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Superlubricity in Gemini Hydrogels

Gemini hydrogels have repeatedly produced low friction under conditions generally not thought to be favorable to superlubricity: low sliding speeds, low contact pressures, macroscopic contact areas, and room temperature aqueous environments. A proposed explanation for this unique behavior is that thermal fluctuations at the interface are sufficient to separate the surfaces, with solvent (water) shearing in this region being the main source of dissipation. In this paper, we demonstrate that very soft and correspondingly large mesh size Gemini hydrogels show superlubricity with the lowest measured friction coefficient being $\mu = 0.0013 \pm 0.0006$. [DOI: 10.1115/1.4032890]

Keywords: friction, hydrogel, Gemini, superlubricity, mesh size

In Fred Ling's monograph *Surface Mechanics*, which evolved into the text *Fundamentals of Surface Mechanics*, he discussed the development of friction theory from the concepts that real surfaces have roughness and asperity contact is distributed broadly across the surfaces with individually microscopic areas of intimate contact [1]. Although Fred Ling's text often focused on hard materials, many of the concepts may hold even for surfaces that are millions of times softer. In the book *Superlubricity*, de Gennes wrote a foreword entitled, "From Hard to Soft," and described soft systems as a "gold mine of friction research" [2]. However, the vast majority of "superlubricity," "superglide," or "superlubrication," conjunctions found and discussed in the literature dealt with diamondlike films [3,4], hard materials, and incommensurate contacts of layered crystals [5,6], and indeed many scientists preferred the term "structural lubricity" [7,8]. But as Erdemir and Martin discussed in their introduction to the text, "the term superlubricity is quite appropriate from a tribological standpoint in the sense that the prefix "super" means extreme; hence, superlubricity means extreme lubricity but in no way suggests zero friction" [2]. What motivates our interests here is the prediction by de Gennes where he concluded that the future direction of material and surface design of biomimetic systems was "relatively clear"—to use branched chains [2]. Although he

described the analysis as primitive, the point that emerges is to make polymer systems where the branches are basically spaced right about their correlation length and are not too large (such that load carrying capacity is lost) or too small (which results in high friction). Although polymer brush systems are substantially different in configuration as compared to branched polymers, highly solvated polymer brushes applied as thin surface coatings have been able to achieve superlubricity [9–20].

A crosslinked hydrogel surface is remarkably similar to the branched polymers described by de Gennes [2], where flexible polymer chains in the semidilute regime are free to fluctuate across their characteristic mesh size (ξ) with an amplitude of fluctuation that is approximately equal to the mesh size [21]. In the case of semidilute hydrogels composed of flexible polymers, the mesh size ξ (the correlation length between all the pairs of molecules comprising the hydrogel network) is approximately the average spacing between crosslinks [21,22]. The crosslinks near the outermost surface of a hydrogel are thus akin to a dynamic form of the anchoring described by de Gennes that set the characteristic spacing between branched polymers. The surface layer of a semidilute hydrogel made from flexible polymers is in near-perfect analogy to the grafted branched chains that de Gennes speculated would produce superlubricity [2].

In our earlier work with self-mated (i.e., twinned) Gemini hydrogels [23,24], we found that the mesh size indeed controls friction and that there was a regime in which the lowest observed friction coefficient appeared to be independent of sliding speed [22]. This low friction regime was termed thermal fluctuation

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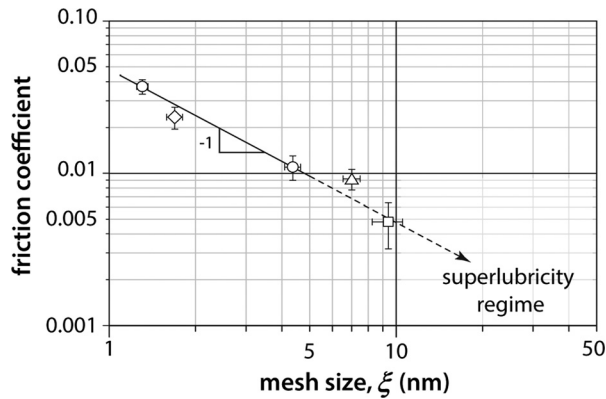


