Are Buckminsterfullerenes “Molecular Ball Bearings”?

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Abstract

Buckminsterfullerenes (C_{60}) are near-spherical molecules which freely rotate at room temperature in the solid state and when dissolved in solution. An intriguing question arises as to whether C_{60} molecules can act as “molecular ball bearings”, i.e. preventing direct contact between two solid surfaces whilst simultaneously dissipating shear stress through fast rotation. To explore this, we performed measurements of friction across a solution of C_{60} in the boundary lubrication regime. High resolution shear and normal force measurements between mica sheets separated by the C_{60} solution were made using a Surface Force Balance to provide a single-asperity contact and sub-nanometer resolution in film thickness. We find that, even at small volume fraction, C_{60} forms a solid-like amorphous boundary film sustaining high normal load, suggesting that this system undergoes a glass transition under confinement. The C_{60} film gives rise to a low friction coefficient up to moderate applied loads, and we discuss the possible relevance of the ball bearing effect at the molecular scale.

Introduction

Human activity has always required the motion of objects, from the building of edifices in

prehistorical ages to the harvesting of energy with wind turbines in present times. The question of whether logs were used as “rollers” to move megaliths has been debated,¹ nonetheless it is clear that the idea of using wheels to replace sliding by rolling was early found to be an efficient way to reduce energy dissipation during motion, i.e. friction. While formulating the first fundamental laws of solid friction, Da Vinci conceived of many ingenious machines involving rotary parts where the friction is limited to the axis.² Ball bearings, consisting of balls running along a groove (e.g. in an axle assembly), are designed to reduce the friction further by transforming sliding into rolling. It is also known, since ancient times,³ that lubricating the contact, i.e. inserting a liquid between the moving solids, is an efficient way to reduce wear and produce a moderate, or at least stable friction. However, finding good lubricants is complex because the appropriate mixture has to remain effective in harsh conditions (high loads/shear stresses/temperatures, humidity etc.), and the field of tribology has been active over the past century and until today.^{4–6} Detailed, mechanistic interpretations of friction are often complicated by processes acting over multiple length-scales and timescales simultaneously. For example a fluid may lubricate motion as a thick film (hydrodynamic regime) or in molecular confinement between close asperities (boundary regime), either at dif-

ferent regions of a rough contact or under different shearing conditions.

Buckminsterfullerene (C_{60}) is a molecule of almost ideal spherical shape⁷ (structure in Figure 1(a)). In its pure form under ambient conditions C_{60} forms a solid in which the molecules are able to rotate freely; inspection of the temperature dependence of the heat capacity shows that the energy associated with rotation of C_{60} in the crystal is smaller than the ambient thermal energy.⁸ This interesting property, combined with relative chemical stability, led to the early proposal that C_{60} could act as an effective boundary lubricant: it might be expected that even when confined between two surfaces it could rotate to dissipate stress, the molecules effectively performing as “molecular ball bearings”. Direct observations have shown that spherical nanoparticles can rotate between sheared surfaces, in a manner which is reminiscent of the rolling without slipping motion of macroscopic ball bearings.⁹ By analogy to the macroscopic mechanism of ball bearings, a molecular ball bearing system should sustain normal load (i.e. keeping the shearing solid surfaces apart) yet without hindering molecular rotations (which serve to dissipate shear stress and so reduce friction). Although this provides a useful motivating concept to consider the effect of rotations in modifying friction at the nanoscale, we note that the macroscopic mechanism of ball bearings does not map perfectly onto molecular systems under ambient conditions: the molecular rotation rate will typically be much higher than the imposed shear under ambient conditions. To differentiate between these two situations, we call the molecular mechanism the “molecular ball bearing effect”. In this work we measure and appraise whether C_{60} might satisfy these criteria.

