

Surviving Structure in Colloidal Suspensions Squeezed from 3D to 2D

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Combining colloidal-probe experiments and computer simulations, we analyze the solvation forces F of charged silica colloids confined in films of various thicknesses h . We show that the oscillations characterizing $F(h)$, for sufficiently large h , are determined by the dominant wavelength of the *bulk* radial distribution function. As a consequence, both quantities display the same power-law density dependence. This is the first direct evidence, in a system treatable both by experiment and by simulation, that the structural wavelength in bulk and confinement coincide, in agreement with predictions from density functional theory. Moreover, theoretical and experimental data are in excellent quantitative agreement.

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One of the most prominent effects of confining surfaces on the behavior of an adjacent fluid consists in the *layer formation* of the particles, indicating that the translational symmetry of the bulk fluid is broken in at least one spatial direction (slit-pore geometry) [1,2]. Layering can induce freezing transitions [3,4], it can support orientational ordering [5], and it affects the flow behavior and dissipation of fluids in nanopores [6,7]. An additional effect attracting increasing interest occurs when the confined fluid acts as a solvent (“depletion agent”) of large colloidal particles: Here, layering of the solvent particles induces *oscillations* in the resulting depletion interactions [8] and in the closely related solvation forces [9] between two planar surfaces. Understanding these interactions and the behavior of the underlying confined solvent is essential in colloid science (e.g., to ensure stability against flocculation, and to control colloidal crystallization for optical devices), in biological contexts (e.g., protein crystallization, stacking of red blood cells), and, generally, for the design of novel materials and devices for micro- and nanofluidics. Indeed, there exist now several techniques allowing precise measurements of colloidal interactions such as the surface force apparatus [9], total internal reflection microscopy [8], optical tweezers [10], thin film pressure balance [11,12], and the colloidal-probe (CP) technique [13]. It turns out that oscillations in the effective interactions are a rather generic feature except at very low solvent concentration. However, a precise understanding of the characteristics, that is the period(s) and decay length of the oscillations in relation to corresponding *bulk* properties of the solvent, is still missing [14,15].

On the other hand, density functional theory (DFT) for inhomogeneous liquids [16,17] clearly demonstrates that some structural features persist when the bulk fluid is squeezed from three towards two dimensions. More precisely, the density profile in the inhomogeneous fluid, $\rho(\mathbf{r})$, which is the prime indicator of layering effects, decays asymptotically with the same decay length and [for density

beyond the so-called Fisher-Widom (FW) line [18,19]] the same oscillatory wavelength as does the bulk radial distribution function, $g_b(r)$, at the same chemical potential and temperature. According to DFT, these features of $\rho(\mathbf{r})$ also determine the asymptotic behavior of depletion and solvation forces [20,21].

In the present Letter we investigate, combining experimental and theoretical techniques, the validity of the DFT predictions in a real colloidal fluid, focusing on the dominant wavelength in bulk and confinement. Our model system is a colloidal suspension of charged silica nanoparticles (LUDOX TMA-34) with a diameter $\sigma \approx 26 \pm 2$ nm [as determined by Cryo-TEM, atomic force microscope (AFM) and small-angle neutron scattering (SANS)] and a charge $Z \approx 35$ determined by electrophoretic mobility measurements. Using the CP-AFM technique [13], we measure the force between a large silica sphere (radius $R = 3.35 \mu\text{m}$) immersed into the colloidal solution and an adjacent flat substrate (silicon wafer). The spring constant of the AFM cantilever is 0.03 N/m. Since $R \gg \sigma/2$ the two surfaces can be considered planar [22], yielding a *slitlike* geometry characterized solely by the film thickness h (Derjaguin limit). The normalized force $F/2\pi R$ then becomes a function of h alone.

