Electronic Supplementary Material (ESI) for Nanoscale.

Supplementary Information

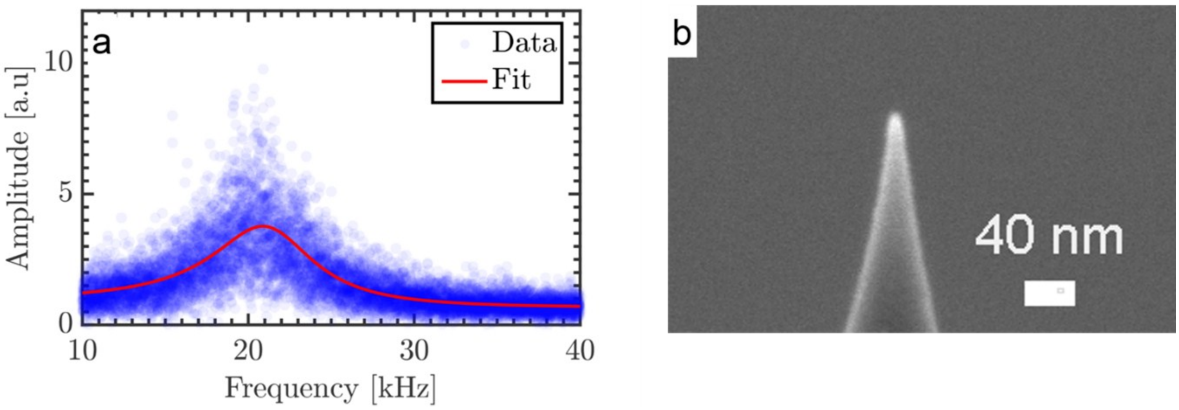
Impact of surface defects on the surface charge of gibbsite nanoparticles

Aram Klaassen, Fei Liu, Dirk van den Ende, Frieder Mugele and Igor Siretanu

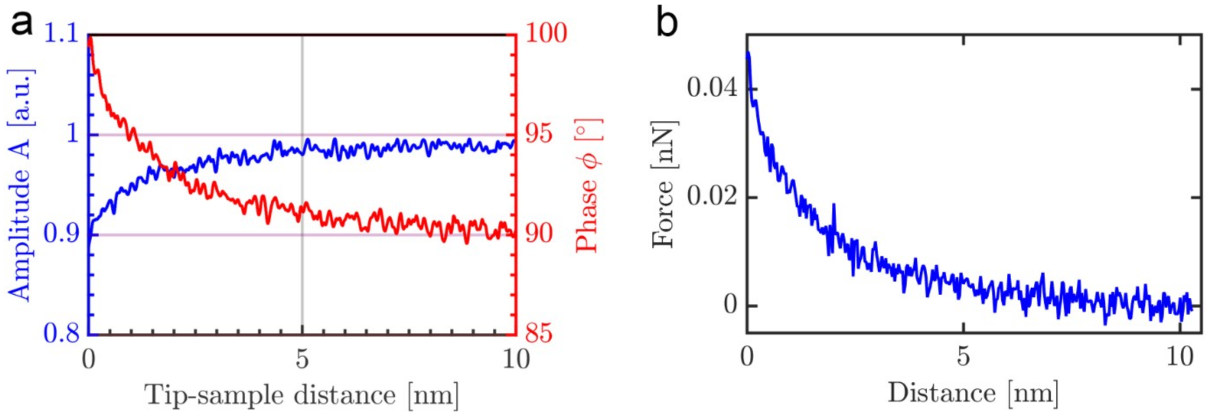
Physics of Complex Fluids Group and MESA+ Institute , Faculty of Science and Technology,