Previous studies have investigated lubrication by C_{60} or fullerene-like molecules in different ways. On one hand, they have been used as a solid lubricant in dry conditions (from simply dispersed powder to carefully sublimated thin film), but they didn’t provide particularly exceptional frictional properties.^{10–14} C_{60} have been used as wheels for single-molecule “nanocars”, and the displacement of

such nanocars was found to be indeed due to the rotation of the C_{60} on the Au-(111) surface at ~ 200 °C.¹⁵ Experimental and numerical studies investigated the frictional behavior on a C_{60} single crystal around an orientational order-disorder phase transition at ~ 260 K, but no significant change of friction coefficient was found.^{16,17} On the other hand, when C_{60} or fullerene-like molecules have been used as an additive in a liquid, they formed a protective boundary film that prevents wear and induces a stable frictional response.^{18–20} In particular, Campbell et al. confined a dispersion of C_{60} in toluene between atomically-smooth mica surfaces in a Surface Force Apparatus, and studied the hydrodynamic lubrication regime by looking at the viscous response to a normal oscillation. They showed that this system exhibits a full slip boundary condition, suggesting a particular “fluidity” of the C_{60} that are adsorbed on the surfaces.¹⁸ In the present paper, we report the first measurements of friction across a dispersion of C_{60} in the boundary lubrication regime.

Methods

Materials. C_{60} was synthesised via the arc discharge method according to the procedure first published by Krätschmer et al.²¹ and was further isolated by high performance liquid chromatography (HPLC) to a purity of 99.5%. Tetralin, 1,2,3,4-tetrahydronaphthalene (Sigma-Aldrich, anhydrous, 99%), was used as solvent (chemical structure in Figure 1(a)). Tetralin was chosen as a good solvent for C_{60} (solubility of C_{60} in tetralin is 16 mg/mL at 25 °C²²) with low volatility (vapor pressure of 0.05 kPa at 25 °C²³) and a moderate viscosity (2.015 mPa.s at 25 °C²⁴). The tetralin was dried with molecular sieves (0.4 nm pore size, from Fisher Chemical) for a week, and filtered before use (Ultra-Cruz Syringe Filter, PTFE, 0.22 μ m). C_{60} molecules were dispersed at a concentration of 5.60 ± 0.01 mg/mL, corresponding to a molar fraction of $0.1065 \pm 0.0002\%$ (given the tetralin density of 0.9645 g/mL at 25 °C²³), or

Figure 1: (a) Chemical structures and sizes of buckminsterfullerene (C₆₀) and tetralin. (b) Schematic of the SFB experiment, that allows to determine the interaction and friction forces between two mica surfaces separated by a liquid film of controlled thickness. (c) Normal force F_N rescaled by the radius of curvature R of the surfaces as a function of the separation D obtained at approach velocities $v_N \sim 1$ nm/s, for tetralin (approach in brown, pull-off force measured on retraction indicated by the black arrow) and the solution of C60 in tetralin (approach in purple, retraction in black).

a mean distance between the C₆₀ molecules of 5.979 ± 0.004 nm $\sim 5 \times$ (C₆₀ diameter).

Force measurements. The measurements were performed with a Surface Force Balance (SFB), which is a method ideal for the study of normal and lateral forces transmitted across fluid and soft films with high resolution. A schematic diagram of the key aspects is in Figure 1(b). The liquid film is held between two optical lenses, hemi-cylindrical in shape (radius of curvature $R \sim 1$ cm) and arranged in crossed-cylinder configuration. This geometry provides a point of closest approach between the two surfaces, which is model experiment for study of a single-asperity contact. The optical lenses are coated with single crystal sheets of mica, so that the roughness is sub-molecular (roughness arising only from the atomic corrugation of the crystalline surfaces). The precise geometry and liquid thickness are measured directly in-situ using white light interferometry; so-called Fringes of Equal Chromatic Order (FECO). The surfaces (lenses) can be translated in both normal and lateral directions relative to one another, and the resulting forces between them are detected via the deflection of normal and lateral springs. These measurements can be performed simultaneously, so that information about film thickness, normal force,

and shear force can be measured in parallel (e.g. during approach of the surface from large distances to contact). The details of the procedure have explained elsewhere;^{25–28} in the following we note the quantities and details particular to the present experiments.

