Supplementary Materials for:

Measurement of no slip and slip boundary conditions in confined Newtonian fluids using Atomic Force Microscopy

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Consistency of methodology and data analysis between cantilever geometries.

Cantilever stiffness. Consideration was given to the stiffness of the cantilever employed, particularly as the later experiments of Honig et al. had used stiffer springs.[1, 2] When performing hydrodynamic measurements the ideal spring stiffness is necessarily a compromise. A weak cantilever will deflect more easily and therefore improve the force resolution of the instrument, however a weak spring will deflect further for a given force and under the large repulsive hydrodynamic forces experienced at short separations this may result in the linear range of the detection optics being exceeded or an inability to drive the surfaces into contact. If the surfaces do not reach true contact the zero of separation will be incorrect as well as the determination of cantilever deflection and hence force. Evanescent wave AFM[3] was used on a subset of our data to confirm that 'hard contact' was reached.

The evanescent wave AFM tracks the relative surface movement of sphere and flat surface.[3] We found that a constant evanescent wave signal (unchanging relative surface position) was achieved even in the case of a very weak spring (0.14Nm^{-1}) being driven at speeds of up to 10μm s^{-1} through 58%w/w sucrose (see Figure 1S.). The finding that hard contact is achieved is backed up by our comparison to 'slow' driving force (100-200nms^{-1}). Identical slope of the compliance region of our graph for fast and slow runs indicates that the cantilever is deflecting similarly in both cases, and not changing position relative to the solid surface. Note that because the evanescent wave AFM only records the relative change in position of the two surfaces, this technique cannot address the possibility, raised by Honig and Ducker,[4] of an asperity in the contact region of the sphere and the flat surface.

We used v-shaped and rectangular springs in the range 0.1-1.0N/m (similar stiffness to those employed by Craig et al.[5]). Considerably stiffer rectangular cantilevers (2-20N/m) similar to those employed by Ducker and co-workers were also tried.[1] The spring constant of the cantilever was found to have no effect on the measured hydrodynamics in this range. Provided the piezo drive rate and solution viscosity are selected with care, there is no reason to exclude the use of weak cantilevers in hydrodynamic measurements.

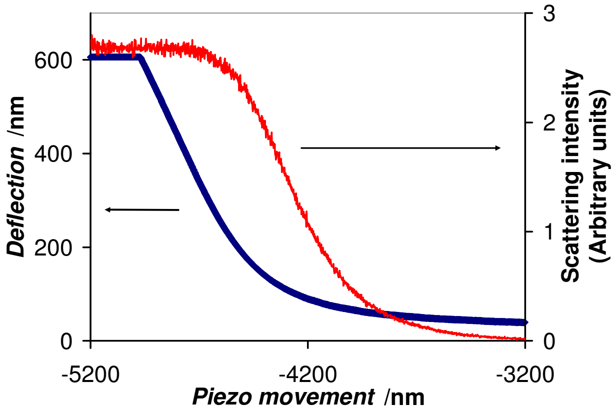

Fig. 1S A weak spring reaches constant separation (taken as surface contact) during piezo approach. Cantilever deflection (◆) and evanescent-wave scattering data (——) as a function of piezo displacement for a v-shaped spring with k~0.14Nm^{-1}. Drive velocity is 6μms^{-1}, medium is 58% sucrose solution. The level evanescent wave trace shows that surfaces have reached constant separation before the photodiode limit is reached. Slip length fit is 5nm.

Only the approach force curves were used for calculating hydrodynamic force and slip length. There are several reasons for this. The ‘turn-around’ of the piezo can introduce ‘ringing’ visible as an oscillation in the withdrawal plot, which can extend even out of contact in our region of interest. The interaction of the tip with the surface, particularly in the presence of nanoscale roughness, is not well characterised. There is a chance that some adhesion or similar interaction may change the tip withdrawal and affect measurements at small separations. In addition, we wished to obtain data at as wide a piezo range as possible, particularly to attempt to settle the question of whether weak springs make contact with the surface. The larger deflection of weak springs means that the range of the photodiode voltage becomes a limit to the contact region measurable. We could stay within the photodiode voltage limits for a larger region of interest if we allowed the deflection due to hydrodynamic attraction on withdrawal to go beyond the limits.

Cantilever drag. Differences in data analysis could lead to a difference in apparent boundary condition. This is possible in these experiments, as the uncertainty in ascribing the position of contact (zero separation) and the force baseline (zero force) is greater than in AFM measurements of quasistatic forces. The force baseline determination is complicated as the influence of the drag on the cantilever (as opposed to the sphere) has to be addressed. Much effort has earlier been devoted to the effect of cantilever drag on the hydrodynamic force measured – which in the simplest analysis is treated under the lubrication approximation for a sphere approaching a flat, with the change in cantilever drag ignored. That is, the small measured drag on the cantilever at far separations is subtracted, and it is assumed that the magnitude of this drag does not change substantially with separation. When a 10μm radius sphere is used the change in separation between the surface and the cantilever is typically less than 5% during a measurement and as this component of the force is already small this change can be neglected. The data of interest is where the separation of the sphere and the substrate changes from <1 micron down to contact, whereas the cantilever-substrate separation changes from approximately 21 microns to 20 microns (depending on the diameter of the sphere) in the same interval. It is not possible accurately to calculate the hydrodynamic force on the cantilever due to the presence of the sphere and changes in the shape of the cantilever during measurement. However because the cantilever is much further away from the substrate in the experiments here the magnitude of the hydrodynamic force on the cantilever is small and does not change much during a measurement. If smaller spheres are employed the influence of the cantilever may become significant. The drag on the cantilever is unlikely to be an explanation for the data obtained with v-shaped springs. During hydrodynamic approach through the fluid, cantilever drag that is not accounted for will provide an additional repulsive component to the force, to the theoretical prediction for a free sphere. This drag should be dependent upon the area of the cantilever that is acted upon. The calculations are complex because the angle of deflection of the cantilever is non-uniform; however for our purposes it is sufficient to know that the area of the v-shaped cantilevers was greater than that of the beam cantilevers tested, and therefore the cantilever drag would increase apparent repulsive force in the v-shaped cantilever data. Instead, our data show a significantly lower repulsion.

1. C. D. F. Honig and W. A. Ducker, *Phys. Rev. Letts*, 2007, **98**, 028305.
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3. S. C. Clark, J. Y. Walz and W. A. Ducker, *Langmuir*, 2004, **20**, 7616-7622.
4. C. D. F. Honig and W. A. Ducker, *J. Phys. Chem. C*, 2008, **112**, 17324-17330.
5. V. S. J. Craig, C. Neto and D. R. M. Williams, *Phys. Rev. Letts*, 2001, **87**, 054504.