University of Twente, PO Box 217, 7500 AE Enschede, The Netherlands

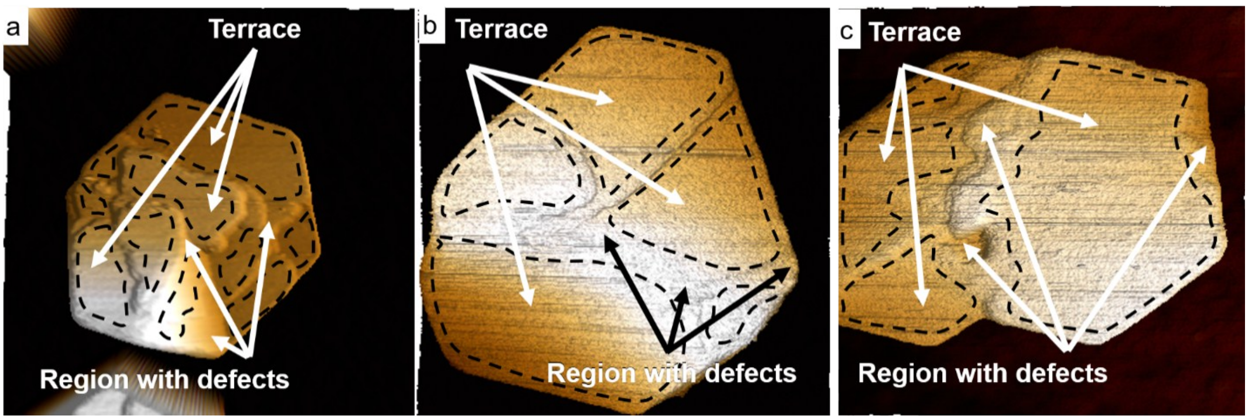
phone: ++ 31 (0)53 489 3089; fax: ++31 (0)53 489 1096; email: i.siretanu@utwente.nl



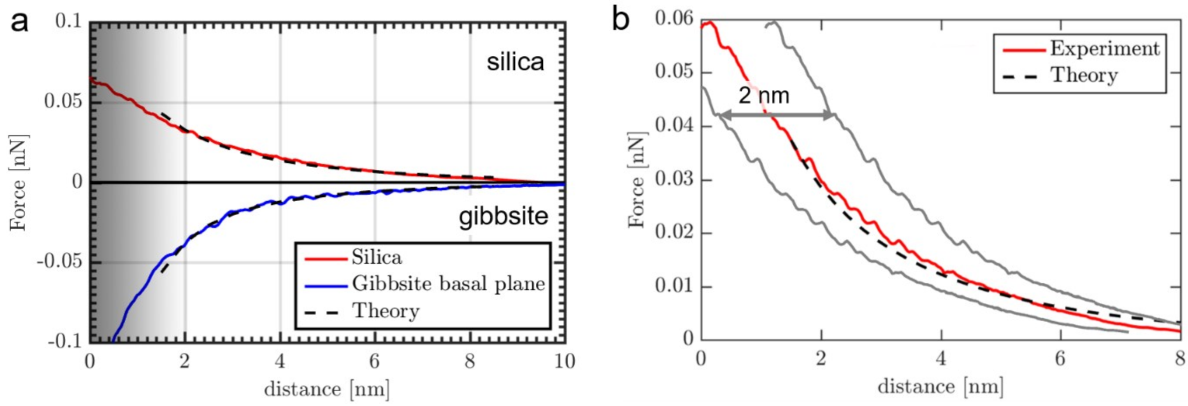
Supplementary Figure 1. (a) The power density spectrum of the cantilever as result of thermal fluctuations recorded in liquid at a distance where the tip-sample interaction is considered zero. In red the fit curve, from which the quality factor and resonant frequency are extracted. In this experiment Q = 2.8 and ω_∞ = 21.6 kHz. (b) Scanning electron microscope image of the cantilever after being used in the experiment. The tip radius is estimated to be around 5 nm.



