Electronic Supplementary Material (ESI) for Nanoscale.

Supporting Information for

Extending the Limits of Direct Force Measurements: Colloidal Probes from Sub-Micron Particles

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S.1 Silica Particle Dimensions

Monodisperse silica particles were purchased from MicroParticles GmbH (Berlin, Germany) in three different sizes. The nominal diameters, as specified by the manufacturer, are compared in Table S1-1 to the particle diameter determined by scanning electron microscopy (SEM). The values in Table S1-1 were obtained from the histograms shown in Figure 1 of the manuscript.

Table S1-1: Diameters of silica particles used in this study.

Material	Nominal diameter [a]	Average diameter [b]
SiO_x	4.28 ± 0.14 µm	4.07 ± 0.20 µm
SiO_x	977 ± 26 nm	983 ± 30 nm
SiO_x	500 ± 13 nm	496 ± 16 nm

[a] as provided by the manufacturer (MicroParticles, Berlin, Germany)

[b] as determined from SEM images

S.2 Summary of Diffuse Double Layer Properties used for Theoretical Calculations

The diffuse double layer potentials and the regulation parameters for the silica particles were determined by the 'classical' colloidal probe method in the sphere/sphere geometry. The fits according to the full-solutions of the Poisson-Boltzmann equation with the constant regulation approximation assume two identical surface chemistries.[1] Based on the data for the silica surfaces, the diffuse layer properties of glass surface have been determined by 'classical' colloidal probe versus a glass surface (sphere/plane geometry). The obtained values are compiled in Table S2-1. These data were used to calculate the theoretical interaction force profiles shown in Figure 6 in the manuscript.

Table S2-1: Compilation of the diffuse layer potential and the regulation parameter for silica colloidal and glass surfaces as determined by 'classical' colloidal probes

	Nominal ionic strength I	Diffuse layer potential Ψ^d	Regulation parameter p
silica	0.1 mM	-71.4 ± 8.1 mV	0.60 ± 0.23
	0.3 mM	-66.1 ± 2.5 mV	0.65 ± 0.16
	1.0 mM	-49.2 ± 3.0 mV	0.66 ± 0.20
glass	0.1 mM	-56.1 ± 3.4 mV	0.61 ± 0.25
	0.3 mM	-37.7 ± 2.3 mV	0.66 ± 0.16
	1.0 mM	-21.2 ± 3.3 mV	0.67 ± 0.15

S.3 Regulation parameter for silica and glass surfaces

The regulation parameter for silica and glass surfaces as a function of the ionic strength was determined at pH 10 from measurements with ‘classical’ colloidal probe technique. The values obtained from the fits are compiled in Table S2-1 and are plotted in Figure S3-1 against the fitted ionic strength. For comparison, the values reported by Pericet-Camara et al. were added, which were obtained from theoretical calculations assuming a 1-p*K* model for the surface chemistry of silica.[1]

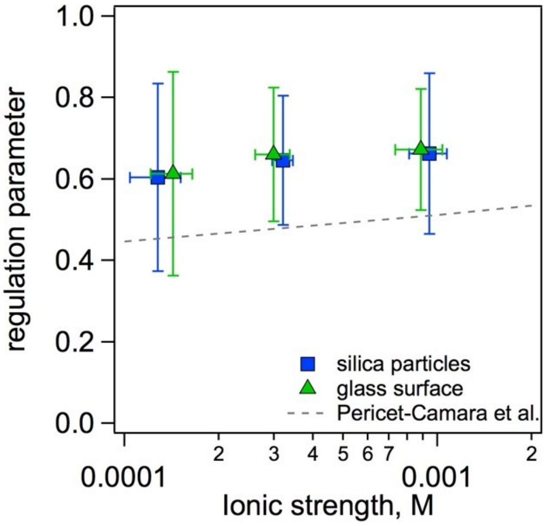
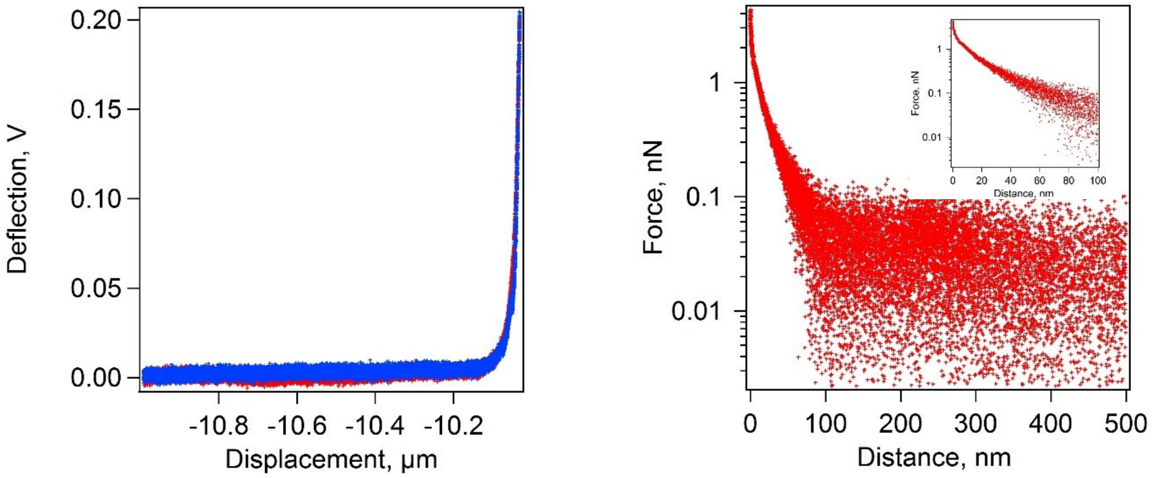