Fig. 1 Friction coefficients decreasing with increasing mesh size as $1/\xi$ was reported in Uruña et al. and predicted superlubricity for $\xi > 5$ nm [22]. All the reported values were below $\mu < 0.05$, with the lowest value $\mu \sim 0.005$ obtained for a mesh size of $\xi \sim 10$ nm. At this order of magnitude and below, the term “superlubricity” is used to describe such friction behavior [2]. Adapted from Ref. [22].

lubrication regime, and the transition away from this regime occurred at a crossover criterion when the shear rate exceeds the polymer relaxation rate. As shown in Fig. 1, the friction coefficient in this thermal fluctuation lubrication regime decreased monotonically with increasing mesh size [22]. The model proposed by de Gennes is in part consistent with these measurements. The hypothesis is that as long as the contact pressure does not

collapse the fluctuating polymer chains, the separation of the surfaces is roughly proportional to the mesh size [25]. At the simplest level of analysis, the dissipation of energy is then related to the viscosity of the solvent (water), the sliding speed, and inversely proportional to the mesh size. This prediction is consistent with our earlier finding of lubricity in Gemini hydrogels, where we observed friction coefficients below $\mu = 0.005$ at speeds below $100 \mu\text{m/s}$ [22]. The trend that emerges from these data (Fig. 1) is that under conditions of mesh sizes greater than 5 nm, these materials may show friction coefficients consistent with superlubricity. An important prediction from this rudimentary analysis is that it predicts lubricity under conditions that are not traditionally thought to promote lubrication, namely, low contact pressures, low sliding speeds, macroscopic contact areas, and aqueous environments at room temperature.

In semidilute hydrogels, the mesh size is related to the polymer concentration, and the mesh size controls both the permeability and the elastic modulus [22]. The hypothesis for superlubricity at large mesh size motivated us to prepare hydrogel samples with an open mesh size. To do this, the hydrogels were prepared following the methods described in Uruña et al. for a 7.5% polymer concentration sample [22], but the countersample was intentionally prepared and polymerized with the sliding surface exposed to laboratory air. Oxygen is an inhibitor to the polymerization process [26] and because these samples are prepared in an aqueous environment, such a process has been found to produce dramatically softer, and thus larger mesh size, hydrogel surfaces.

Tribology experiments were performed on a microtribometer and analyzed following the methods described previously [22,23,27,28]. These experiments were performed at an applied

