Electronic Supplementary Material (ESI) for Nanoscale.

Supporting Information

Friction between soft contacts at nanoscale on uncoated and protein-coated surfaces

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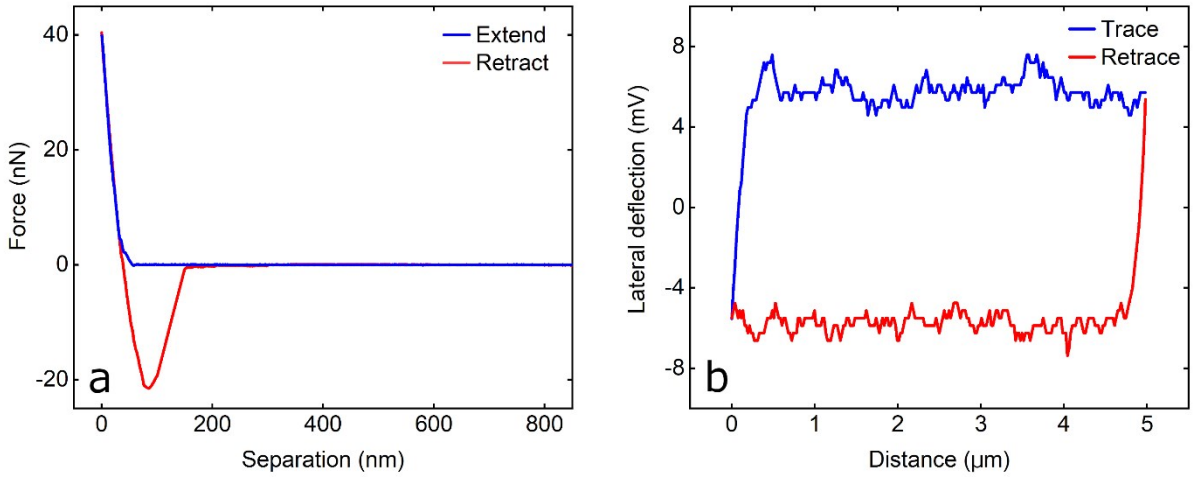

Figure S1. Representative force-distance (F-d) curve and friction loop. a) The curves represent a characteristic force versus distance relationship of a hard borosilicate glass (BSG) colloidal probe against soft PDMS surface. The blue colour indicates the extending part, where the BSG probe travels towards the PDMS surface, while the red is the retracting part where the probe withdraws from the PDMS surface. The retracting part of the curve exhibits the adhesion between the BSG probe and the PDMS, this was also fitted with JKR model for the calculation of the elastic modulus of the surfaces. b) The curves represent a typical friction loop acquired by means of atomic force microscopy upon sliding of a BSG probe against PDMS surface in presence of buffer solution. The different colours correspond to the trace (blue) and the retrace (red) part of the loop.