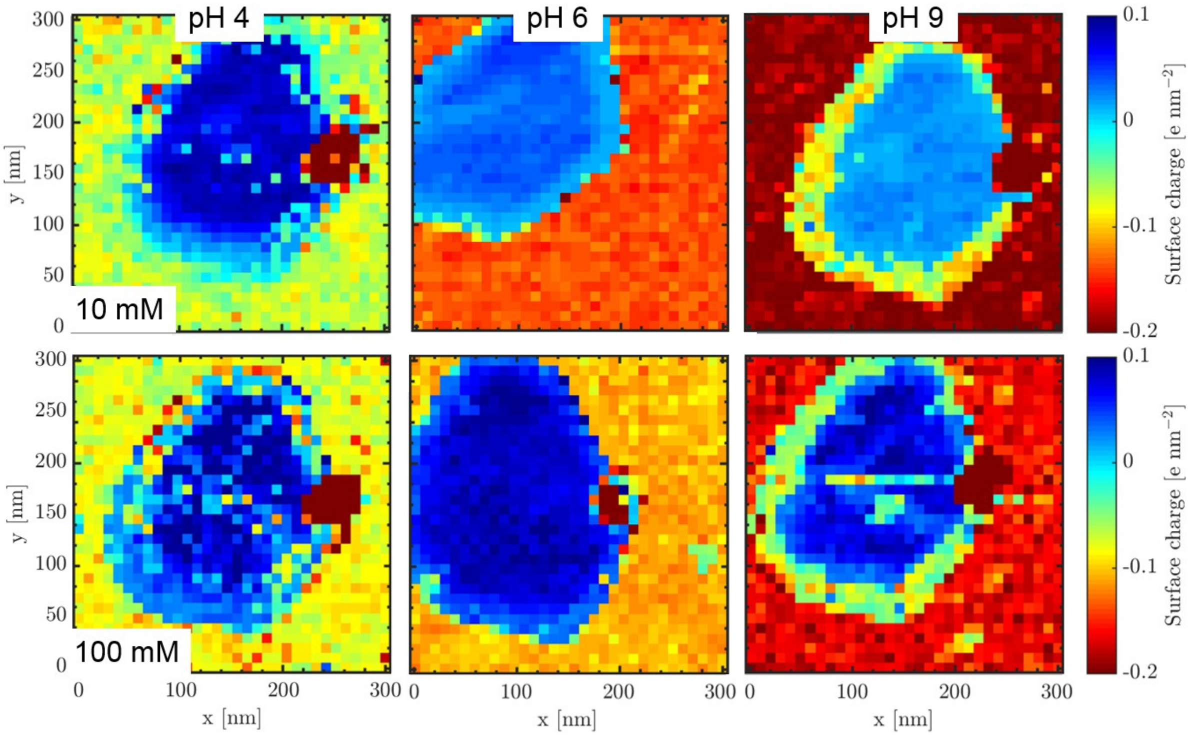
Supplementary Figure 2. (a) Amplitude and phase data recorded on silica in a 10 mM NaCl pH 6 solution during the force volume method. The amplitude is normalized to the amplitude at 20 nm from the surface A_∞. (b) Amplitude and phase are converted to the interaction force using equation 3. Experimental parameters in liquid: Mikromash NSC36/Au-BS, k_{int} = 0.64 N/m, ω_∞ = 21.6 Khz, Q = 2.8.