Muscovite mica is cleaved, backsilvered and glued on glass cylindrical lenses using dextrose, D-(+)-glucose (Sigma-Aldrich, 99.5%, chosen for its insolubility in tetralin). Two surfaces are mounted in a crossed-cylinder geometry to make a single contact between atomically smooth surfaces, and the liquid is injected in between to form a capillary bridge. The chamber is dried with P₂O₅, phosphorus pentoxide (Sigma-Aldrich, 99%) and the room is regulated to 25°C. FECO are analyzed to measure the radius of curvature R of the surfaces and the liquid thickness, D . D is measured with a precision of 0.02 nm (RMS noise) and accuracy of 1 nm and $D = 0$ is defined as the mica-mica contact position measured in dry air before liquid injection. The refractive indices of 1.5413 at 20°C for tetralin²³ and 1.5417 at 22°C for the mixture were measured with a Bellingham+Stanley Abbe 60 ED refractometer.²⁹ A stepper motor is used to approach or retract the top surface at a normal velocity v_N and a piezo-electric tube allows application of

a shearing motion at lateral velocity v_L . Normal force F_N and lateral force F_L are then measured using springs, with respective stiffness of 133.8 ± 3.0 N/m and 441 ± 4 N/m.

Results

Normal force. The normal force profiles obtained are shown in Figure 1(c). For pure tetralin, the surfaces experience a (van der Waals) attractive interaction on approach of the surfaces to ~ 10 nm causing a jump-in to contact. The surface separation just after the jump-in is close to the direct mica-mica contact value (within the systematic experimental error). The finite gradient of this soft wall is due to the compression of the mica, the single material remaining in the optical interferometer. On retraction the two surfaces jump-out when reaching a pull-off force of $F_{adh}/R = -435$ mN/m, which according to the JKR theory corresponds to an adhesion energy of $W = 2F_{adh}/(3\pi R) = -92$ mN/m.²⁵ This value is comparable with the adhesion energy between -160 mN/m and -108 mN/m measured previously for mica-mica contact in dry nitrogen.³⁰ It is not clear why a structural force is not observed in this case, as might be expected by comparison with similar measurements with apolar liquids like cyclohexane, benzene or toluene which do each give rise oscillatory structural surface forces.^{26,31-35} However, a similarly strong adhesion minimum has also been observed for these liquids, and attributed to the presence of traces of water that wets the mica surfaces. Particular care was taken to use tetralin in dry conditions (storage in molecular sieves, measurements with P_2O_5 in the chamber), however it is still possible that traces of water may remain giving rise to an adsorbed layer or part-layer on the mica. In the subsequent experiments we take this control measurement with pure tetralin as the reference situation in order to investigate the effect of the addition of small quantities of C_{60} under the same conditions.

When 0.1 mol % C_{60} is added to the tetralin the normal force between the surfaces is mod-

ified significantly, as clear in Figure 1(c). On approach of the surfaces a repulsive soft wall is reached at ~ 6 nm, compressing by several nm with increased load (appearing even more clearly in Figure 3(b)). The onset of repulsion corresponds to the thickness of approximately 5 C_{60} molecules, and the soft wall holds for loads up to 80 μ N, corresponding to a pressure of ~ 6 MPa (given the contact radius of ~ 2 μ m), and on retraction an adhesive minimum of $F_{adh}/R = -2.7$ mN/m is obtained. This value is comparable with what Campbell et al. measured for C_{60} in toluene between mica.¹⁸

In summary of the normal force profiles, we find that very small volume fractions of C_{60} lead to substantial modification to the interaction force between confining surfaces, giving rise to a monotonic repulsive force extending to ~ 5 molecular diameters. This insight allows us subsequently to interpret the direct friction measurements, as follows.