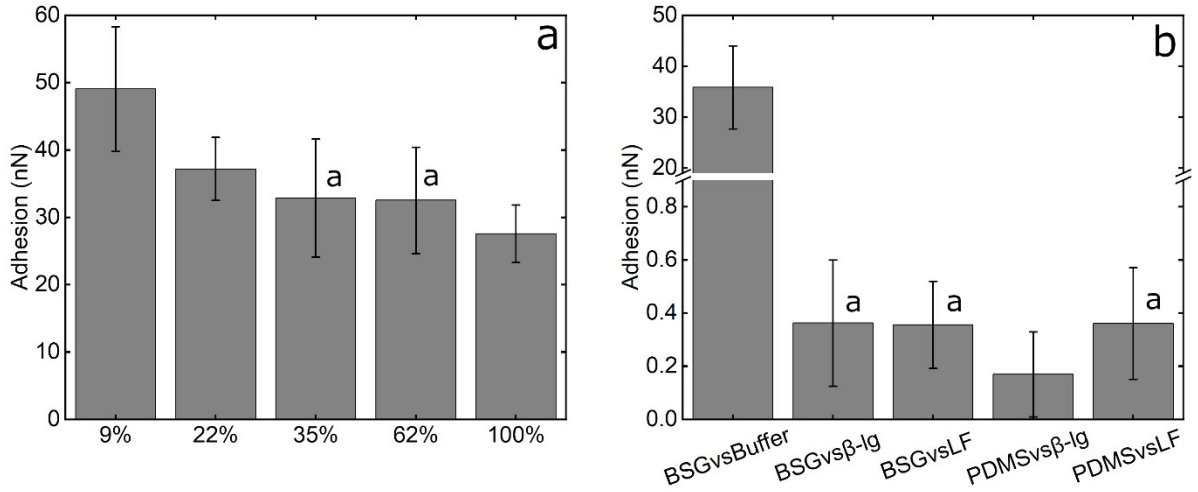

Figure S2. Adhesion measurements. a) The bar chart represents the adhesion (n = 50, mean ± SD) between hard borosilicate glass (BSG) probe and PDMS substrate with various elastic modulus. The measurements were acquired by AFM. The labels correspond to the weight percentage of Sylgard®184 as a percentage of combined weight of Sylgard®184 and Sylgard®527. Samples with the same letter do not differ significantly ($p > 0.05$) in adhesion values according to Tukey's test. b) The bar chart represents the adhesion (n = 50, mean ± SD) between colloidal probes (BSG or PDMS) and PDMS substrates in buffer and in protein solutions. Samples with the same letter do not differ significantly ($p > 0.05$) in adhesion values according to Tukey's test.

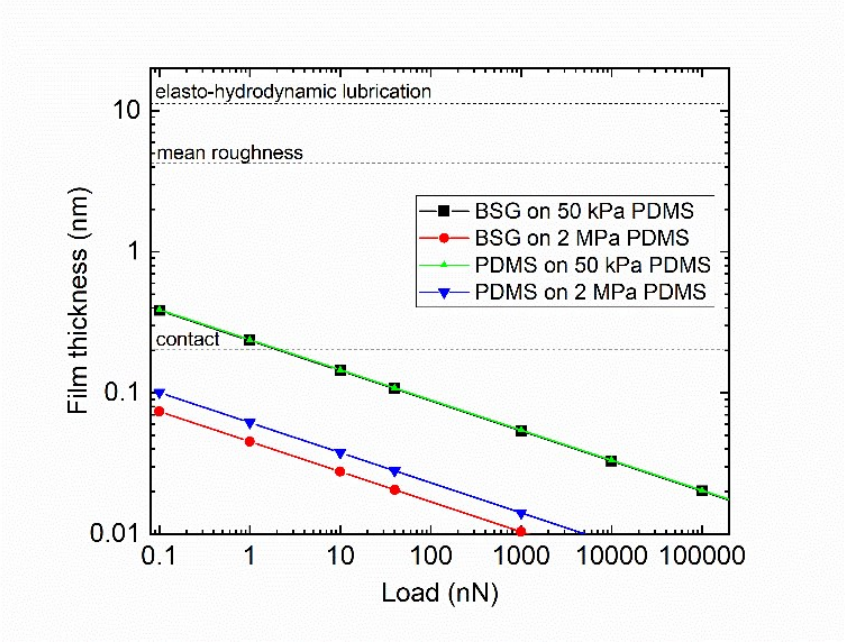

Figure S3. Theoretical film thickness as a function of load. Curves represent the film thickness of water as a function of load, at different probe (BSG and PDMS) and surface (50 kPa and 2 MPa) combinations. The calculations were performed for a sliding speed of 5 μm s^{1}. Dotted lines represent the film thickness where elasto-hydrodynamic lubrication commences (without considering deformation of roughness), the mean roughness of the PDMS surfaces, and the thickness where clear probe-sample contact occurs at less than the diameter of a water molecule. The colours represent to different probe/surface systems.