Theoretically, we model the suspension on an effective level via the electrostatic part of the Derjaguin-Landau-Verwey-Overbeek (DLVO) potential [23] involving only the negatively charged silica macroions. The resulting interaction reads $u(r) = \tilde{Z}^2 e_0^2 \exp(-\kappa r)/4\pi\epsilon_0\epsilon r$ where e_0 is the elementary charge, ϵ_0 and ϵ are the permeability of vacuum and the solvent dielectric constant, respectively, and $\tilde{Z} = Z \exp(\kappa\sigma/2)/(1 + \kappa\sigma/2)$ is an effective valency involving the inverse Debye screening length $\kappa = (e_0^2/\epsilon_0\epsilon k_B T)^{1/2} (Z\rho + 2IN_A)^{1/2}$ (with ρ being the particle number density). The ionic strength of the added salt is set to $I = 10^{-5}$ mol/l corresponding to the experimental system. In addition to the DLVO potential, the particles interact (for numerical reasons) via a soft-sphere repulsion,

which strength, however, is negligible against the DLVO repulsion (of about $50k_B T$) at typical interparticle distances. Also, we have checked that attractive van der Waals interactions do not influence the quantities considered. Indeed, the resulting model correctly describes (as compared to experiment) [24] structural features not only in the bulk but, more interestingly, also in slitlike confinement. The latter is modeled by two plane parallel, smooth, uncharged surfaces separated by a distance h along the z direction and of infinite extent in the x - y plane. The fluid-wall potential $u_{fw}(z)$ is chosen to be purely repulsive and decays as z^{-9} . This simple choice is motivated by the fact that, according to DFT arguments [17], the precise shape of $u_{fw}(z)$ should influence only the fluid's behavior close to the wall but not the *asymptotic* decay of $\rho(z)$ and related quantities.

To study the bulk structure of our model, we have numerically solved integral equations for $g_b(r)$ consisting of the exact Ornstein-Zernike equation combined with the approximate hypernetted chain (HNC) closure [25]. The latter is known to yield reliable results for Yukawa-like interactions with not too high interaction strengths [26]. As a test we have additionally performed canonical Monte Carlo (MC) simulations. Within the HNC, the dominant wavelength and decay length of the function $h_b(r) = g_b(r) - 1$ [with $h_b(r)$ being the total correlation function] can be determined via an analysis of the (complex) poles $q = \pm q_1 + iq_0$ of the function $1 - \rho \tilde{c}_b(q) = (S_b(q))^{-1}$, with $S_b(q) = 1 + \rho \tilde{h}_b(q)$ being the structure factor [16]. It follows that $rh_b(r) = (2\pi)^{-1} \sum_n R_n \times \exp(iq_n r)$ where R_n is the residuum of $q \tilde{h}(q)$ related to pole q_n . The pole with the smallest imaginary part determines the slowest exponential decay and thus the *asymptotic* behavior of $h_b(r)$, i.e., $rh_b(r) \rightarrow A_b \exp(-q_0 r) \times \cos(q_1 r - \theta_b)$, $r \rightarrow \infty$, with q_0 playing the role of an inverse correlation length (i.e., $q_0 = \xi^{-1}$) and $q_1 = 2\pi/\lambda_b$ determines the wavelength λ_b of the oscillations (at the state points considered all poles have both a real and an imaginary part, in agreement with earlier findings for Yukawa-like systems [26]). In addition, we have determined q_0 and q_1 from MC data by plotting the function $\ln(r|h_b(r)|)$. Wavelength and correlation length then follow from the oscillations and the slope of the straight line connecting the maxima at large r . Our HNC and MC results for λ_b as a function of the volume fraction $\phi = \pi\rho\sigma^3/6$ are given in the main part of Fig. 1, showing that the two approaches are in good agreement. This is consistent with the observations reported in [26] and justifies the use of HNC in the bulk system. Also, more importantly, λ_b strongly depends on the density and can thus be very different from the particle diameter, $\sigma = 26$ nm. More precisely, our theoretical data can be fitted according to the power law $\lambda_b = a\phi^{-b}$ with $b^{\text{MC}} \approx 0.36$, $b^{\text{HNC}} \approx 0.39$.

