms variation in F_k rose from ~1% to ~5%. However, the kinetic friction coefficient μ_k hardly changed during the "smooth-to-rough" sliding transition, being $\mu_{\rm k} = 0.17 \pm 0.01$ for smooth sliding and $\mu_{\rm k} = 0.14 \pm$ 0.01 for rough sliding, independent of the sliding velocity over the range $0.2-4 \mu \text{m/s}$ (Figures 2 and 3). We note that the measured friction coefficient for rough sliding $(\mu_{\rm k} \approx 0.14)$ agrees with previously reported values of $\mu_{\rm k}$ \approx 0.15 obtained on macroscopic surfaces coated with solid layers of C₆₀. ^{25,26}

The wear or surface damage was recorded on video tape as it occurred (cf. Figure 1C) and later also analyzed by viewing the damaged regions with an optical microscope. Initially, the damaged surfaces consisted of wear tracks and uprooted particles having dimensions of order 15 nm. The damage remained localized even after prolonged sliding over the same area, i.e., it did not spread out outside the contact area or deep into the material, otherwise we would have seen much larger wear tracks and greater distortions of the FECO fringes as occurs when mica becomes damaged

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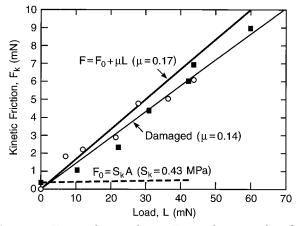


Figure 2. Kinetic friction forces F_k as a function of applied load L for two 512 Å thick layers of crystalline C_{60} on mica sliding at $V=0.5~\mu\text{m/s}$. (A) Smooth sliding, before damage, S_c (kinetic) = 0.34 MPa, $\mu_k \approx 0.17$. Note that a line passing through the square data points can be split up into an adhesion-controlled force (dashed line) and a load-controlled contribution expressed by a straight line passing through the origin of slope 0.17. (B) Rough sliding (open circles), after damage, $S_c \approx 0$, $\mu_k \approx 0.14$. Note that the solid line of slope 0.14 passes through the origin, i.e., there is no friction at zero load.

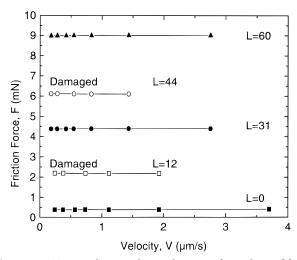


Figure 3. Kinetic friction forces for smooth surfaces (black points) and rough or damaged surfaces (white points) as a function of sliding velocity, V, at different loads, L.

by delaminating right from the start. These observations also allow us to conclude that the initial damage remained wholly within the C_{60} layers. Only after many traverses over the same area did it reach the underlying mica substrates. The type of damage observed with C_{60} was similar to what was previously observed with crystalline alumina and silica.²⁰

Once damage was initiated at a particular point, it rapidly (within seconds) spread throughout the whole "contact" area until the two surfaces continued to slide while separated by an average distance of 15 nm, being kept apart by the asperities created on each surface. Once the surfaces became roughened by damage, the high starting friction or "stiction spike" (F_s in Figure 1A) decreased in magnitude and disappeared altogether once the damage had spread across the whole contact area (Figure 1C). Increasing humidity resulted in damage occurring more easily, and in a slightly reduced friction force.

The errors in our fitted friction coefficients (± 0.01) suggest that the values for the smooth and rough surfaces may be the same. However, the finite friction that was measured at zero load with the smooth, undamaged surfaces is clearly different from the zero friction measured between damaged surfaces, so that the two sets of data points are actually qualitatively different, especially at low loads (cf. Figure 2). The reason for this difference is probably as follows: the finite adhesion force of molecularly smooth surfaces ensures that there is a finite contact area even at zero load and hence a finite friction force. For rough surfaces, however, the zero load adhesion and friction negligible because—as discussed below-adhesive contact now occurs only at the tips of a few asperities.

Discussion

Adhesion. To understand the unusually low surface adhesion energy of C_{60} , we turn to theories of intermolecular forces. Conventional theories usually assume that small spherical molecules interact via a "central potential" function. For example, if the interaction is predominantly van der Waals, as is the case for C_{60} molecules, we may write²⁷

$$w(r) = -C/r^6 \tag{1}$$

where r is the distance between the *centers* of the interacting atoms or molecules $[C={}^3/_4h\nu\alpha^2]$, where h, ν , and α are Planck's constant, the absorption frequency in the UV, and the molecular polarizability.] In this approximation, when two molecules are in adhesive contact, their equilibrium separation, r, is the same as their molecular diameter, σ , so that the contact adhesion energy per pair is

$$w(\sigma) = -C/\sigma^6 \tag{2}$$

Theories based on such simple expressions can nevertheless accurately predict the bulk cohesive energies, latent heats, and surface energies of nonpolar compounds, such as hydrocarbons. ¹⁴ But they cannot provide a reasonable theoretical estimate for the low value of $\gamma = 2.0$ mJ/m² obtained here for C₆₀.