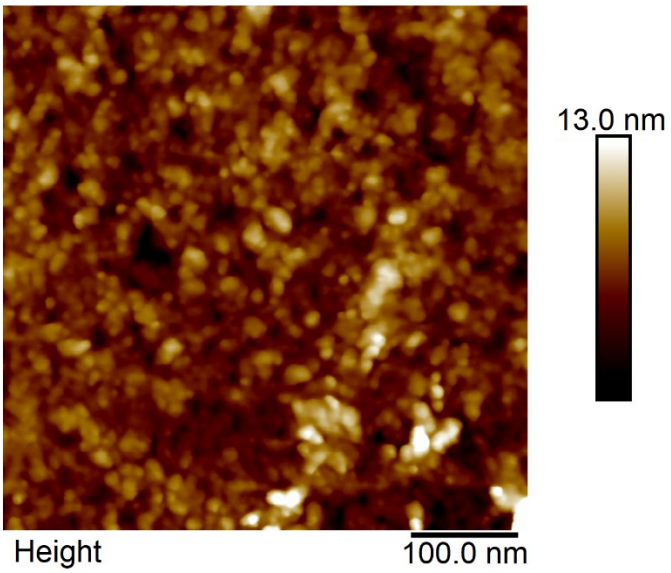

Figure S4. Topographic image of borosilicate glass (BSG) colloidal probe. AFM image showing the surface of the BSG particle attached on the AFM cantilever. Analysis revealed RMS roughness equal to 1.74 nm.

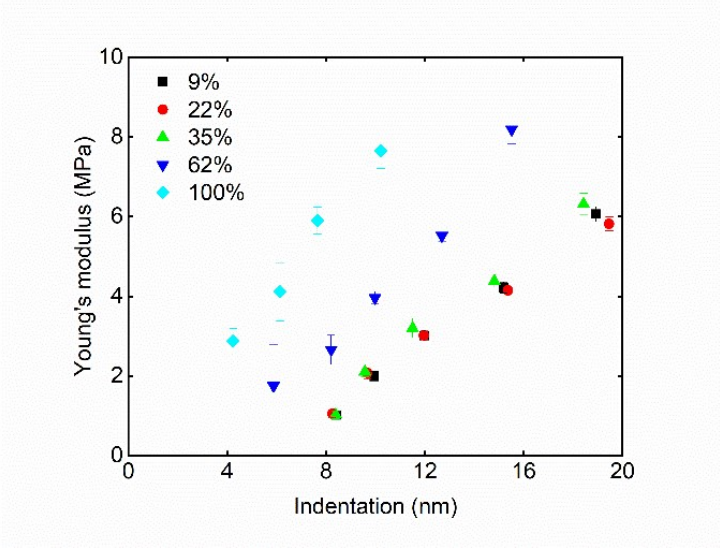

Figure S5. Determination of the elasticity of the hydrophilic PDMS substrates. The Young's modulus was determined by means of AFM using a hard borosilicate glass (BSG) probe with a radius of approximately 2.5 µm and fitted with a JKR model. The data points (n = 50, mean ± SD) represent the Young's modulus of hydrophilized PDMS surfaces as a function of the indentation depths. The colours correspond to the weight percentage of Sylgard®184 as a percentage of combined weight of Sylgard®184 and Sylgard®527.

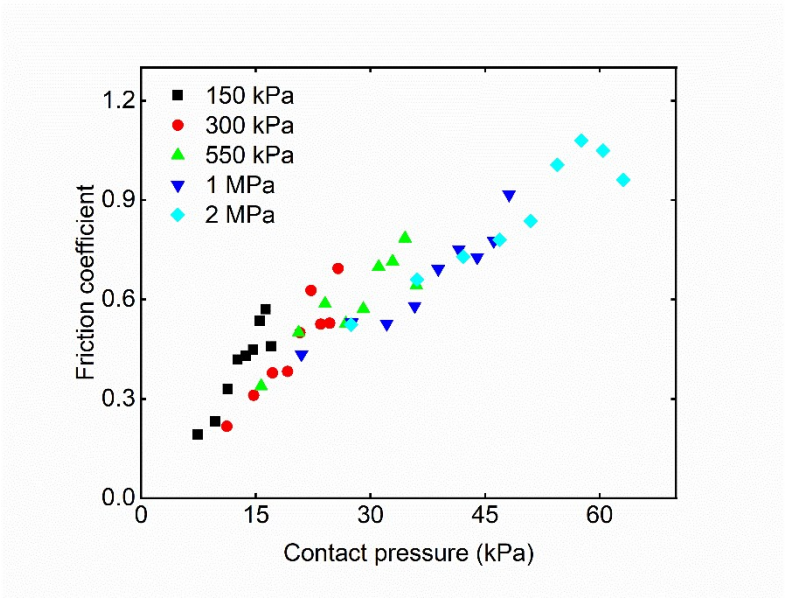

Figure S6. Friction coefficient as a function of mean contact pressure. The measurements were acquired by friction force microscopy, using a PDMS colloidal probe sliding over PDMS substrates with different modulus in presence of protein (β-lactoglobulin, β-lg). The data points represent friction coefficient (calculated by the tangent at every individual measurement on Figure 4c) as a function of mean contact pressure. The colours correspond to the Young's modulus of the PDMS substrates.