From the experimental side, it is difficult to determine directly the quantity λ_b related to the real-space distribu-

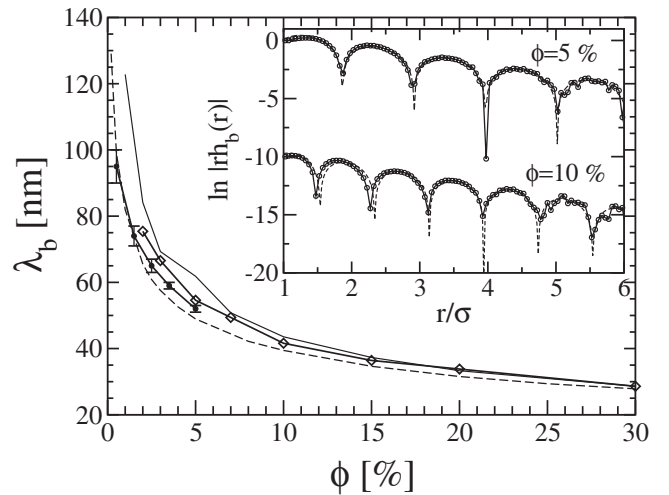


FIG. 1. Dominant wavelength λ_b characterizing $h_b(r) = g_b(r) - 1$ as a function of the volume fraction according to HNC (solid line) and MC (diamonds). Also shown are the HNC data for λ_s (dashed line) and the corresponding SANS data (filled circles, with error bars). The inset shows two MC results for the function $\ln(r|h_b(r)|)$ (circles). The asymptotic fit functions are plotted as dashed lines.

tion function $h_b(r) = g_b(r) - 1$. Instead, we have measured (using SANS) the position of the main peak of $S(q)$ [24], q_{max} , which may be related to a wavelength $\lambda_s = 2\pi/q_{\text{max}}$. Experimental details are given in [24]. The structure factor $S(q)$ is the Fourier transform of the *full* function $h_b(r)$ involving all poles. Thus, λ_s may be considered as a wavelength averaged over all particle separations, which does not need to coincide with λ_b . The latter determines the asymptotic behavior via the leading pole. Still, one expects these two wavelengths to be very close to each other. This is confirmed by our HNC results for λ_s , which conform well with the MC/HNC data for λ_b and also with the experimental data for λ_s [24] (see Fig. 1). Thus, we consider the experimental data for λ_s as an approximation of the true wavelength λ_b characterizing $g_b(r)$ in the real (bulk) system.

We now investigate to which extent the bulk length λ_b persists in the presence of confinement. DFT [16,17] predicts that, for sufficiently large h allowing a bulklike region in the middle of the pore, the microscopic density profile should decay as $\rho(z) - \rho_b \rightarrow A_\rho \exp(-q_0 z) \cos(q_1 z - \theta_\rho)$, where q_0 and q_1 are *exactly* the same as in the bulk system at equal chemical potential (with bulk density ρ_b), whereas the amplitude A_ρ and phase θ_ρ depend on the nature of fluid-wall interactions. The same asymptotic behavior is expected for the so-called normal (solvation) pressure, $f(h) = P_{zz}(h) - P_{\text{bulk}}$, integration of which then gives $F(h)$ (assuming validity of the Derjaguin approximation [22]).

To test these predictions within our DLVO model, we have calculated, for various packing fractions, the function