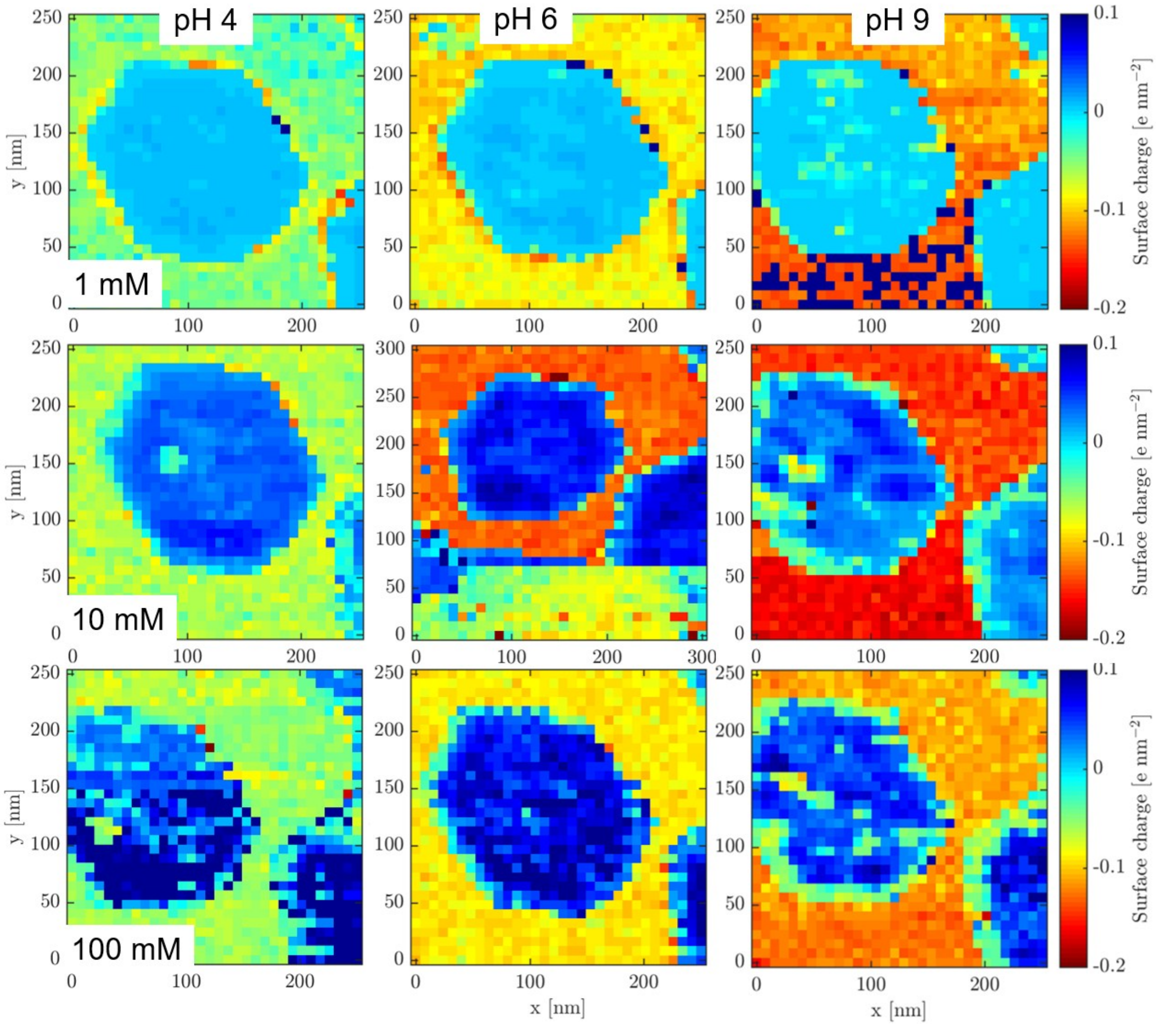
Supplementary Figure 3. Topographic images of single gibbsite particles on silica in 10 mM NaCl pH 6, showing the presence of smooth terraces and regions with defects. (a) Particle used in the charge maps found in Figure S6. (b) Particle used in the charge maps found in Figure S5.