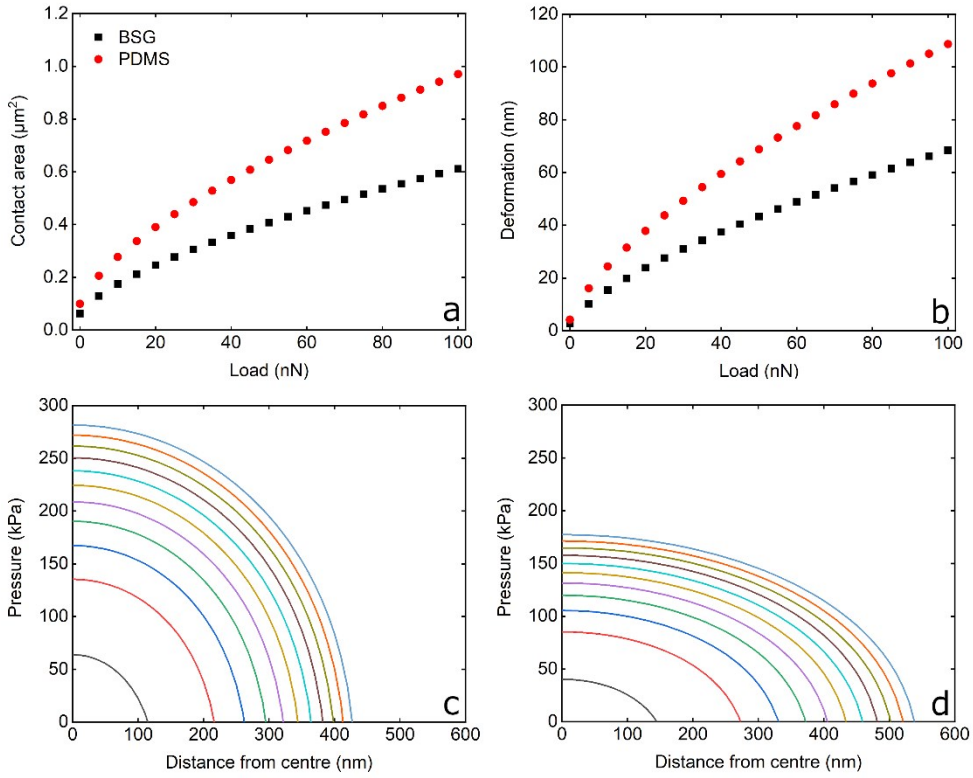

Figure S7. Contact area, deformation, and pressure distribution in hard-soft versus soft-soft contacts. a) The data points represent the dependence of contact area on normal load. b) The data points represent the dependence of deformation at the centre of contact on normal load. Note, deformation is the combined deformation of probe and surface, hence for soft-soft contact both deform to a similar degree. This explains the apparently counter-intuitive result of greater deformation of the soft-soft contact, when it would be expected that the hard probe would deform the soft surface more. If only surface deformation was measured, the PDMS surface would indeed be deformed more by the BSG probe. c) The data lines represent the pressure distribution as applied by a borosilicate (BSG) probe on a PDMS surface. The normal load is ranging from 0 nN (black line) to 100 nN (blue line) with 10 nN increments. d) The data lines represent the pressure distribution as applied by a PDMS probe on a PDMS surface. The normal load is ranging from 0 nN (black line) to 100 nN (blue line) with 10 nN increments. All calculations were performed using the JKR model, using the theoretical values (adhesion 1 nN, probe radius 2.5 μm) of BSG and PDMS probes against PDMS surfaces with elastic modulus of 2 MPa.

