Colloids with a tunable dipolar interaction: equations of state and order parameters via confocal microscopy

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Received 20th May 2009, Accepted 5th November 2009
First published as an Advance Article on the web 21st December 2009
DOI: 10.1039/b909953k

Laser scanning confocal microscopy studies were carried out on charged screened colloidal silica microspheres in sedimentation equilibrium in the presence of a tunable external alternating electric field. The external a.c. field controls the averaged dipolar interaction between the silica microspheres. From the equilibrium sedimentation profiles, equations of state were obtained as a function of the dipolar strength and volume fraction. The colloidal fluid at zero field follows the hard-sphere equation of state but with an effective larger hard-sphere diameter. At non-zero fields, the average colloidal fluid isothermal compressibility was obtained as a function of a dipolar strength parameter. We then investigated bond order parameters upon increasing the field, and monitored an orientational order parameter associated with the field dependence of the average orientation of dual-particle bonds. The orientational order parameters were found to be very sensitive measures of anisotropy. The field dependence strongly confirms the use of the point dipolar approximation in this system.

1 Introduction

Colloids with tunable interactions are very promising systems for studying the fundamental physics of the liquid state, crystallization kinetics, martensitic transitions and kinetic arrest at glass and gel transitions. These studies would benefit greatly from systems where these tunable interactions can be switched on and off instantaneously to provide the equivalent of temperature or pressure quenches in the study of colloidal phase transitions.

One of a few such systems is a colloidal suspension with a tunable dipolar interaction, controllable by the strength of an external (linear or rotating) a.c. electric field. The dipolar interaction is an important driving force for nanoparticle self-organization. Simulations of magnetic dipolar colloids with an additional Lennard-Jones interaction have shown numerous variants (linear aggregates, droplets, columns) of phase separation into regions of higher and lower densities. Recent experiments in Brownian dipolar colloids also exhibit an unusual void phase at very low packing (\(\varphi < 1\%\)). It is important, however, to establish quantitatively the relation between the applied external field and the resultant modulation of the inter-particle interaction, especially in light of questions regarding the limitations of the point dipole model. The fluid phase can be used to test quantitatively whether the interaction of two particles in the presence of a sea of other spheres is still effectively captured by the point dipolar approximation (as has been shown in the case of two isolated spheres), and to obtain experimentally the equation of state of dipolar fluids. Thus far this has not been done.

The equilibrium sedimentation profile of colloidal suspensions has been utilized to obtain the colloidal hard-sphere equation of state. It has also been used to obtain the equation of state for colloid–polymer mixtures. However, while many studies of local dynamics in both hard-sphere colloids as well as colloids with longer-range interactions are carried out using confocal microscopy, i.e. in thin cells close to a bounding surface, quantitative tests of colloid thermodynamics (measurement of the equation of state) have been limited to bulk samples. A test of colloid thermodynamics in the realistic case of colloids experiencing external forcing (either bounding surfaces or electric-field-tunable interactions or both) is thus of broad importance.

In this work, we obtain sedimentation profiles for thin colloidal sediments obtained via confocal microscopy. We use these sedimentation profiles to obtain the equations of state and isothermal compressibilities for a colloidal suspension as a function of the magnitude of an applied external electric field, i.e. as a function of increasing dipolar strength, with the field direction being perpendicular to gravity. In this geometry both the electric field and gravity are simultaneously important. Going beyond the equation of state, we directly calculate an orientational order parameter to shed light on local anisotropy in the fluid state at small fields well below the field strength at which long chains form. From the functional dependence of the order parameter, we conclude that an effective dipolar approximation is quantitatively valid.

The equation of state in bulk systems of screened, charge-stabilized colloids has been shown to exhibit quantitative agreement with the Carnahan–Starling relation which expresses the osmotic pressure in a colloidal suspension at packing fraction \(\varphi\) as \(\Pi(\varphi) = nk_bT\zeta(\varphi)\), where the particle number density \(n\) is related to the packing fraction by \(\varphi = n(4\pi a^3/3)\) (where \(a\) is the particle radius) and \(\zeta(\varphi) = (1 + \varphi + \varphi^2 - \varphi^3)/(1 - \varphi)^3\) is the Carnahan–Starling compressibility factor.

