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Supporting information for"Experimental evaluation of additional short ranged repulsion in structural oscillation forces"

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In the present paper we analyzed the additional repulsion, that has been observed in the structural oscillation forces of silica nanoparticle suspensions [REF]. It has been proposed by other groups that the additional repulsion is linked to the diffusive double layer forces [REF]. A comparison between the additional decay length ξ_2 and the Debye length κ^{-1} for silica nanoparticle suspension of different concentrations seems to support this notion. On the other hand, the increase of the additional repulsive energy $E_{rep} = B \cdot \xi_2$ with increasing suspension concentration conflicts with it. As an alternative source for the additional repulsion the contribution of the hydrodynamic drag forces in normal direction to the colloidal probe has been investigated. The formulas for calculating the hydrodynamic drag as well as the conditions for the approximations used are presented in the following[1].

A force F acting on a spherical particle in a fluid will lead to a steady state velocity v of:

$$v = \mu \cdot F \tag{1}$$

With μ being the hydrodynamic mobility. In the steady state the force F is balanced by the hydrodynamic force F_{hydro} with:

$$F = -F_{hydro} \tag{2}$$

The hydrodynamic mobility for a spherical particle under creeping flow conditions (Reynolds number Re « 1) is given by the Stokes-Einstein equation:

$$\mu = \frac{1}{6\pi\eta R} \tag{3}$$

R confers to the Radius of the moving particle, in our case the colloidal probe (R = $3.35 \cdot 10^6$ m) and η to viscosity of the fluid.

The Stokes-Einstein equation is valid for a particle in an infinite fluid. When the particle is close to a wall, as in our case, the hydrodynamic interactions between wall and particle must be considered. Correction factors for the mobility have been developed by Brenner *et al.*[2,3] for both cases of motion direction, namely parallel and normal to the confining wall. For a particle approaching a wall in normal direction the mobility is given as:

$$\mu_\perp = \frac{1}{6\pi\eta R\lambda_\perp} \tag{4}$$

In case of small separations (x<R) the correction factor $\lambda_\perp$ can be approximated according to Cox and Brenner[4] to:

$$\lambda_\perp = \frac{R}{x} - 0.21ln\left(\frac{x}{R}\right) + 0.97 \tag{5}$$

Combination of equations 1, 2 and 4 gives the hydrodynamic force acting on a particle moving in normal direction to a confining wall in a fluid.

$$F_{hydro,\perp} = \frac{v}{\mu_\perp} = -6\pi\eta R\lambda_\perp v \tag{6}$$

Concerning our presumption of creeping flow conditions (Re«1), the Reynolds number can be calculated as follows:

$$Re = \frac{2Rv\rho}{\eta} \tag{7}$$

Here ρ is the density of the fluid. The density of the silica nanoparticle suspension was calculated according to:

$$\rho\,(x\,wt\%) = \frac{1}{\frac{x}{100\cdot\rho_{SiO_2}} + \frac{100-x}{100\cdot\rho_{H_2O}}} \tag{8}$$

With ρ_{SiO_2} = 2650 kg/m^3 and ρ_{H_2O} = 997 kg/m^3 we get a value of $\rho_{10wt\%}$ = 1063 kg/m^3 for the 10 $wt\%$ silica nanoparticle suspension used in our speed dependent experiments. Comparision between the calculated value for the density and actual measurements of different samples of 10 $wt\%$ silica nanoparticle

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suspensions shows a maximum deviation of 0.6%. Further calculations containing the density of the suspension have therefore been performed with the calculated values. The viscosity of the silica nanoparticle suspension was obtained by measuring the kinetic viscosity at different concentrations and multiplcation with the density of the silica nanoparticle suspension. The results were plotted, and a linear fit was applied see **Fig.** 1. The results from the fit were then used to calculate the value of the dynamic viscosity accordingly ($\eta(\rho_{10wt\%}) = 3.54 \cdot 10^{-3} Pa \cdot s$).

