Supplementary Information

Friction Force Microscopy of Lubricin and Hyaluronic Acid between Hydrophobic and Hydrophilic Surfaces

Debby P. Chang[1, 2], Nehal I. Abu-Lail[3], Jeffery Coles[1, 2, 4,], Farshid Guilak[4, 5], Gregory Jay[6], and Stefan Zauscher[1, 2, 4*]

1 Department of Mechanical Engineering and Materials Science, Duke University
2 Center for Biologically Inspired Materials and Material Systems, Duke University
3 Chemical Engineering and Bioengineering, Washington State University
4 Center for Biomolecular and Tissue Engineering, Duke University
5 Department of Surgery, Duke University
6 Department of Emergency Medicine, Rhode Island Hospital

*Corresponding Author
Professor Stefan Zauscher
Department of Mechanical Engineering and Materials Science
144 Hudson Hall, P.O. Box 90271, Durham, NC 27708
Email: zauscher@duke.edu
Phone: (919) 660-5360
Fax: (919) 660-5409

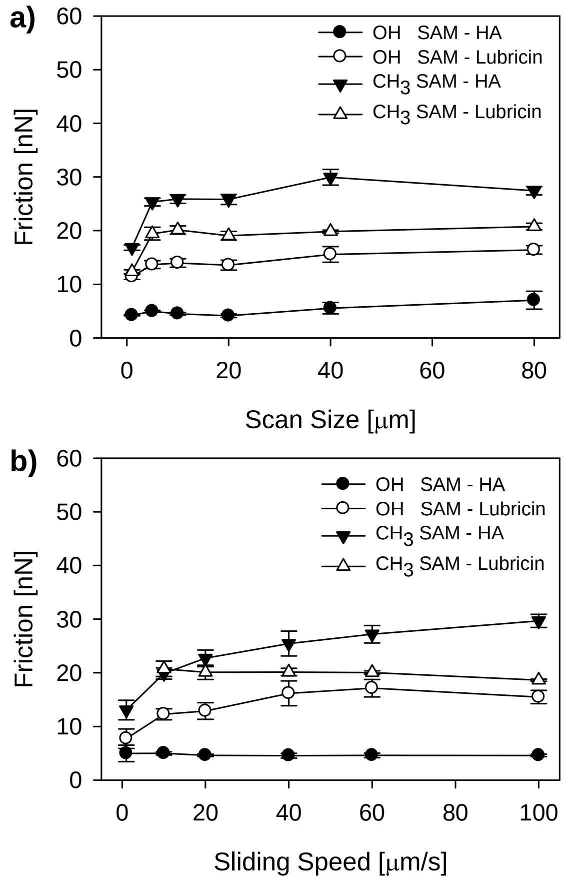

Figure S1: Friction forces measured as a function of a) scan size and b) sliding speed between hydrophobic (CH_3-terminated SAM, triangle), hydrophilic (OH-terminated SAM, circle) surfaces in the presence of lubricin/HA solutions under a constant applied normal load of 100 nN.