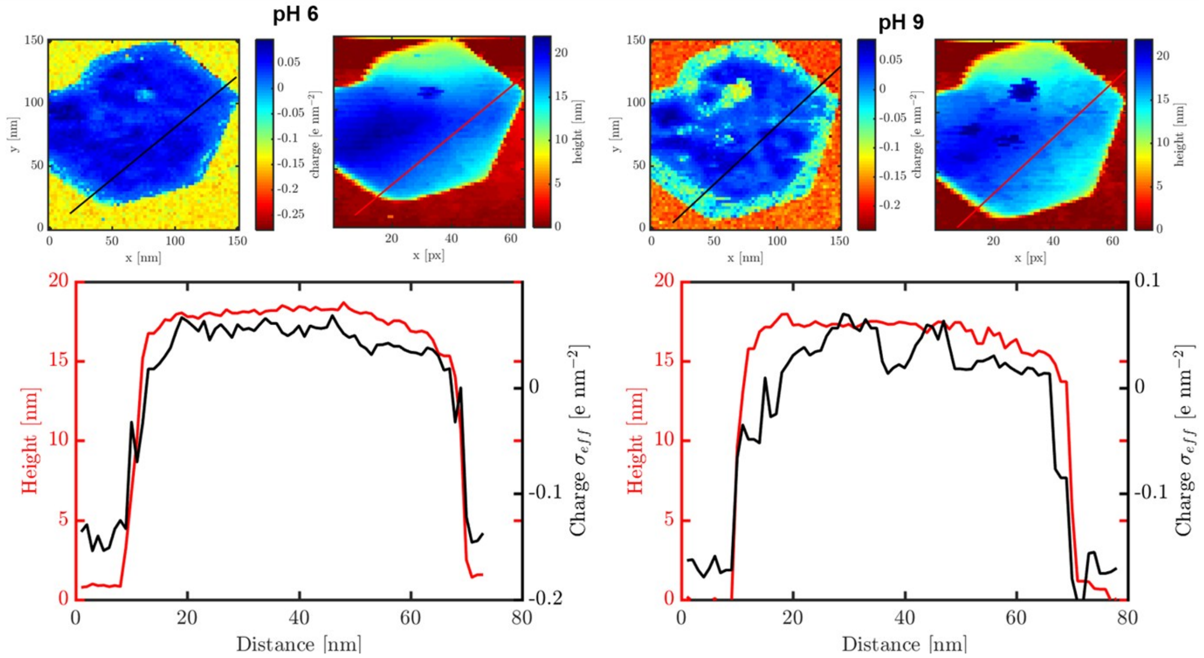
Supplementary Figure 4. (a) Plot of the electrostatic part of the tip sample interaction force on silica and gibbsite in a 10 mM NaCl pH 9 solution. The charge is calculated using DLVO theory with charge regulation boundary conditions. The charge and pK values resulting from this fitting for silica are $pK_H = 1.4$, $pK_C = 2.3$, $\sigma = -0.173$ e/nm^2 and gibbsite $pK_{H2} = 5.0$, $pK_A = 2.1$, $\sigma = 0.056$ e/nm^2 (b) Calculation of the effect of the uncertainty in zero on the surface charge. We fit the surface charge for 32 approaches while we shift each tip-sample distance by -0.5 and 0.5 nm (Figure S2b). We calculate the mean error for both shifts, which results in a 20% error in the average surface charge. (Tip parameters in liquid: $Q = 2.8$, $\omega_\infty = 21.6$ kHz, $\omega_d = 20.2$ kHz, $A_0 = 1.7$ nm, $k = 0.64$ N/m, $R \approx 5$ nm)



Supplementary Figure 5. Surface charge maps of a single gibbsite particle on silica (Figure S3b) in several solutions (10 and 100 mM NaCl at pH 4, 6 and 9). Red and blue are negative and positive charge respectively. With increasing pH, the negative charge on silica increases, , while the charge on gibbsite decreases. At pH 9, charge reversal is observed at the rim of the gibbsite particle. The pixel size is 9.4 nm/px. (Tip parameters in liquid: Q = 3.5, ω_∞ = 48.6 kHz, ω_d = 49.4 kHz, A_0 = 0.55 nm, k = 0.65 N/m, R ≈ 9 nm)



Supplementary Figure 6. Surface charge maps of a single gibbsite particle on silica (Figure S3a) in several solutions (1, 10 and 100 mM NaCl at pH 4, 6 and 9). Red and blue are negative and positive charge respectively. With increasing pH, silica gets more negatively charged, while gibbsite gets less positively charged. At pH 9, charge reversal is observed at the rim of the gibbsite particle. The pixel size is 7.8 nm/px. (Tip parameters in liquid: Q = 2.6, ω_∞ = 17.8 kHz, ω_d = 16.5 kHz, A_0 = 2.0 nm, k = 0.65 N/m, R ≈ 7 nm)



Supplementary Figure 7. Surface charge maps, topography and line sections at pH 6 and pH 9. At pH 6 and pH 9, the surface charge characteristics (in black) on gibbsite do not follow the surface roughness (in red). The pixel size is 2.3 nm/px. (Tip parameters in liquid: Q = 2.8, ω_d = 21.6 kHz, k = 0.64 N/m, R ≈ 5 nm)