Supplementary Information

Effect of particle size and Debye length on order parameters of colloidal silica suspensions under confinement

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We calculated the Debye length with formula $\kappa=(e^2/\varepsilon_0\varepsilon k_B T)^{1/2}(Z\rho+2I_{salt}N_A)^{1/2}$ as we described in the section of Theoretical Modelings. This equation is also the one we used in the theoretical modelings to set the Debye length of the systems. In this equation, we include the contribution of nanoparticle's dissociation. In the case of no additional salt (salt free), the counterions of the solution is dissociated solely from the colloidal particles and charge neutrality between counterions and colloidal particles is assumed, the valency of the counterions is assumed as 1(univalent). Thus $\rho_c=Z\rho$. The valency of the colloids, Z, is determined from Grahame equation with known value of measured zeta potential.

In the meantime, we also measured the conductivity of the nanoparticle suspension. The conductivity of Ludox suspensions at varying particle concentrations (weight percentage) is shown in Table 1. In Table 1, one can also find the Debye length κ^{-1} obtained from conductivity measurement and from eqn of $\kappa=(e^2/\varepsilon_0\varepsilon k_B T)^{1/2}(Z\rho+2I_{salt}N_A)^{1/2}$ which we used in the manuscript. The Debye lengths estimated from conductivity measurement are very similar to our calculated ones used in the manuscript.

To convert conductivity to ionic strength, an accurate prefactor is needed. Instead of using a simple Russell prefactor, $1.6 *10^{-5}$, which is valid for simple electrolytes, we determined the prefactor for our system individually.

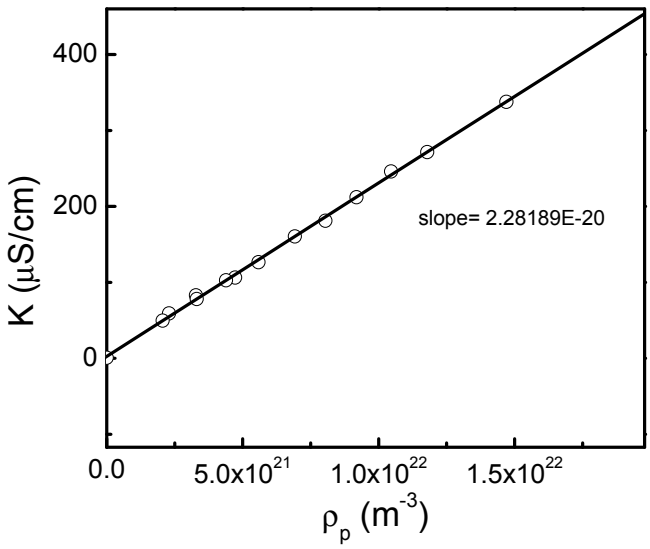
The conductivity is known to be proportional to the number density of ions, $K=\alpha*\rho_c+\beta*\rho_p$, where α and β are the conductivity factor of counterions and colloidal particles, respectively. (Note in real system, β is very small compare to α due to the larger size thus the smaller mobility.)

We assume the counterions in a salt-free colloidal suspension are dissociated by the charged colloidal particles, and the charge neutrality between counterions and colloidal particles requires, $z_c\rho_c=|Z|\rho_p$, where z_c is the valency of counterions (generally univalent counterions is assumed, $z_c=1$), ρ_p is the particle number density, and $|Z|$ is the valency of the colloidal particle which estimated from the Grahama equation for the surface charge density. For 26 nm sized particle, $|Z|=35$.

Thus the above equation can be written as

$K= \alpha*|Z|*\rho_p+ \beta*\rho_p = \gamma*\rho_p$

We plot of K versus ρ_p and find the factor γ being $2.282*10^{-20}$.



At meanwhile, ionic strength of salt-free colloidal suspensions is defined as

$2IN_A=(z_c)^2*\rho_c$

where N_A is Avogadro's constant. Due to the charge neutrality of the system, $2IN_A=|Z|*\rho_p$

Thus we build a relation between the measured conductivity and ionic strength of the samples.

$I=|Z|/(2N_A* \gamma)* K$

This equation yields a prefactor $1.27* 10^{-6}$ to convert conductivity K in the unit of μS/cm to ionic strength I in the unit of mol/l, for 26 nm sized silica nanoparticle suspensions.

Table 1: Experimental results of conductivity K at varying particle concentration, the corresponding ionic strength and Debye length, and the previous calculated Debye length from equation of $\kappa=(e^2/\varepsilon_0\varepsilon k_B T)^{1/2}(Z\rho+2I_{salt}N_A)^{1/2}$, and the ratio of Debye lengths from two methods.

Conc.(wt%)	Cond.(μS/cm)	I (mol/l)	Mea. κ_1^{-1}(m)	Calc. κ_2^{-1}(m)	$\kappa_2^{-1}/\kappa_1^{-1}$
3.87	58.8	7.4676E-5	3.51944E-8	3.72511E-8	1.05844
5.54	82.8	1.05156E-4	2.96583E-8	3.11344E-8	1.04977
7.97	106.1	1.34747E-4	2.62002E-8	2.59577E-8	0.99074
9.42	126.5	1.60655E-4	2.39948E-8	2.38764E-8	0.99507
13.57	181	2.2987E-4	2.00596E-8	1.98932E-8	0.99171
17.65	246	3.1242E-4	1.72066E-8	1.74431E-8	1.01374
3.47	49.3	6.26872E-5	3.84126E-8	3.93396E-8	1.02413
5.58	77.9	9.8933E-5	3.05769E-8	3.10226E-8	1.01458
7.41	102.6	1.30366E-4	2.66368E-8	2.69207E-8	1.01066
11.67	160.2	2.0353E-4	2.13181E-8	2.14516E-8	1.00626
15.50	212.1	2.69316E-4	1.85324E-8	1.86135E-8	1.00438
19.90	271.6	3.44894E-4	1.63765E-8	1.64274E-8	1.00311
24.80	337.8	4.2907E-4	1.46825E-8	1.47153E-8	1.00223