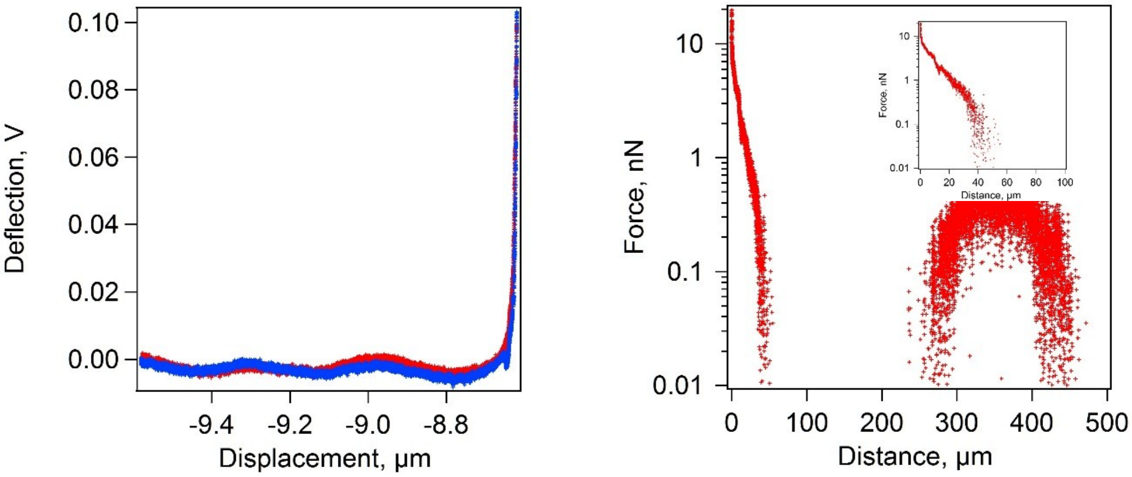
Figure S3-1: Determined regulation parameter as a function of the fitted total ionic strength for silica (blue squares) and glass surfaces (green triangles). The dashed line are the theoretical calculations by Pericet-Camara et al.[1]

S.4 Influence of Optical Interferences on the Force Profiles Acquired by FluidFM

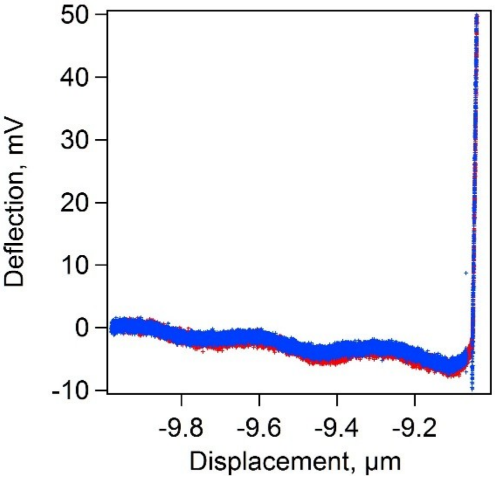
The following raw data demonstrate the influence of optical interferences at FluidFM-cantilever on the quality of converted interaction force profiles. All interaction force profiles were acquired under the same conditions ($I = 0.1$ mM and pH 10) but with different FluidFM-cantilevers. Two different types of FluidFM-cantilevers have been used termed as MicroPipettes (2 μm aperture) and NanoPipettes (300 nm aperture at apex of pyramidal tip).