Lateral force. Having characterised the normal interaction between the surfaces, we next applied a lateral (shearing) motion of the top surface relative to the bottom surface and detected the resulting lateral force transmitted across the liquid. In the SFB this can be performed at the same time as approaching the surfaces and measuring the film thickness and normal force; in this section we present results of the measured friction as a function of separation and load. We compare the case of pure tetralin, as control, to the tetralin with C_{60} . In Figure 2 we show the result of measurements with pure tetralin (part (a)) and with C_{60} in tetralin (part(b)). For the control experiment with pure tetralin, we show the temporal evolution of the liquid thickness D and the lateral force F_L when the top surface is moved downward and then upward at $v_N = 0.92 \pm 0.05$ nm/s and simultaneously oscillated laterally at $v_L = 287 \pm 1$ nm/s. When the surfaces are separated by a finite film of tetralin, before reaching surface contact, no measurable lateral force is detected (smaller than the sensitivity of ~ 1 μ N), meaning there is no mechanical coupling between the surfaces. At the point of jump-in to contact the lateral force instantaneously increases

Figure 2: (a) Temporal evolutions of liquid thickness D (red traces) and lateral force F_L (blue traces) when approaching and retracting mica surfaces separated by tetralin with simultaneous constant-velocity shearing of one surface. The lateral force is below the experimental resolution until the surfaces reach direct contact, at which point they are rigidly coupled. (b) Temporal evolution of liquid thickness D when approaching the surfaces and simultaneously applying constant-velocity lateral motion to one surface across the solution of C_{60} in tetralin. The insets show the lateral force F_L at two time intervals (or equivalently two loads F_N as indicated), showing how the lateral force during shearing cycles evolves as the applied load is increased. At higher loads a clear yield spike followed by smooth sliding is observed; from this the kinetic friction $F_{L,k}$ is deduced.

in magnitude and varies directly with the ap-
 plied shearing amplitude; the saw-tooth shape
 is the signature that the surfaces are rigidly cou-
 pled, i.e with no relative motion throughout the
 cycle. Because of the strong adhesion between
 the surfaces, friction is controlled by adhesion³⁶
 and is so high that the yield point of the con-
 tact is not reached within the range of lateral
 force explored. Thus we find that the yield force
 of the contact must be higher than 110 μN in
 this case. In experiments with higher shear-
 ing amplitudes, we found that the yield force
 was in fact higher than 330 μN ; corresponding
 to a lower limit for the contact shear stress of
 $\sigma_L \sim 26 \text{ MPa}$. During retraction, a damped os-
 cillation at the resonance frequency of $\sim 25 \text{ Hz}$
 is obtained when the surfaces jump-out, and
 then no lateral force is detected, consistently
 with the behavior on approach. In sum, we find
 that tetralin alone cannot support any applied
 load, and so squeezes out of a contact when fi-
 nite load is applied, giving rise to high friction
 in accordance with direct mica-mica contact.
 Lateral forces measured across the solution of
 C_{60} in tetralin as a function of load - examples
 of which are in Figure 2(b) - show an entirely
 different behavior. When the surfaces approach
 to the distance corresponding to the repulsive
 wall the lateral force is still below the sensi-
 tivity limit. It was necessary to increase the
 load before any detectable lateral force could
 be recorded between the surfaces; the left-hand
 inset show the emergence of tiny lateral forces
 when the surfaces are being pushed together
 with a force of 28 μN . The amplitude of the
 lateral force then increases with the load, and
 the signal exhibit a strong stiction spike fol-
 lowed by a plateau (right-hand side inset). The
 clear yield point followed by sliding behavior is
 typical of a solid-like response to lateral applied
 stress. We systematically extracted the ampli-
 tude of the plateau, which we identified as the
 kinetic friction force $F_{L,k}$. In Figure 3(b) we
 compare the normal force and kinetic friction
 force profiles as a function of surface separation,
 D . In this representation, we clearly see that
 the range of the friction force is much smaller
 than the range of the normal force, becoming
 measurable only at separations of $\sim 4 \text{ nm}$ at