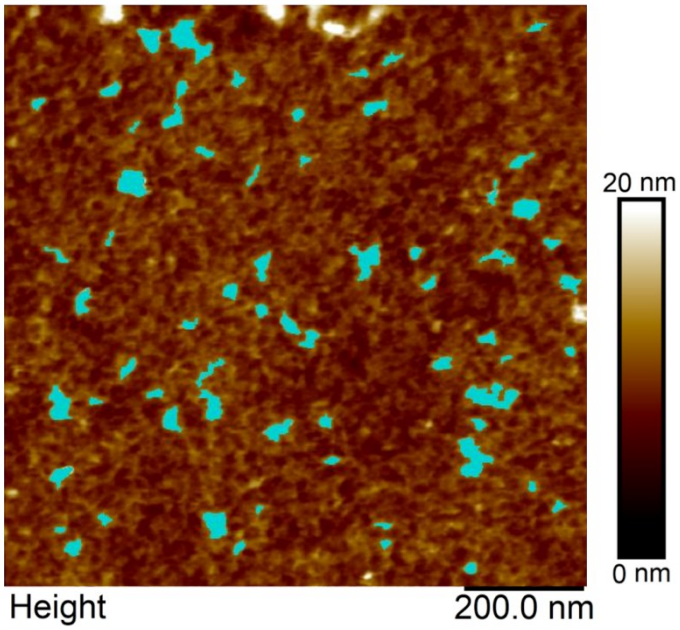

Figure S8. Topographic image of lactoferrin (LF) film on PDMS substrate. AFM image showing LF adsorbed onto PDMS substrates. Analysis on the largest aggregates (teal colour) revealed a mean height of 7 nm (ranging between 2 nm and 23 nm), and a mean diameter of 22 nm (ranging from 11 nm to 50 nm).

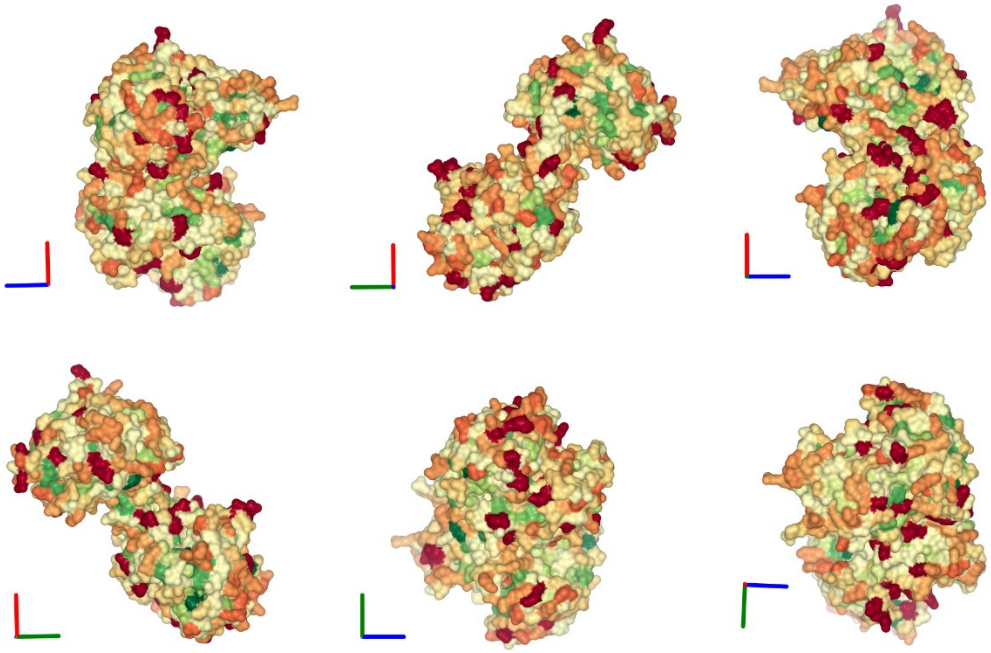

Figure S9. Hydrophobicity of lactoferrin. The figure shows the hydrophilic residues coloured with shades of orange and the hydrophobic residues coloured with shades of green of lactoferrin, as seen from the six different planes around the protein molecule. The molecular structure was found in RCSB protein data bank (PDB code:1QJM). A molecular surface representation was selected, depicting the hydrophobicity of the residues, as shown in the Mol* Javascript viewer.