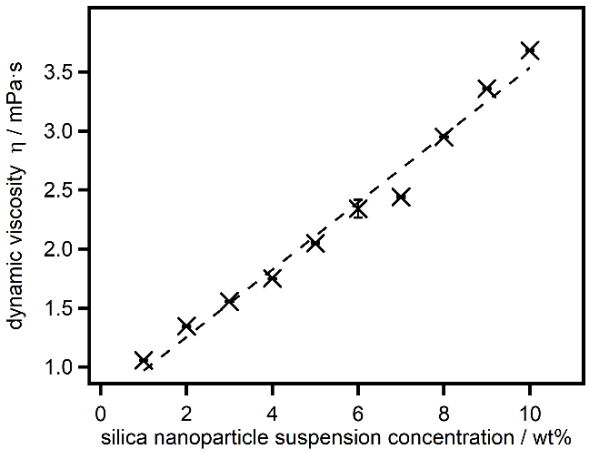

Fig. 1 : Dynamic viscosity of silica nanoparticle suspensions (x) at different concentrations. Errors are small vs symbol size.

With the values known, for viscosity and density of the 10 *wt%* silica nanoparticle suspension, we can now calculate the Reynolds number. The highest approach speed used during the experiment was $v = 4 \cdot 10^{-7}$ *m/s* while the radius of the colloidal probe was $R = 3.35 \cdot 10^{-6}$ *m*, this gives a Reynolds number according to equation 7 of $Re = 8.05 \cdot 10^{-7}$ which is indeed small compared to one. Concerning the second assumption of small separations x<R, forces were measured in the range from 0 to 1000 μm separation. Structural oscillation forces occurred below 0.4 μm and the additional repulsion declined to zero at approxamatley 0.2 μm. This is indeed small compared to the radius of the colloidal probe R=3.35 μm, allowing the use of the approximation for $\lambda_{\perp}$.

Equation 6 has been used to calculate the hydrodynamic forces F_{hydro} acting on the colloidal probe at different approach speeds in normal direction to the substrate.

Fig. 2 displays two sets of hydrodynamic forces. The dashed lines show the results as obtained with equation 6, while the solid lines have been background corrected. The correction is necessary as the hydrodynamic drag force after a fast decline at small separations levels off and does not decline to zero. Especially in case of the higher approach speeds – 200 and 400 *nm/s* – a significant contribution of approximately 1 *pN* remains. In contrast to that, the force profiles of the structural oscillation forces, have been adjusted for zero force at large separations during the initial analysis of the deflection and z senor signals as obtained from the AFM. Therefore, the background correction for the hydrodynamic forces is needed, to calculate the contribution to the structural oscillation forces. The background has been determined in the range from 600-1000 *nm* separation with a linear fit. The inset

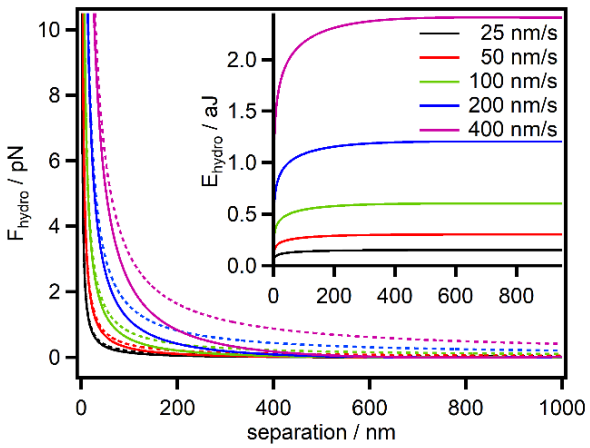

Fig. 2 : Hydrodynamic drag force and energy (inset) over separation for a colloidal probe of 6.7 μm diameter approaching a confining wall in a silica nanoparticle suspension of 10 *wt%*, at different speeds. Dashed lines show the forces as calculated with equation 6, solid lines have been background corrected

shows the hydrodynamic drag energy E_{hydro} as obtained from integration of the background substracted hydrodynamic force. The hydrodynamic drag energy as displayed in Figure 4 of the main paper is the value of the curve shown here at separation x in the range of 160-250 *nm* depending on the approach speed and the corresponding additional decay length ξ_2.

$$x = -\xi_2 \cdot ln(0.001) \tag{9}$$

We did not simply choose the maximum of the hydrodynamic drag energy, as it is only reached at large separations especially in case of the higher approach speeds of 200 and 400 *nm/s*. We explicitly wanted to compare the contribution of E_{hydro} to the additional repulsive energy $E_{rep} = B \cdot \xi_2$, as obtained from the second term in the extended fit equation. Therefore, the value of x was chosen to match a separation where this second term $B \cdot e^{-\frac{x}{\xi_2}}$ declined to 0.1 %.

Notes and references

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