It is known that the central potential approximation fails once the molecular diameter exceeds about 5 Å. 13 This is because the interactions now occur between the effective surfaces of the molecules rather than between their centers. Thus, molecules such as C_{60} should be treated as (small) macroscopic spheres, rather than as conventional molecules, and when this is done, a number of unusual properties are readily explained. Thus, referring to Figure 4, for two molecules of diameter ϕ , but composed of submolecular groups or atoms with diameter σ and interaction constant C, their contact pair energy is 13

$$w(\sigma) \approx -\left(\frac{\phi}{\sigma}\right)\frac{C}{\sigma^6}$$
 for $\phi > \sigma$ (3)

which is a factor ϕ/σ *larger* than the value given by the central potential equation, eq 2. When the molecules are small so that $\phi = \sigma$, eq 3 reduces to eq 2. Note that when $\phi > \sigma$, the interaction energy and force scale with the diameter ϕ of the molecules. [For example, the van

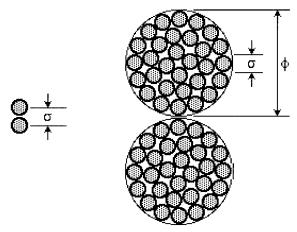


Figure 4. Interaction of a pair of atoms or small spherical molecules (left) compared to the interaction of a large molecule composed of many atoms (right). The two large molecules shown here have ~ 60 atoms each (30 per side).

der Waals interaction energy $w(\sigma)$ and force $F(\sigma)$ between two macroscopic spheres of radius R in contact is $w(\sigma) = AR/6\sigma$ and $F(\sigma) = AR/6\sigma^2$, respectively, where A is the Hamaker constant.¹⁴] On the other hand, concerning the surface energy, γ , this is the adhesion energy per unit area of surface, which is composed of molecules of surface density $1/\sigma^2$. For small molecules γ therefore scales as (using eq 2)

$$\gamma = \frac{\mathbf{w}(\sigma)}{\sigma^2} \approx \frac{C}{\sigma^8} \tag{4}$$

However, for large molecules, since the density of surface molecules is now proportional to $1/\phi^2$, the surface energy γ will scale as

$$\gamma pprox rac{\omega(\sigma)}{\phi^2} pprox \left(rac{\phi}{\sigma}\right) rac{C}{\sigma^6 \phi^2} pprox \left(rac{\sigma}{\phi}\right) rac{C}{\sigma^8}$$
 for $\phi > \sigma$ (5)

which is a factor σ/ϕ *smaller* than the conventional value that would be calculated from eq 4 for small molecules.

On the basis of this calculation, one might expect other large molecules to have low surface energies, but-like C60-they would also have to be rigid and maybe even have a smooth outer surface or else the number of intermolecular van der Waals contacts will not be small. Thus, large but deformable molecules such as hydrocarbons and polymer melts of high MW would not fall into the C₆₀ category because their internal bond flexibility allow their submolecular groups to behave like a liquid with the result that the density of van der Waals contacts between neighboring molecules is always high. On the other hand, smooth rigid molecules, such as some fluorocarbons (where the bulky C-F groups are much less flexible than C-H bonds) do indeed exhibit unusually low surface energies—well below the values expected from their polarizability or refractive index. For example, while surfaces composed of hemispherical -CH₃ groups have a "normal" surface energy of $\gamma = 24$ mJ/m², those composed of $-CF_3$ groups (of diameter ~ 5 Å) have $\gamma = 6$ mJ/m²,²⁸ even though the intermolecular pair interaction, w, is larger between $-CF_3$ groups.²⁹

The above simple calculations show why the surface energy of C_{60} and, presumably, other large rigid molecules, may be expected to be low when expressed *per unit area*. On the other hand, properties that depend on the strengths of the intermolecular pair interactions *per molecule* or per mole, such as the heat of sublimation, may be expected to be large, since these are magnified by the same factor (compare eqs 3 and 5). Thus, C_{60} appears to have a surface energy that is about 10 times *smaller*, but a latent heat of sublimation¹¹ (40 kcal/mol) that is about 5 times *larger* than typical values for van der Waals solids and liquids.

