Untangling superposed double layer and structural forces across confined nanoparticle suspensions

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Electronic Supplementary Information (ESI)

Potentiometric titration of nanoparticle suspensions Potentiometric titration of pure nanoparticle (NP) suspensions (initial volume = 10 mL) at three different volume concentrations of NPs was carried out upon addition of hydrochloric acid solution (HCl, Titrisol, Merck, Germany). The pH was measured using a pH-electrode (inoLab pH 720, VWR). The surface charge density σ of NPs in pure, aqueous dispersions can be calculated from the point of inflection x_0 in the titration curve ($0.159 \pm 0.002\,\mathrm{mmol\,g^{-1}}$), the density of silica NPs ρ and the mean diameter d of the NPs, assuming spherical particles.

$$\sigma = x_0 N_\mathrm{A} \rho \frac{d}{6} \tag{S1}$$

Equation S1 results in a surface charge density $\sigma = 0.50 \pm 0.01\,\mathrm{nm^{-2}} = 0.080 \pm 0.002\,\mathrm{C\,m^{-2}}$, irrespective of the NP concentration. This is in good agreement with literature values [1–3].

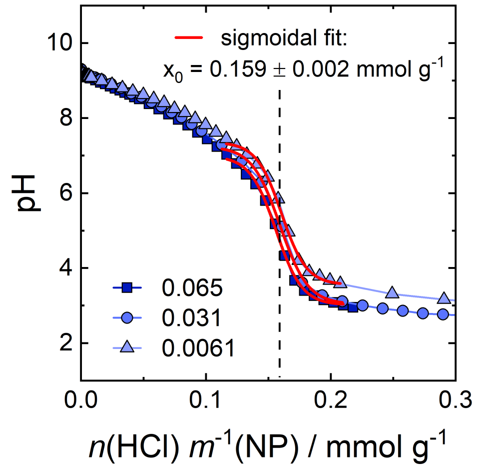

Figure S1: Potentiometric titration of pure NP suspensions (without added salt) upon addition of HCl for various volume fractions of NPs. The amount of added HCl is normalised by the total mass of NPs in the suspension. Sigmoidal fitting is used to extract the point of inflection x_0 with the mean value being displayed in the graph.

Interaction forces between charged surfaces in pure electrolyte solution Interaction forces of negatively charged silica surfaces in pure NaCl solutions were measured for reference.

Figure S2 shows the measured interaction force profiles in pure NaCl solutions. While (a-c) is in linear representation, (d-f) shows the same data in semilogarithmic representation, for emphasis of the double layer force. The blue dotted lines are the fit to the double layer force, with the effective surface potential ψ_{eff} being the only parameter to enter the fitting. Effective surface potentials ψ_{eff} are determined as - 70.0 ± 4.4 mV, - 44.9 ± 1.5 mV, and - 25.1 ± 0.9 mV in 0.1 mM, 1 mM, and 5 mM NaCl solutions, respectively. In figures S2 (a,d) also a black dotted line is shown, which represents the fit of the double layer force with the ionic strength I also as free fit parameter. Best fit result is obtained for an ionic strength I of 0.136 mM which shows the difficulty to work at such low ion concentrations, since *e.g.* adsorption of CO_2 may change the ionic strength to this amount.

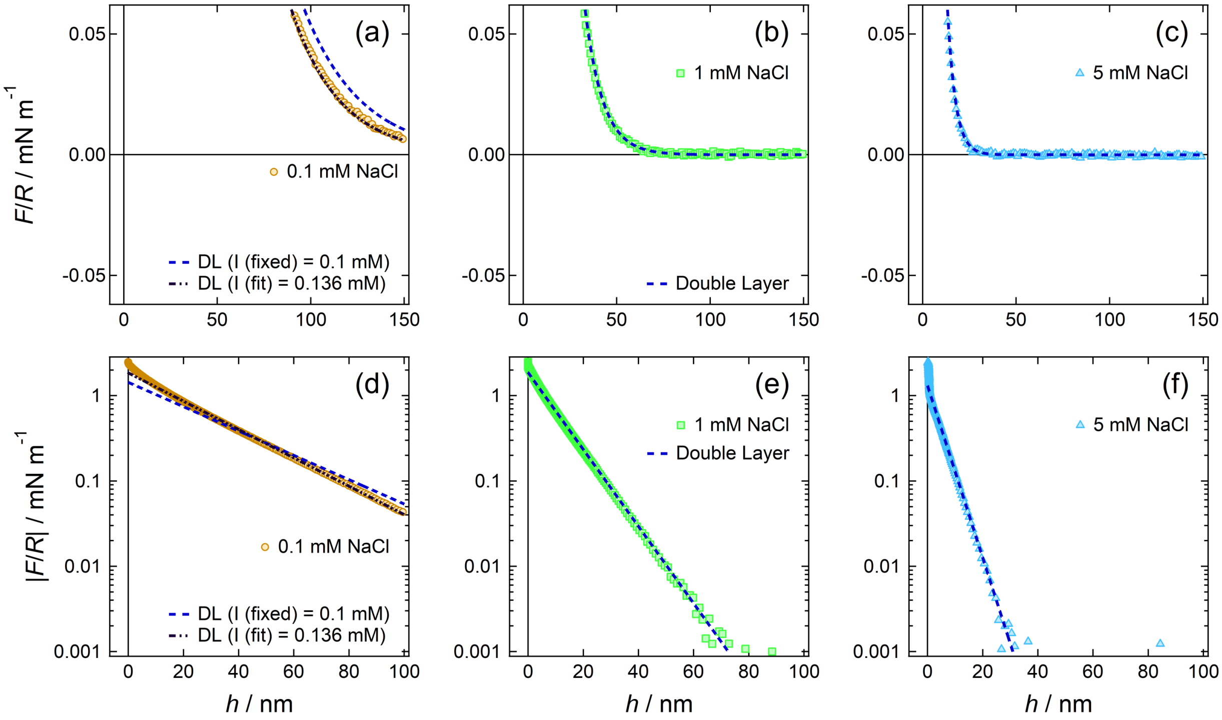

Figure S2: Interaction forces between silica surfaces in aqueous NaCl solutions. Experimental data (dots) is compared with the fitted double layer force (dashed line). (a-c): linear representation, (d-f): semilogarithmic representation for emphasis of the double layer force. For 0.1 mM NaCl (a,d) two different fits were performed with either the ionic strength I being fixed or entering as free fit parameter of the double layer force.

References

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