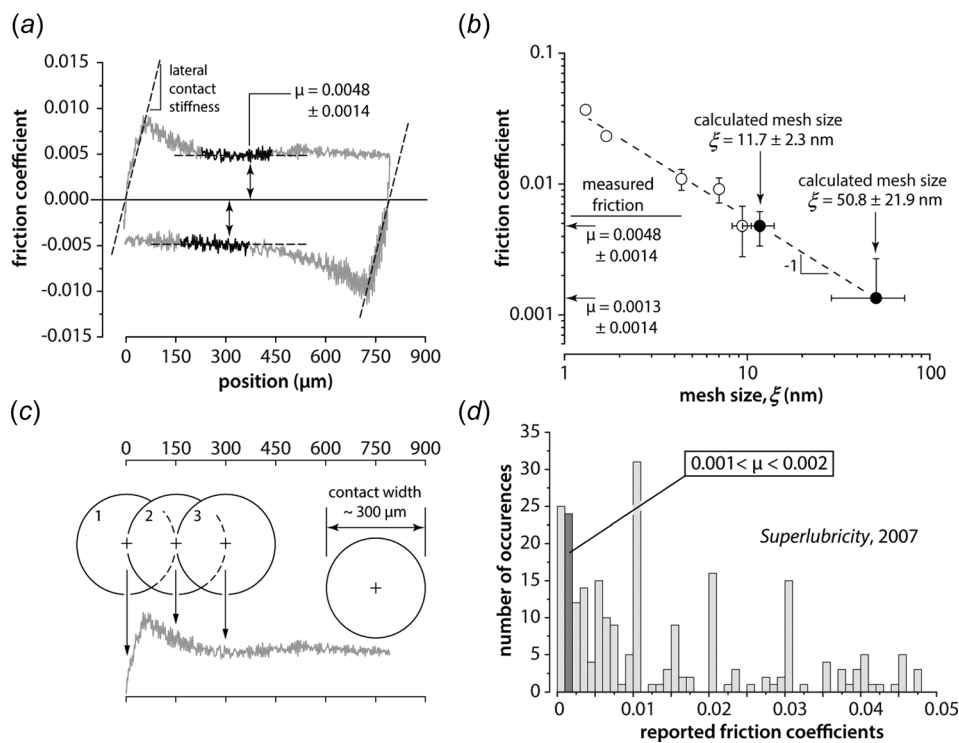


Fig. 2 (a) A representative friction loop from the Gemini hydrogel sliding interface (probe radius of curvature ~ 2 mm and countersample thickness ~ 5 mm) subjected to a normal load of $500 \mu\text{N}$, stroke length of $800 \mu\text{m}$, and sliding speed of $200 \mu\text{m/s}$. The black data in the free sliding region were used to calculate the average friction coefficients and associated uncertainties. (b) Friction coefficients from Fig. 1 were plotted together with those in this paper, and the relation in Uruña et al. was used to calculate the mesh size for the two measurements shown [22]. (c) The friction coefficient loop shows a low contact stiffness [29,30] as the probe moved from the reversal locations (1) to overcome breakloose friction [31] and eventually left the mutual overlap criterion [32] (2 and 3) to achieve superlubricity for the duration of sliding. (d) Friction coefficients of $\mu = 0.001$ – 0.002 are among the lowest values reported in the book *Superlubricity* [2].

normal load of 500 μN , a reciprocating stroke length of 800 μm , and a sliding speed of 200 $\mu\text{m/s}$. The friction loops (Fig. 2(a)) revealed that the samples are truly in sliding contact with clear trends of increasing friction coefficient at the reversal locations (Fig. 2(c)). The friction coefficients in the midregion of the tracks reached values between $\mu=0.005$ down to below $\mu=0.001$, depending on the sample. For the friction loop shown, the friction coefficient is calculated to be $\mu=0.0048 \pm 0.0005$. In Fig. 2(b), we have reported two values of friction coefficient, $\mu=0.0048$ and $\mu=0.0013$, which fall within the regime of superlubricity as shown in Fig. 2(d). As discussed by Erdemir and Martin, measurements below $\mu=0.001$ are extremely challenging (our best efforts yielded experimental uncertainties of $\mu=0.0005$, which are nearly identical to the noise observed in the measurements) [2]. While mesh size measurements are often performed by small angle X-ray scattering, polymerizing hydrogel samples in open air precludes the ability to directly measure the mesh size by this method. Using the data from Fig. 1, we performed a Monte Carlo analysis to estimate the mesh size of the samples and found $\xi=11.7 \pm 2.3$ nm and $\xi=50.8 \pm 21.9$ nm, for $\mu=0.0048$ and $\mu=0.0013$, respectively. These surfaces were extremely soft (consistent with these mesh size estimates) and while we obtained some representative images of the contact areas under static loading, we were not able to accurately compute an elastic modulus. From these static measurements, we approximated the contact pressures to be on the order of 3–7 kPa, which is extremely close to our estimates of the elastic modulus of these surfaces.

The ability of Gemini hydrogel interfaces to achieve superlubricity at low contact pressures, speeds, and macroscopic contact areas in a submerged aqueous environment is contrary to the majority of sliding configurations traditionally described for superlubricity, but is aligned with de Gennes' predictions [2]. The hypothesis of thermal fluctuation lubrication correctly predicted the superlubricity behavior of these Gemini hydrogels [22,24]. Despite these experiments being performed on macroscopic contacts at 500 μN of load, they may have been right on the edge of collapse; thus, the lowest range of friction coefficients reported herein may lie toward the practical limit of friction coefficient measurements (Fig. 2(d)). An additional aspect of this practical limit is also the very formation of a hydrogel with such a large mesh size. A single acrylamide chain with a radius of gyration comparable to the 50 nm mesh size estimated here would have a molecular weight approaching 1×10^6 . Thus, the results described here suggest that Gemini hydrogel interfaces exhibiting superlubricity exist close to, if not on the edge of, the dilute/semidilute crossover concentration, below which individual chains are so disperse in space that they cannot link into hydrogels. By our estimates, it is these most dilute hydrogels that will be capable of exhibiting superlubricity.