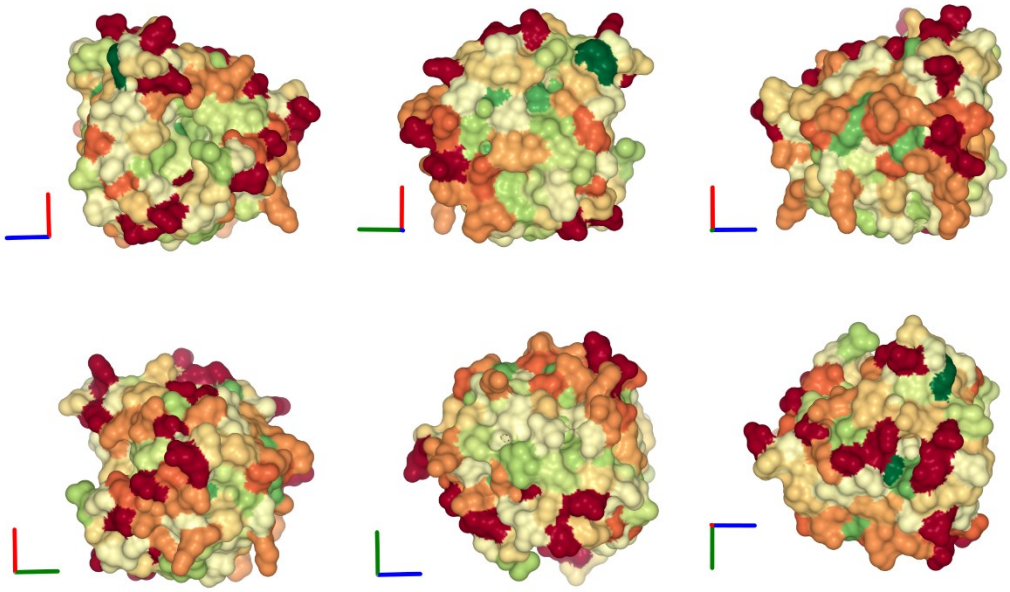

Figure S10. Hydrophobicity of β-lactoglobulin. The figure shows the hydrophilic residues coloured with shades of orange and the hydrophobic residues coloured with shades of green in β-lactoglobulin, as seen from the six different planes around the protein molecule. The molecular structure was found in RCSB protein data bank (PDB code:5IO5). A molecular surface representation was selected, depicting the hydrophobicity of the residues, as shown in the Mol* Javascript viewer.

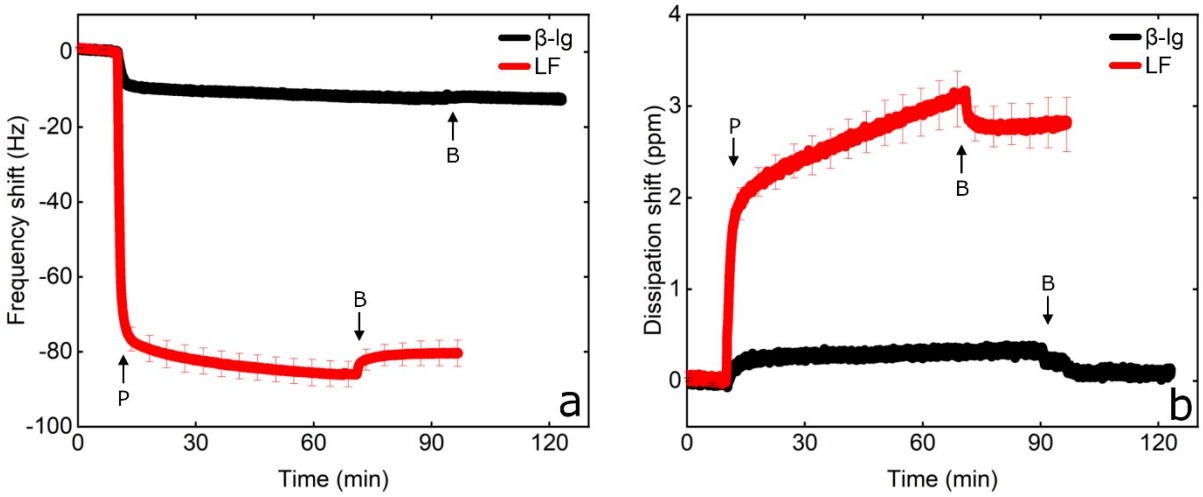

Figure S11. Characterisation of adsorbed protein films. Adsorption of β-lactoglobulin (β-lg) and lactoferrin (LF) on PDMS surfaces acquired by quartz crystal microbalance with dissipation. a) The curves (n = 3, mean ± SD) represent the frequency shift as a function of time. b) The curves (n = 3, mean ± SD) represent the dissipation shift (ΔD) as a function of time.