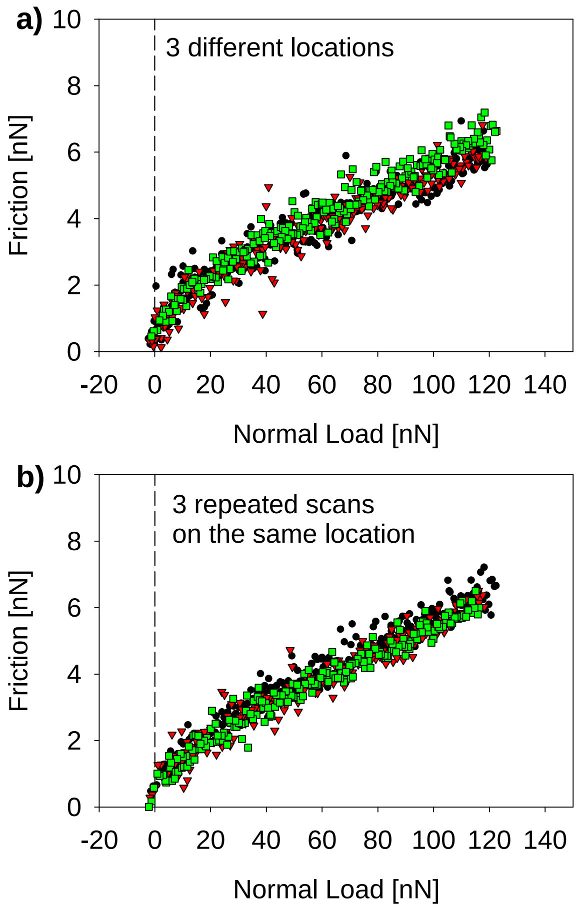

Figure S2. Typical set of friction vs. load measurements obtained on a) different locations and b) repeated scans on the same location between methyl-terminated SAM surfaces in the presence of 200 μg/ml lubricin. The different symbols correspond to different sets of measurements.

Friction Force Fit

Friction versus load at the microscopic contact can be explained by continuum mechanic models showing that friction increases with increasing contact area. A model for non-adhesive contact was developed by Hertz. This model estimates the contact area between a homogenous, isotropic and linear elastic material. For a sphere with radius R, pressed onto a flat surface with a force, F, the contact radius, a, is

$$a = \left(\frac{FR}{K}\right)^{1/3}, \qquad \text{[Eq. 1]}$$

where K is the effective elastic modulus of contact

$$K = \frac{4}{3}\left(\frac{1-\nu_1^{\,2}}{E_1} + \frac{1-\nu_2^{\,2}}{E_2}\right)^{-1}, \qquad \text{[Eq. 2]}$$

calculated from the Young's moduli, E_1, E_2, and Poisson's ratios, ν_1, ν_2, of the sphere and flat surface, respectively.

To capture and compare the observed non-linear friction versus load behavior in adhesive contact, the Carpick, Ogletree, and Salmeron (COS) equation[3, 4], which describes the contact radius for both JKR and DMT models, was used. The COS equation is an analytical approximation of the contact area based on Maugis-Dudgdale model[5], and later physically justified by Schwarz[6]. The model estimates the contact radius,

$$a = a_0 \left(\frac{\alpha + \sqrt{1 - L/L_c}}{1+\alpha} \right)^{2/3} \qquad \text{[Eq. 3]}$$

where α_0 is the contact radius at zero load, L_c is the pull-off force and α is the transition parameter (α=1 corresponds to JKR model and α=0 corresponds to the DMT model).

To fit the COS equation to friction versus load data, friction is assumed to be directly proportional to the contact area ($F_f = \tau * \pi a^2$, where τ is the constant interfacial shear stress). By substituting contact radius with friction force, $a = (F_f / \tau * \pi)$ ^ (1/2), and defining the friction at zero load, $F_{f0} = \tau * \pi a_0^2$, the following equation can be used to fit the friction data,

$$F_f = F_0 \left(\frac{\alpha + \sqrt{1 - L/L_c}}{1+\alpha} \right)^{4/3} . \qquad \text{[Eq. 4]}$$

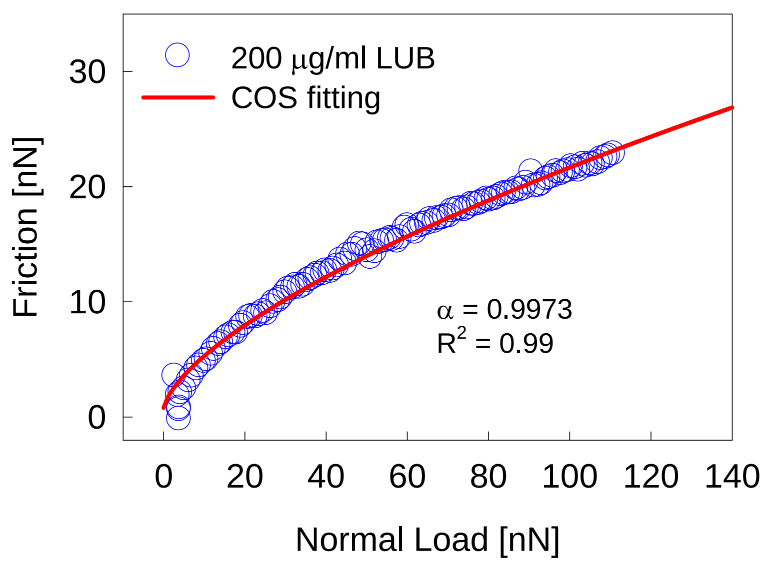

Figure S3. Friction force versus normal load measurement between two hydrophobic surfaces in presence of 200 μg/ml lubricin. Solid line represents the fit using the COS equation.