which point the layer is already substantially
 compressed and the load is high, qualitatively
 similar to what has been observed for lubrica-
 tion by polymer brushes.³⁷ As shown in Fig-
 ure 3(a), the relationship between the kinetic
 friction force and the load is not linear, instead
 it has a strongly convex shape. At small loads,
 kinetic friction is proportional to the load, with
 no significant contribution from adhesion (zero
 friction at zero imposed load) and a coefficient
 of proportionality $\mu = 0.072 \pm 0.002$ (with
 the coefficient of friction defined as the local
 slope $\mu = dF_{L,k}/dF_N$). This quantity increases
 with the load, and reaches $\mu = 4.1 \pm 1.6$ at the
 maximum imposed load. Thus the friction coef-
 ficient evolves from a very low value, indicating
 efficient lubrication at moderate load, up to a
 high value under strong compression. To com-
 ment on these values, it is useful to compare
 them to the friction coefficient of different liq-
 uids between mica surfaces, all measured with
 a Surface Force Balance. Simple apolar liquids
 are generally characterized by a single friction
 coefficient: 1.1 for octamethylcyclotetrasiloxan
 (OMCTS), 2.2 for cyclohexane.³⁸ Ionic liquids
 exhibit quantized friction,³⁹ i.e. a friction co-
 efficient indexed by the number of ordered lay-
 ers of ions in the film, typically varying from
 0.007 to 0.5 for 1-decyl-1-methylpyrrolidinium
 bis[(trifluoromethane)sulfonyl]imide, $[\text{C}_{10}\text{C}_1\text{Pyr}][\text{NTf}_2]$.⁴⁰ Regarding the low-load friction coef-
 ficient, the C_{60} solution is thus between apo-
 lar liquids and ionic liquids, and is compara-
 ble with the 0.12 obtained for 2,6,10,15,19,23-
 hexamethyltetracosane (squalane), a branched
 hydrocarbon liquid that has been reported for
 exhibiting glassy behavior in certain confine-
 ment conditions.⁴¹

Discussion

A solid film. We now propose a simple qual-
 itative picture of what is happening at the
 molecular scale to interpret the observed behav-
 ior. The molecular forces governing the inter-
 action between C_{60} , tetralin and mica include
 van des Waals and steric forces. Mica is po-
 lar, and maybe covered with a (sub-)molecular

Figure 3: (a) Kinetic friction $F_{L,k}$ as a function of load F_N . Friction in pure tetralin was above the range limit of the experiment, as indicated by the shaded bar, whereas the solution of C₆₀ in tetralin gave rise to measurable friction (in purple). The two stars correspond to the lateral force traces shown in insets of Figure 2(b), and the red lines are the linear fits used to deduce the local friction coefficient μ . (b) Normal (red) and kinetic friction (blue) force profiles, for the solution of C₆₀ in tetralin. (c) Schematic representation of the system in confinement: the C₆₀ molecules are randomly packed, steric interactions lead to a significant repulsion between the solid surfaces, but fast rearrangements induce a relatively small shearing resistance.