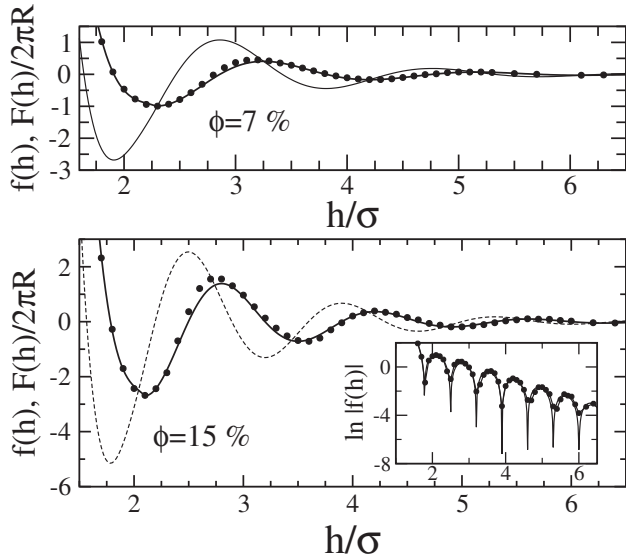


FIG. 2. Two examples of the solvation pressure $f(h)$ as obtained by GCMC (filled circles) together with the asymptotic fits (solid line) obtained with the bulk values of $q_1 = 2\pi/\lambda_b$ and q_0 . Included are the resulting structural forces $F(h)/2\pi R$ (dashed line). The inset shows a logarithmic plot of $f(h)$.

$f(h)$ via grand canonical (GC) MC simulations; see Fig. 2 for two representative examples. In the whole density range considered the oscillatory asymptotic decay of our $f(h)$ (determined by a wavelength λ_f), is indeed very well described by the leading *bulk* wavelength (and correlation length), implying $\lambda_f = \lambda_b$. This is particularly clearly demonstrated by the logarithmic representation in the inset of Fig. 2. Thus, our GCMC simulation results for the charged silica particles confirm the DFT predictions. Moreover, the asymptotic expression is found to provide a good approximation of the oscillations already at remarkably small wall separations. Indeed, the full curve is well described by the asymptotic formula already after the first minimum at $h = h_{\min}$, combined with a cubic polynomial fit for $h \leq h_{\min}$. Then, having found an accurate fit formula for $f(h)$, one may immediately integrate [20] to obtain the solvation force $F(h)/2\pi R$, results for which are included in Fig. 2.

Experimental results for $F(h)$ from CP-AFM measurements are shown in Fig. 3. For all but the highest concentration considered, the data may well be fitted by an exponentially damped oscillation with wavelength λ_f . Moreover, the data clearly show that λ_f decreases and the oscillations become more pronounced with increasing particle concentration (the corresponding behavior of the decay length is less clear due to significant statistical errors). At the highest concentration one observes a deviation from the fit function for very small wall separations (of about 1σ – 2σ), indicating a different spatial distribution in ultrathin films. We also note that, irrespective of the concentration considered, the amplitudes and phases charac-

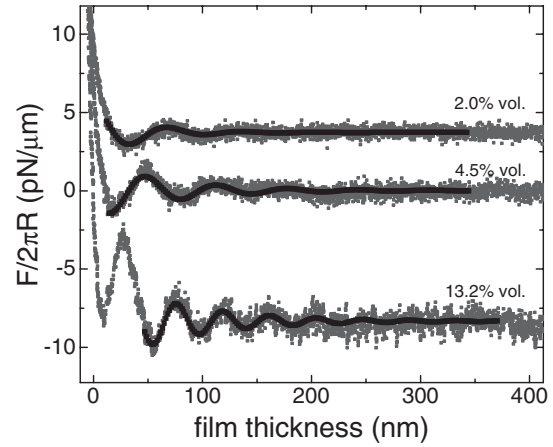


FIG. 3. Experimental curves for $F(h)$ obtained by CP-AFM for three different particle concentrations (the data have been vertically offset for ease of viewing). The curves are fitted according to the formula $F/2\pi R = A \exp(-h/\xi_f) \cos(2\pi h/\lambda_f + \theta_f) + \text{offset}$.

terizing the experimental data are different from those of the theoretical functions $F(h)$ illustrated in Fig. 2. This is expected in view of the simplified fluid-wall potential $u_{\text{fw}}(z)$ used in the theoretical calculations. In the present Letter we rather focus on the wavelength λ_f of the oscillations, which should be independent of u_{fw} [17].