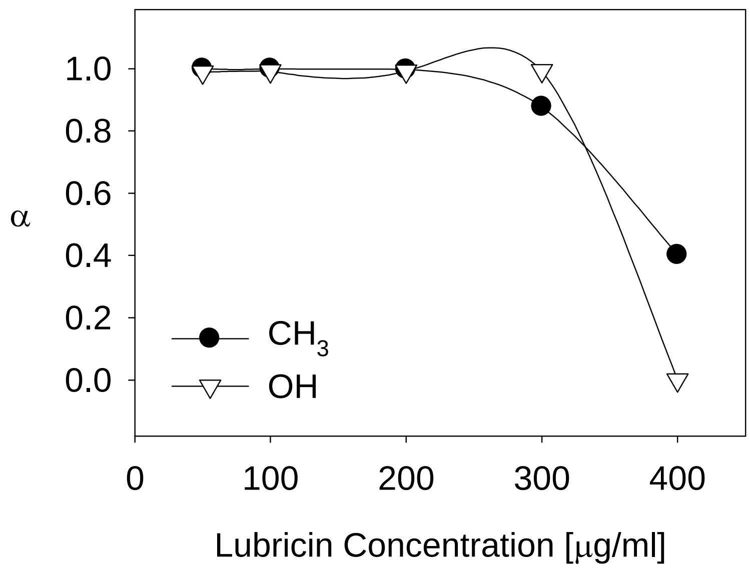

Figure S4. The transition parameter, α, obtained from the COS model fit over a range of lubricin concentrations.

Figure S3 shows a typical friction versus load data in the presence of 200 μg/ml lubricin with the COS fit. The COS fit was determined by letting the pull-off force P_c, friction at zero load F_{f0}, and transition parameter α, be free parameters in the curve fit optimization. The model fit gives a qualitative estimate of the frictional behavior. The fitted transition parameter α=0.99 suggests that the JKR model best describes the frictional behavior at this lubricin concentration. **Figure S4** shows the transition parameter obtained from the COS model fit between hydrophobic or hydrophilic surfaces for a range of lubricin concentrations. At lower concentrations of lubricin, the JKR model predominates the frictional behavior (α=1), indicating that short-ranged adhesive forces are most prevalent. At higher lubricin concentration, the frictional behavior transitions towards the DMT model (α=0), indicating that long-ranged adhesive force slowly dominates.

The contact mechanic model used here can qualitatively captures the shape of the friction versus normal load curves; however, it should not be applied quantitatively because it is only truly valid for homogeneous, isotropic and linear elastic materials. The adsorbed lubricant layer can substantially alter the contact mechanics model, making the system inhomogeneous and maybe anisotropic and non-linear.

1. K. L. Johnson, K. Kendall and A. D. Roberts, *Proceedings of the Royal Society of London Series a-Mathematical and Physical Sciences*, 1971, **324**, 301-.
2. B. V. Derjaguin, V. M. Muller and Y. P. Toporov, *J. Colloid Interface Sci.*, 1975, **53**, 314-326.
3. D. S. Grierson, E. E. Flater and R. W. Carpick, *J. Adhes. Sci. Technol.*, 2005, **19**, 291-311.

4. R. W. Carpick, D. F. Ogletree and M. Salmeron, *J. Colloid Interface Sci.*, 1999, **211**, 395-400.
5. D. Maugis, *Journal of Colloid and Interface Science*, 1992, **150**, 243-269.
6. U. D. Schwarz, *J. Colloid Interface Sci.*, 2003, **261**, 99-106.