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References

- [1] Ling, F. F., Lai, W. M., and Lucca, D. A., 2002, *Fundamentals of Surface Mechanics*, Springer, New York.
- [2] Erdemir, A., and Martin, J.-M., 2007, *Superlubricity*, Elsevier, Amsterdam, The Netherlands.
- [3] Erdemir, A., 2001, "The Role of Hydrogen in Tribological Properties of Diamond-Like Carbon Films," *Surf. Coat. Technol.*, **146**–**147**, pp. 292–297.
- [4] Erdemir, A., 2004, "Genesis of Superlow Friction and Wear in Diamondlike Carbon Films," *Tribol. Int.*, **37**(11–12), pp. 1005–1012.
- [5] Lançon, F., Pénisson, J.-M., and Dahmen, U., 2007, "Quasicrystalline Gold Interface With a Hypo-Friction Property," *Europhys. Lett.*, **49**(5), pp. 603–609.
- [6] Friedel, J., and de Gennes, P.-G., 2007, "Friction Between Incommensurate Crystals," *Philos. Mag.*, **87**(1), pp. 39–49.
- [7] Müser, M. H., 2004, "Structural Lubricity: Role of Dimension and Symmetry," *Europhys. Lett.*, **66**(1), pp. 97–103.
- [8] Dietzel, D., Feldmann, M., Schwarz, U. D., Fuchs, H., and Schirmeisen, A., 2013, "Scaling Laws of Structural Lubricity," *Phys. Rev. Lett.*, **111**(23), p. 235502.
- [9] Klein, J., Kumacheva, E., Mahalu, D., Perahia, D., and Fetters, L. J., 1994, "Reduction of Frictional Forces Between Solid Surfaces Bearing Polymer Brushes," *Nature*, **370**(6491), pp. 634–636.
- [10] Grest, G. S., 1999, "Normal and Shear Forces Between Polymer Brushes," *Adv. Polym. Sci.*, **138**, pp. 149–183.
- [11] Raviv, U., Giasson, S., Kampf, N., Gohy, J.-F., Jérôme, R., and Klein, J., 2003, "Lubrication By Charged Polymers," *Nature*, **425**(6954), pp. 163–165.
- [12] Gong, J. P., 2006, "Friction and Lubrication of Hydrogels: Its Richness and Complexity," *Soft Matter*, **2**(7), pp. 544–552.
- [13] Müller, M., Lee, S., Spikes, H. A., and Spencer, N. D., 2003, "The Influence of Molecular Architecture on the Macroscopic Lubrication Properties of the Brush-Like Co-Polyelectrolyte Poly(L-lysine)-g-Poly(ethylene glycol) (PLL-g-PEG) Adsorbed on Oxide Surfaces," *Tribol. Lett.*, **15**(4), pp. 395–405.
- [14] Kenausis, G. L., Vörös, J., Elbert, D. L., Huang, N., Hofer, R., Ruiz-Taylor, L., Textor, M., Hubbell, J. A., and Spencer, N. D., 2000, "Poly(L-lysine)-g-Poly(ethylene glycol) Layers on Metal Oxide Surfaces: Attachment Mechanism and Effects of Polymer Architecture on Resistance to Protein Adsorption," *J. Phys. Chem. B*, **104**(14), pp. 3298–3309.
- [15] Pasche, S., De Paul, S. M., Vörös, J., Spencer, N. D., and Textor, M., 2003, "Poly(L-lysine)-Graft-Poly(Ethylene Glycol) Assembled Monolayers on Niobium Oxide Surfaces: A Quantitative Study of the Influence of Polymer Interfacial Architecture on Resistance to Protein Adsorption by ToF-SIMS and in Situ OWLS," *Langmuir*, **19**(22), pp. 9216–9225.
- [16] Li, A., Benetti, E. M., Tranchida, D., Clasohm, J. N., Schönherr, H., and Spencer, N. D., 2011, "Surface-Grafted, Covalently Cross-Linked Hydrogel Brushes With Tunable Interfacial and Bulk Properties," *Macromolecules*, **44**(13), pp. 5344–5351.