Our experimental results for λ_f as a function of the particle volume fraction are plotted in Fig. 4. Also shown are the theoretical (MC) data for λ_f (which, as demonstrated in Fig. 2, equals the bulk wavelength λ_b plotted in Fig. 1), and the experimental (SANS) data for the bulk wavelength λ_s deduced from the structure factor. Clearly, there is very good agreement between the experimental data for λ_f and λ_s . Therefore, and since we may consider

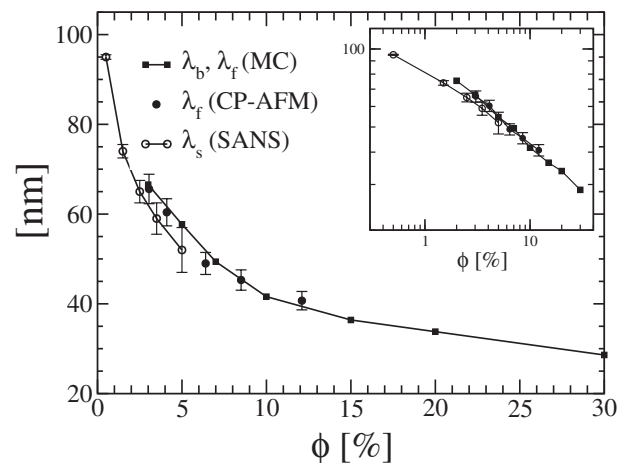


FIG. 4. Comparison of the various wavelengths from theory and experiment in bulk and confinement. Not included are the theoretical results for λ_s since these are very similar to the SANS data (see Fig. 1). The inset shows the same data on a logarithmic scale.

λ_s (i.e., the *average* bulk wavelength) as a very accurate approximation for the wavelength λ_b determining the *asymptotic* oscillations in $g_b(r)$, our experimental results are completely consistent with DFT predicting $\lambda_f = \lambda_b$. Moreover, we see from Fig. 4 that there is excellent agreement between experimental and theoretical data for λ_f . This is a strong (yet indirect) evidence that the actual shape of the fluid-wall interactions (which is too simplified in our theoretical model) is *irrelevant* for the asymptotic decay of surface forces, which conforms with the DFT predictions. The very similar behavior of the wavelengths λ_f and λ_s is also reflected by the close values of the exponents b governing their power-law density dependence (i.e., $\lambda = a\phi^{-b}$). Indeed, we find for λ_s that $b^s = 0.27$ (0.30) from experiment (theory), while for λ_f , $b^f = 0.35$ (0.36). We understand the somewhat lower values of b^s as a consequence of the averaged character of λ_s , which results in a somewhat weaker density dependence (as compared to that of λ_f).

To summarize, we have shown by experiment and theory that the dominating wavelengths of the oscillations in characteristic distribution functions of bulk and confined charged silica solutions are in excellent agreement with each other. This is the first experimental proof of corresponding DFT predictions. Moreover, our experimental results are reproduced very well by theoretical calculations based on the DLVO interaction potential. Strictly speaking, the latter is an effective potential derived for *bulk* systems with spherical counterion distribution. Clearly, this will change in a nanoscopic system where many particles are close to an interface (where image charge effects may also play a role) [27,28]. From that point of view, the good performance of our calculations indicates that the confinement-induced changes of the effective silica interactions are irrelevant for the quantities considered.

Of course, the wavelength λ_f considered in this Letter is associated with the density distribution *perpendicular* to the walls, and we have seen that this wavelength strongly depends on the particle volume fraction (ϕ). Clearly, one would also expect an increase of *lateral* order with ϕ , including the possibility of wall-induced crystallization. Hints for such behavior were already observed in x-ray experiments [29] and also in the present study via a deviation of the measured force $F(h)$ from simple oscillatory behavior in ultrathin films. More detailed studies on this topic are under way.

Finally, the results presented in this study are relevant not only for the specific silica suspension considered here, but we rather expect our findings to be transferable to the packing (and fluidics) of other confined nano-objects from colloidal particles via micelles and macromolecules to biological entities, e.g., cells.

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