404 film of water. Tetralin is slightly polar and 453
 405 polarizable (calculated static polarizability of 454
 406 $1.8 \times 10^{-39} \text{ C} \cdot \text{m}^2/\text{V}$), whereas C_{60} is more 455
 407 polarizable because of the highly delocalized 456
 408 π electrons (measured static polarizability of 457
 409 $8.6 \times 10^{-39} \text{ C} \cdot \text{m}^2/\text{V}$ ⁴²). When the mica sur- 458
 410 faces are far apart, the C_{60} molecules in the 459
 411 bulk are separated by an average distance of 460
 412 about 5 times their diameter (deduced from the 461
 413 chosen concentration) and are attracted by a 462
 414 dispersion (London) interaction but the liquid 463
 415 dispersion is thermodynamically stable because 464
 416 the concentration is (just) below the saturation 465
 417 limit. A monolayer of C_{60} is probably initially 466
 418 adsorbed on each mica surface due to the induc- 467
 419 tion (Debye) interaction and the preference of 468
 420 mica for the more polar C_{60} rather than tetralin. 469
 421 When confining the liquid, tetralin tends to be 470
 422 squeezed-out, as shown by the reference mea- 471
 423 surement. The local concentration of C_{60} in 472
 424 the gap therefore increases as the surfaces ap- 473
 425 proach and the C_{60} molecules - which are al- 474
 426 ready close to the aggregation limit in the bulk 475
 427 solution - are expected to agglomerate, forming 476
 428 a strongly bound solid film (as shown by the 477
 429 soft wall in the normal force profile). The fact 478
 430 that this film holds for pressures up to $\sim 6 \text{ MPa}$ 479
 431 is remarkable, given that a yield stress of about 480
 432 $\sim 1 \text{ MPa}$ is measured when compressing a C_{60} 481
 433 single crystal along the $\langle 110 \rangle$ direction.⁴³ This 482
 434 is probably due to the fact that we are dealing 483
 435 with a nanometric film, the C_{60} having attrac- 484
 436 tive interactions with the confining surfaces and 485
 437 being packed in a disordered arrangement with 486
 438 no cleaving plane. 487

439 **A disordered film.** The absence of order 488
 440 in the film is revealed by the normal force pro- 489
 441 file showing a soft wall at distance of approx- 490
 442 imately 5 C_{60} diameters. This behavior was 491
 443 unexpected, because a structural force is usu- 492
 444 ally observed for apolar liquids between mica. 493
 445 When Campbell et al. studied a solution of 494
 446 C_{60} in toluene between mica, they observed 495
 447 a soft wall at $\sim 3.4 \text{ nm}$ at approach veloci- 496
 448 ties higher than 5 nm/s , or a structural force 497
 449 of period of 1.1 nm equal to the diameter of 498
 450 the C_{60} molecules at smaller velocities.¹⁸ They 499
 451 interpret this transition as C_{60} molecules be- 500
 452 ing kinetically trapped between the surfaces 501

and having no time to order. We never ob-
 served a structural force over the explored spots
 on the surfaces, experiments and velocities be-
 tween $\sim 1 \text{ nm/s}$ and $\sim 12 \text{ nm/s}$. This is most
 likely to be due to the different solvent and
 concentration chosen: Campbell et al. used
 a concentration of 0.095 mg/mL correspond-
 ing to a molar fraction of $\sim 0.001\%$ or $\sim 3\%$
 of the saturation limit in toluene (2.8 mg/mL
 at 25°C ²²), whereas here we use a concentra-
 tion of 5.60 mg/mL corresponding to a molar
 fraction of $\sim 0.1\%$ or $\sim 35\%$ of the saturation
 limit in tetralin (16 mg/mL at 25°C ²²). In our
 case, the C_{60} molecules in the bulk are much
 more concentrated and close to the agglomera-
 tion limit, and the order/disorder kinetic tran-
 sition may have been shifted to approach ve-
 locities much smaller than 1 nm/s . Combining
 the observations of no structural force and of
 a solid-like friction response, we conclude that
 under the experimental conditions used the C_{60}
 must form a disordered/amorphous solid, i.e. a
 glass, where the molecules are randomly packed
 in the gap (as illustrated in Figure 3(c)). The
 situation is thus related to the difficult prob-
 lem of glass transition in confinement, already
 investigated for various systems⁴⁴ like simple
 liquids,⁴⁵ polymers,⁴⁶ liquid crystals⁴⁷ or col-
 loids.⁴⁸ It is then tempting to interpret our mea-
 sured kinetic friction-load curve as a kind of
 Angell plot, that conventionally represents how
 the logarithm of the viscosity increases with the
 inverse temperature (for molecular liquids) or
 with the packing fraction (for colloidal liquids)
 when approaching the glass transition.^{49,50} Fol-
 lowing this scenario, it would be the increase
 of the C_{60} packing fraction with the load (as
 shown by the compression of the film) that leads
 to a dramatic slowing down of the dynamics,
 i.e. of the rearrangement timescale of the glassy
 film in the gap, as measured by the increase of
 the friction force.

