

Methods

We have chosen to investigate the normal forces and sliding resistance in systems comprising spherical thiolated gold particles sliding against smooth polytetrafluoroethylene (PTFE) substrates in various liquid media. Quantitative measurements of normal and friction¹ forces were conducted using a commercial AFM² in colloid probe mode³ with force sensitivity in the sub-picoNewton range; see the schematic Figure 2.

The deflection of a micro-fabricated AFM cantilever (dimensions typically: length ~200µm, width ~30µm, thickness ~1µm) is measured by the change in position of a laser beam reflected off the back of the cantilever onto a photodiode detector in a commercial AFM (Nanoscope, Digital Instruments). The surface force is obtained from the normal deflection of the cantilever while the friction force is obtained from a twist in the cantilever as the lower surface is moved below the sphere (at right angles to the cantilever) at a given load. The methods, including details of normal and torsional spring constant determination, cantilever preparation etc are described more fully elsewhere.^{4,5}

Surfaces. Spherical smooth gold particles (radius between 5.0 and 10.0µm) were produced by electrical discharge between gold wires (0.25mm) under an argon atmosphere. They were glued onto standard contact mode AFM cantilevers under an optical microscope using a motorized micromanipulator device. The gold particles were hydrophobized by treatment with mercaptopentadecane solution in ethanol to avoid adsorption of trace amounts of residual water in the solutions. Smooth PTFE surfaces (rms roughness < 0.2 nm over 1µm²) were produced by compressing pieces of PTFE between freshly cleaved atomically flat mica sheets in an oven (500°C) overnight. Molecular sieves were used to ensure that the solvents were free from dissolved water, except for the experiments in which water was intentionally added to the ethanol. The liquids were filtered (Nucleopore 0.25µm) and introduced into the AFM liquid cell via syringe.

Surface Forces and Friction. Normal (surface) forces were measured as a function of surface separation as the substrate was ramped towards and away from the cantilever.³

Sliding friction forces were measured by applying a continuous triangle wave displacement in the plane of the PTFE surface perpendicular to the axis of the cantilever.⁴ The amplitude of the displacement was 1 µm and the frequency 1 Hz. The torsional deflection of the cantilever is monitored in each direction, providing a “friction loop”. The friction force at each load is obtained from the average of 10 such loops, each of which returns the average of approximately 400 points. The diameter of the sphere acts a lever arm and must be accounted for.

It is important to note that the absolute zero of separation in such measurements is ambiguous, due to the asymptotic nature of the force couple with the fact that with the AFM technique, there is no absolute measurement of zero separation. The apparent position of contact is ordinarily inferred from the region of constant compliance – where the spring deflects linearly with the relative motion of the surfaces. As Milling *et al* pointed out such a force leads to a “pseudo constant compliance” region and they developed a linearisation procedure to obtain the true separation.⁶ Here we used an alternative approach by determining the slope of the constant compliance region unambiguously from force measurements in the adhesive case (inset figure 2). Equation 1 is then used to *calculate* the separation at the maximum *measured force* and this value is then set as the minimum separation achieved in figure 2 between the gold and PTFE surfaces. As with the method of Milling *et al* this assumes that the functional form of equation 1 is correct even at small separations. As an independent check the linearisation was also employed and returned an *identical* separation of 2.9 nm at the maximum applied force of 2mN/m.

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