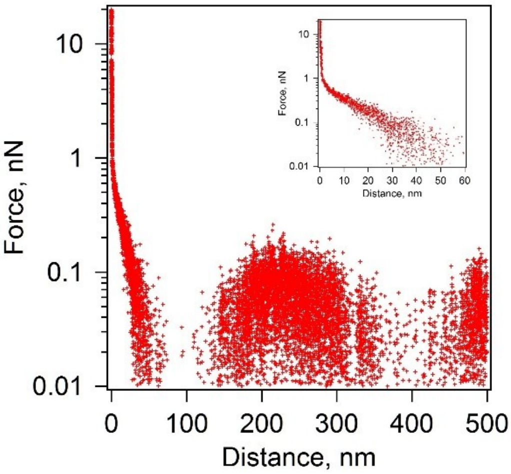


S.4.1 MicroPipette showing few interference fringes

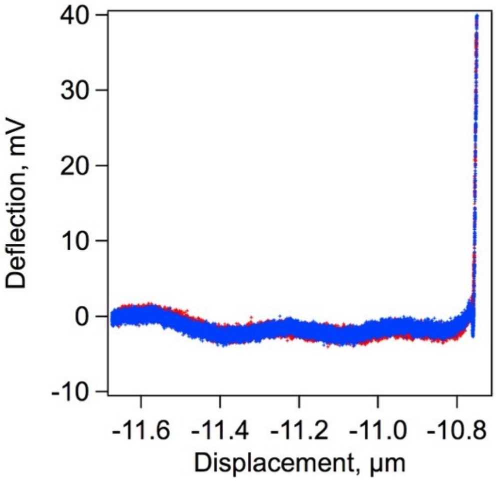


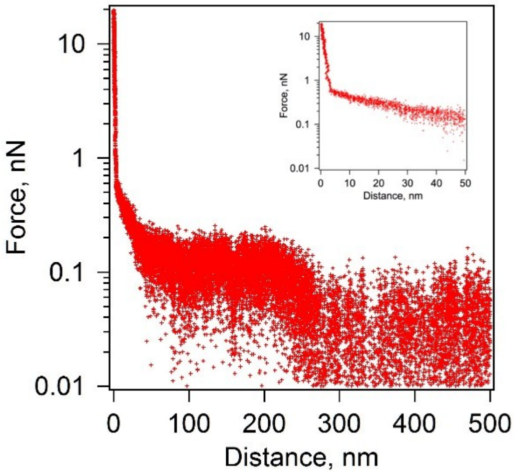
S.4.2 MicroPipette with pronounced interference fringes





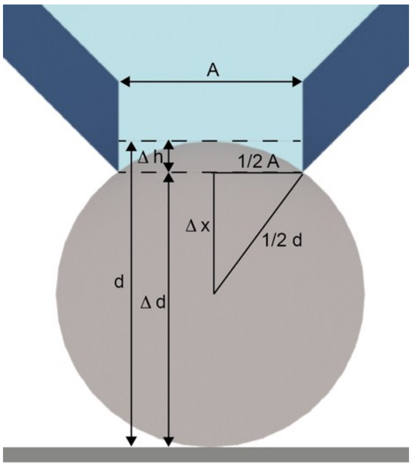
S.4.3 NanoPipette





S.5 Aspiration of Nanoparticles to the Aperture – Geometrical Effects

Upon aspiration of colloidal particles to the aperture of a FluidFM-cantilever, the total particle diameter is reduced by Δh. Hence, in the deflection vs. displacement data a shift of Δd is detected, with $d - \Delta h$. One finds by the theorem of Pythagoras:



$$\Delta h = d - \Delta d = ½\, d - \Delta x = ½\,(d - \sqrt{d^2 - A^2})$$

With the nominal values for the aperture diameter and particle diameter (A = 300 nm and d = 496 nm) one obtains $\Delta h \approx 50$ nm, which is approximately the double of the standard deviation found for the diameter of the smallest silica particles (*cf.* Table S1-1).

S.6 Real-time movie of direct force measurements using the FluidFM technology

The enclosed real-time movie illustrates the temporary aspiration of a single silica particle to the aperture of a FluidFM-cantilever and shows a single force versus distance cycle with this temporary colloidal probe against the glass surface (sphere/plane geometry).

References

(1) Pericet-Camara, R.; Papastavrou, G.; Behrens, S. H.; Borkovec, M. Interaction Between Charged Surfaces on the Poisson−Boltzmann Level: the Constant Regulation Approximation. *J. Phys. Chem. B* **2004**, *108*, 19467–19475.