Role of rotation. One can finally ask
 whether the rotation of C_{60} contributes to the
 frictional behavior. As shown by a 2D molecu-
 lar dynamics simulation of lubrication by cir-
 cular molecules, a high concentration in the
 gap can lead to jamming, which hinders the
 molecular rotation because the two sides of two

502 molecules in contact would have to rotate in 548
 503 opposite directions.⁵¹ So if the rotation of C₆₀ 549
 504 plays a role in our system, it is likely to happen 550
 505 at small loads, for which we indeed measured a 551
 506 small friction coefficient. Because of the rela- 552
 507 tively strong adhesion of the C₆₀ on mica (De- 553
 508 bye interaction), the lateral motion is probably 554
 509 distributed in the middle of the gap and not 555
 510 at the film/mica interfaces. The small resis- 556
 511 tance to flow in the gap indicates that energy 557
 512 is dissipated efficiently in the film; the mech- 558
 513 anism for this could originate from (at least) 559
 514 three modes. First, there is only small adhesion 560
 515 between C₆₀ molecules (London interaction).¹⁸ 561
 516 Second, there is room and time for rearrange- 562
 517 ments, since C₆₀ molecules are randomly packed 563
 518 with vacancies, at a packing fraction far enough 564
 519 from the glass transition. Third, the C₆₀ may 565
 520 rotate freely in the thin disordered film, like 566
 521 they do in the bulk crystal, and this free ro-
 522 tation could contribute to a dissipation mecha-
 523 nism leading to low friction. In other words, a
 524 “molecular ball bearing” effect may be occurring
 525 and be partly responsible for the low friction
 526 regime.

527 Conclusions

528 To summarize our findings, C₆₀ performs as
 529 an excellent boundary lubricant additive in our 567
 530 system; $\sim 0.1\%$ of C₆₀ is sufficient to form a 568
 531 strong boundary film that reduces wear by pre- 569
 532 venting direct contact between the sliding sur- 570
 533 faces and gives rise to a small friction coefficient
 534 at moderate loads. A key ingredient leading to 571
 535 this useful outcome is that C₆₀ has a finite sol- 572
 536 ubility and tends to solidify when the concen- 573
 537 tration exceeds the saturation point locally in
 538 confined contacts thus preventing squeeze-out 574
 539 of the film. The fact that the C₆₀ appears to 575
 540 form a disordered solid, evidenced by no regu- 576
 541 lar oscillatory structural force despite solid-like 577
 542 mechanical response, indicates that the convex 578
 543 friction-load relationship may be the manifes- 579
 544 tation of a glass transition under confinement. 580
 545 The friction coefficient at moderate loads is re- 581
 546 markably small, and so it is hypothesised that
 547 the molecular rotations intrinsic to C₆₀ – the

“molecular ball bearing effect” – may be impor-
 tant for reducing shear stress.

Future investigations should involve a sys-
 tematic study of the effect of the concentra-
 tion on kinetic trapping and on friction re-
 sponse. To clarify the role of molecular rota-
 tion, comparative Surface Force Balance mea-
 surements with C₆₀ chemically grafted to the
 surfaces and thus unable to rotate^{52,53} could be
 performed. It would also be of interest to study
 different surface materials such as graphene;⁵⁴
 with only *sp*²-hybridized carbon materials ex-
 ceptional properties can emerge.^{55–57}

Author Contributions

R.L. and C.D. performed the experiments. S.P.
 and R.L. conceived of the project, interpreted
 the data and wrote the paper. K.P. and S.S.
 synthesised the fullerenes and contributed to
 the experimental design.

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