Friction. Previous experimental and theoretical work²⁴ has shown that, in general, the friction force associated with the sliding of two smooth surfaces may be divided into an adhesive contribution that is independent of load (adhesion-controlled friction) and a contribution that is proportional to the externally applied load (load-controlled friction). The former is proportional to the "real" (molecular) area of contact, A, the latter is proportional to the load, L. To a good approximation, the total friction force can therefore be expressed as

$$F = F_{\mathsf{A}} + F_{\mathsf{L}} = S_{\mathsf{c}} A + \mu L \tag{6}$$

where S_c (the critical shear stress) and μ (the friction coefficient) are constants. Dividing through by the area, A, the above may also be written in terms of the total shear stress, S:

$$S = S_{c} + \mu P \tag{7}$$

where P is the applied pressure. For each of the above two equations, one may distinguish between the static friction forces, $F_{\rm s}$ and $S_{\rm s}$, and the kinetic friction forces, $F_{\rm k}$ and $S_{\rm k}$ (cf. Figure 1) where the latter values are strictly velocity-dependent rather than real constants.

Fitting the above equations to the kinetic data of Figure 2, we find good fits for both smooth and damaged sliding. In the case of smooth sliding, the best-fit parameters are $S_c = 0.43$ MPa and $\mu = 0.17$, while for damaged sliding they are $S_c = 0$ and $\mu = 0.14$. As expected, 24 the adhesion-controlled contribution S_c is finite for smooth, self-adhering surfaces but is small or zero for damaged surfaces. We note, however, that these values apply to the kinetic friction force, i.e., the force during steady-state sliding, and not to the static friction force, i.e., the initial force or critical shear stress needed to initiate sliding, which was much higher.

Our values of $\mu=0.14-0.17$ agree with the value of $\mu=0.15$ obtained in a friction force microscope (FFM or AFM) study of C_{60} surfaces. ³⁰ But the low value for the shear stress quoted in that work (0.1 MPa) is much lower than our measured value of 0.4 MPa for smooth surfaces. However, the molecular area of contact during sliding is not directly measurable in AFM experiments (as in SFA experiments) and so has to be estimated, and this value is needed to calculate the shear stress.

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In another AFM study,³¹ the friction of C_{60} surfaces was measured over a large range of loads (applied pressures) and velocities. At low pressures (estimated as <10 Pa) and velocities (a few μ m/s) corresponding to those used in our study, there is good agreement (μ = 0.15) with our values. At higher velocities, μ fell which, according to the "time-temperature superposition principle",²⁴ is consistent with our theoretically based conclusion (see later) and the experimental findings reported in ref 32 that μ is highly temperature-dependent.

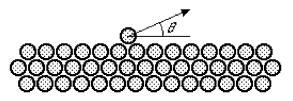
Previous experiments have found C_{60} to be an unexceptional or even disappointing lubricant, $^{6-9.25,26,33}$ exhibiting a "normal" friction coefficient of $\mu\approx 0.15$ (as found in refs 25 and 33 as well as here) with no obvious beneficial tribological properties. This has come as a surprise because C_{60} is known to rotate rapidly in the solid lattice, suggesting that it could function as a molecular ball bearing and thus act as a good (dry) lubricant. It is possible that the much reduced friction force on going from the static to the kinetic (sliding) regime is a reflection of precisely such a phenomenon. However, the kinetic friction force, particularly as characterized by S_c (but not μ_k)—while somewhat low—was not found to be *exceptionally* low, in agreement with the previous findings by others. $^{6-9.25,26,33}$

Theoretically, the friction of two solid crystalline surfaces should anyway not be predicated on the mobility of the molecules but on the energy or force needed to raise one lattice over the other in order to move it laterally,²⁴ and this force is the same regardless of whether the molecules are rotating or stationary. This is the basis of Coulomb friction and the Cobblestone model.²⁴ Another way of looking at this is to consider the lateral force needed to push a cart along a cobblestoned road. The pushing force moves the cart forward because it first moves it upward against the force of gravity, and this force is the same if the stones and wheels are dry or wet (slippery). Thus, the measured load-dependent kinetic friction coefficient of $\mu_k = F_k/L$ = 0.17, which is typical of many solid surfaces, is simply related to the average angle θ by which one lattice has to move up to overcome the normal load, L, by

$$\mu_{\mathbf{k}} = F/L = \tan \theta \tag{8}$$

which in this cased gives $\theta = \tan^{-1}0.17 = 10^{\circ}$. Furthermore, as illustrated in Figure 5, this purely geometric value need not be very different for smooth and rough surfaces.