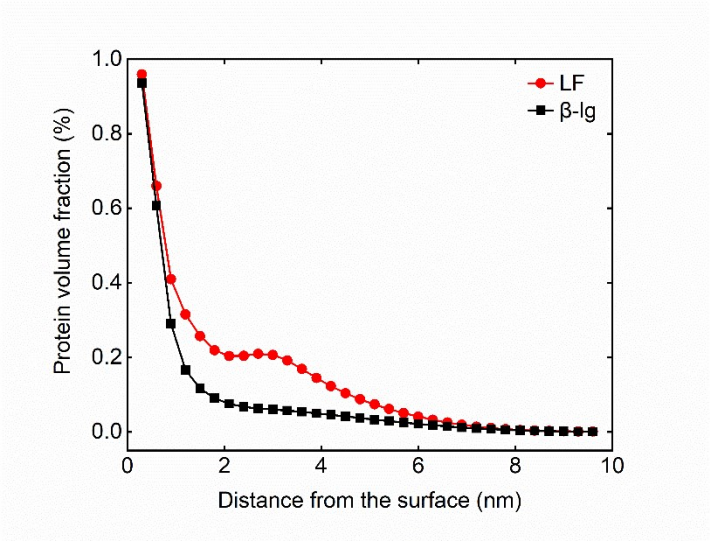

Figure S12. Theoretical calculation of total segment density profiles for the adsorbed protein films. Curves represent the volume fraction of lactoferrin (LF) and β-lactoglobulin (β-lg), plotted as a function of distance away from a solid surface. Bulk volume fraction of remaining protein in solution was 1×10^{-7} in each case, as it is assumed that most of the protein will be adsorbed onto surfaces rather than remaining in bulk. The volume fraction of ions is 0.002 (equivalent to 10 mM NaCl) at neutral pH. Calculations were performed using self-consistent field theory (SCF).

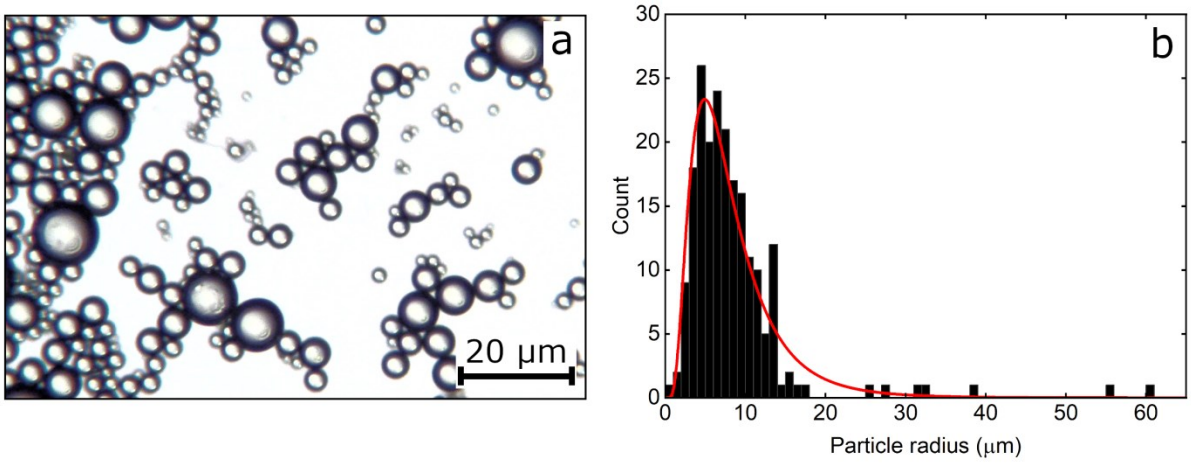

Figure S13. Images and size distribution of PDMS microspheres used for the friction force microscopy for soft-soft contact. a) Images of PDMS microspheres acquired by optical microscopy. b) Particle radius size distribution of the PDMS microspheres, measured from multiple optical images using the Particle Analysis function in ImageJ (NIH). Peak of the log-normal distribution (red fit line) = 4.9 µm.