- [17] Morgenthaler, S., Zink, C., and Spencer, N. D., 2008, "Surface-Chemical and -Morphological Gradients," *Soft Matter*, **4**(3), pp. 419–434.
- [18] Ohseido, Y., Takashina, R., Gong, J. P., and Osada, Y., 2004, "Surface Friction of Hydrogels With Well-Defined Polyelectrolyte Brushes," *Langmuir*, **20**(16), pp. 6549–6555.
- [19] Giasson, S., and Spencer, N. D., 2014, "Aqueous Lubrication With Polymer Brushes," *Aqueous Lubrication*, World Scientific Publishing Company, Singapore, p. 284.
- [20] Li, A., Ramakrishna, S. N., Nalam, P. C., Benetti, E. M., and Spencer, N. D., 2014, "Stratified Polymer Grafts: Synthesis and Characterization of Layered 'Brush' and 'Gel' Structures," *Adv. Mater. Interfaces*, **1**(1).
- [21] de Gennes, P.-G., 1979, *Scaling Concepts in Polymer Physics*, Cornell University Press, Ithaca, NY.
- [22] Uruña, J. M., Pitenis, A. A., Nixon, R. M., Schulze, K. D., Angelini, T. E., and Sawyer, W. G., 2015, "Mesh Size Control of Polymer Fluctuation Lubrication in Gemini Hydrogels," *Biotribology*, **1**–2(352), pp. 24–29.
- [23] Dunn, A. C., Sawyer, W. G., and Angelini, T. E., 2014, "Gemini Interfaces in Aqueous Lubrication With Hydrogels," *Tribol. Lett.*, **54**(1) pp. 1–8.
- [24] Pitenis, A. A., Uruña, J. M., Schulze, K. D., Nixon, R. M., Dunn, A. C., Krick, B. A., Sawyer, W. G., and Angelini, T. E., 2014, "Polymer Fluctuation Lubrication in Hydrogel Gemini Interfaces," *Soft Matter*, **10**(44), pp. 8955–8962.
- [25] Dunn, A. C., Uruña, J. M., Huo, Y., Perry, S. S., Angelini, T. E., and Sawyer, W. G., 2013, "Lubricity of Surface Hydrogel Layers," *Tribol. Lett.*, **49**(2), pp. 371–378.
- [26] Shi, Q., and Jackowski, G., 1998, "One-Dimensional Polyacrylamide Gel Electrophoresis," *Gel Electrophoresis of Proteins: A Practical Approach*, Oxford University Press, Oxford, UK, pp. 1–52.
- [27] Schmitz, T. L., Action, J. E., Ziegert, J. C., and Sawyer, W. G., 2005, "The Difficulty of Measuring Low Friction: Uncertainty Analysis for Friction Coefficient Measurements," *ASME J. Tribol.*, **127**(3), pp. 673–678.
- [28] Burris, D. L., and Sawyer, W. G., 2009, "Addressing Practical Challenges of Low Friction Coefficient Measurements," *Tribol. Lett.*, **35**(1), pp. 17–23.
- [29] Carpick, R. W., Ogletree, D. F., and Salmeron, M., 1997, "Lateral Stiffness: A New Nanomechanical Measurement for the Determination of Shear Strengths With Friction Force Microscopy," *Appl. Phys. Lett.*, **70**(1), pp. 1548–1550.
- [30] Dickrell, D. J., and Sawyer, W. G., 2010, "Lateral Contact Stiffness and the Elastic Foundation," *Tribol. Lett.*, **41**(1), pp. 17–21.
- [31] Persson, B. N. J., Albohr, O., Mancosu, F., Peveri, V., Samoilov, V. N., and Sivebaek, I. M., 2003, "On the Nature of the Static Friction, Kinetic Friction and Creep," *Wear*, **254**(9), pp. 835–851.
- [32] Blanchet, T. A., and Kennedy, F. E., 1991, "Effects of Oscillatory Speed and Mutual Overlap on the Tribological Behavior of PTFE and Selected PTFE-Based Self-Lubricating Composites," *Tribol. Trans.*, **34**(3), pp. 327–334.