The only unusual aspect of the friction of the C_{60} surfaces—measured between molecularly smooth surfaces but not between rough surfaces—was the high static but low kinetic critical shear stress, S_c . According to the Coulomb or Cobblestone models, 24 a large static friction force under zero external load normally arises only if the surface adhesion energy per unit area is high. This is because S_c is related to the energy γ associated with separating the two surfaces against their inter-



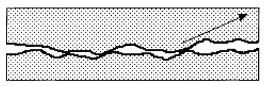


Figure 5. Geometric effects that determine the initial direction of motion when molecules and/or rough solid surfaces slide over each other (based on the Coulomb and Cobblestone models of friction²⁴).

molecular forces according to²⁴

$$S_{c} = F/A \approx 2\epsilon \gamma/\sigma \tag{9}$$

where σ is a molecular dimension and where ϵ is the fraction of energy dissipated as heat per molecular hop, which is different for static and dynamic conditions, where typically

$$\epsilon_{\rm s} \approx 1$$
 (9a)

$$\epsilon_{\mathbf{k}} < 1$$
 (9b)

Inserting the measured value of $\gamma=2.0~\text{mJ/m}^2,~\sigma=1~\text{nm},~\text{and}~\epsilon_s\approx 1~\text{for}~C_{60},~\text{we obtain}~S_c\approx 4~\text{MPa}$ which is typical of hydrocarbon boundary lubricants but an order of magnitude lower than the measured static value of 40 MPa for C₆₀. However, putting $\epsilon_k\approx 0.1,~\text{which}$ is typical for kinetic sliding, gives a value of $S_c\approx 0.4~\text{MPa}$ in good agreement with the measured value. The unexpectedly high static friction measured between smooth C₆₀ surfaces is, however, consistent with the unexpectedly high values measured for the shear stresses of C₆₀ monolayers and multilayers at the water—air interface and when incorporated into thin hydrocarbon films³⁴ (which was one of the early indications that C₆₀ might not be a good solid lubricant).

It is possible that the high static friction of smooth C₆₀ surfaces is related to their high pair interaction which, unlike for many organic molecules, is well above kT at room temperature. A high pair interaction means that the molecules are sitting deeply inside their potential well, even if they are rotating. Thus, a high shear force will be needed to initiate sliding. In contrast, for smaller molecules whose pair interaction is closer to kT, the shear stress to initiate motion will be much lower since they are already thermally activated well above their potential minimum. If this interpretation is correct, the friction of smooth C_{60} surfaces should be very temperature sensitive and, by the time-temperature superposition principle,²⁴ also velocity-dependent, both of which have been found to be the case. 31,32

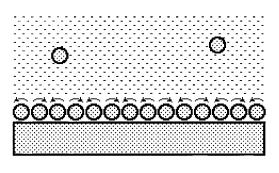
The unusually high static friction appears to apply only to smooth, crystalline surfaces. As already described, once sliding commences or when the surfaces

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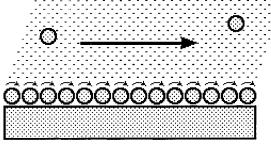


Figure 6. Freely rotating C_{60} molecules adsorbed on a solid surface from solution (e.g., toluene, benzene). Top: at rest. Bottom: during flow. Illustration based on refs 36-38.

become rough or damaged, the friction falls to lower, more "normal", values.

All these findings apply only to the adhesion and friction of pure solid C₆₀. When C₆₀ molecules adsorb onto a solid surface from solution, i.e., when C₆₀ is an additive in a mixture, its tribological effects may then be very different.³⁵ As recently reported by us³⁶ and Zhao et al.,37,38 the ability of C₆₀ to rotate freely on a surface can change the boundary conditions of the solid-liquid interface from no-slip to full-slip or partialslip (Figure 6), thereby dramatically reducing the viscous drag of the system below the value obtained in the absence of C₆₀. The tribological behavior of lubricated and unlubricated C₆₀ surfaces or surface layers is thus very different.

Surface Damage (Wear). On the basis of our observations and comparison with the way other smooth surfaces (alumina, silica, mica) become damaged during sliding, 20,39 we tentatively conclude that damage and wear of C₆₀ and other isotropically crystalline surfaces can remain highly localized—a form of localized "ductile damage", but that layered materials (such as micas) become worn by delaminating over large distances-a form of extended "brittle damage".

Summary and Conclusions

Due to its large size, C₆₀ exhibits a high lattice energy (per mole) but an unusually low surface energy (per unit area). These results suggest that, at least as far as their intermolecular interactions are concerned, C₆₀ and other large spherical molecules should be treated more as small macroscopic particles than as conventional molecules. The kinetic friction coefficient of C₆₀ appears to be "normal", both for molecularly smooth and rough surfaces, but the smooth surface has an unusually high static shear stress which, however, disappears once the surfaces become roughened (damaged) during sliding. C₆₀ on its own does not appear to have any beneficial tribological properties, but if it can be dissolved in a suitable solvent (base oil) from which it can also be made to adsorb onto a surface, it may then act as a very effective drag reducing additive.

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