The decrease in osmotic pressure for an increment in vertical position \(dz\) in a colloidal sediment is given by \(d\Pi = -g\Delta p \rho(z) dz\). Here \(\Delta p\) is the particle–solvent density mismatch. Integrating this from position \(z\) until a height where no more particles are found yields the equation of state:
\[ \Pi(z) = \int z g \Delta \rho \phi(z') dz' \]  \hspace{1cm} (1)

One can also calculate the isothermal compressibility
\[ \chi_T = k_B T \left( \partial \Pi / \partial n \right)_T \]  \hspace{1cm} (2)

For hard spheres, \( \chi_T \) is independent of particle radius \( a \). At low density, \( \chi_T = \chi_T^{\text{app}} \) is often taken as a constant (although this is not strictly valid) and eqn \( (2) \) reduces to \( \phi = \phi_0 \exp(- \chi_T^{\text{app}} z l_g) \). Here \( \chi_T^{\text{app}} \) is the apparent compressibility in the barometric regime and \( l_g \) is the gravitational length defined as \( l_g = k_B T (4 \pi a^3 / g \Delta \rho) \).

More detailed structural information may be obtained at different depths \( z \) in the colloidal sediment to detect the presence of the field. We do so by way of an order parameter based on the angle a bond between two particles makes with respect to the field direction.

In what follows we obtain the equation of state (via eqn \( (1) \)) and the isothermal compressibility (via eqn \( (2) \)), as well as orientational order parameters, from sedimentation profiles obtained via confocal microscopy.

\section{Experimental}

We prepare our colloidal samples with fluorescent core–nonfluorescent shell silica microspheres (synthesized as by van Blaaderen and Vrij\textsuperscript{21}) suspended in a water–dimethyl sulfoxide mixture (15 : 85 in volume for refractive index matching). The diameter of the fluorescent core is 0.46 \( \mu \text{m} \) ± 6.9%. The two batches of core–shell spheres have diameters \( a = 2a \) of 0.77 \( \mu \text{m} \) (3.8\% polydispersity) and 1.14 \( \mu \text{m} \) (3.4\% polydispersity). Sandwich cells were made using 75 \( \mu \text{m} \) thick polyethylene terephthalate film as spacers and UV epoxy. A 1 MHz a.c. electric field was generated using a dual-channel function generator and a wide-band amplifier, and the potential between gold electrodes was monitored by a two-channel digital storage oscilloscope. In order to apply linear and rotating fields, gold electrodes were patterned onto the microscope slide (top plate) and the cover slip (bottom plate) of a “sandwich cell” by gold vapor deposition through masks machined with the required geometry. For geometry 1 (linear field), two parallel electrodes were patterned on bottom and top plates. Each electrode on the bottom plate was shorted to the electrode above it on the top plate. Geometry 2, with 4 electrodes on each plate instead of 2 to create two diagonal electrode pairs, was used to achieve a switchable rotary or linear field. For a rotary field, we used a dual channel signal (one 90° phase shifted with respect to the other) and separately connected them to each pair. The instantaneous field direction at the center then rotates at mega-Hertz frequency (the Lissajous figure on the oscilloscope is circular). By switching the phase shift between the two channels from 90 to 0°, we switch from a rotary to linear field in the same colloidal system and switch the anisotropy of the system without altering the energy that might be pumped into the system. The center of the electrodes where no gold is deposited is the place we probe our colloids under external fields using a VisiTech VT-Eye confocal scanner attached to a Nikon inverted microscope and equipped with a 491 nm laser.

In what follows we obtain the equation of state (via eqn \( (1) \)) and the isothermal compressibility (via eqn \( (2) \)), as well as orientational order parameters, from sedimentation profiles obtained via confocal microscopy.

\section{Equations of state}

The equation of state can be extracted from the equilibrium sedimentation profile in a colloidal suspension. Shown in Fig. 1(a) is the evolution of sedimentation profiles (for zero applied field) after a sample is first inverted and placed on the microscope stage. For our systems, the Brownian time \( \tau_B = 6 \pi a^2 / k_B T \) and the Stokes time \( \tau_S = h / v_s \) where \( h \approx 30 \mu \text{m} \) is the sediment height and \( v_s = (2 \Delta \rho g \eta a^3) \) is the Stokes velocity of a sphere) are roughly 0.5 s and 2 min respectively. For times larger than 15 min, the sedimentation profiles can be seen to approach the equilibrium profile. We typically waited a minimum of 15 min before obtaining equilibrium profiles (on the order of 1000 Brownian and 10 Stokes times).

The sedimentation profile is a sensitive indicator of residual electrostatic effects in a nearly hard-sphere-like charge-stabilized...
colloidal suspension. Fig. 1(a) shows layering oscillations close to the bottom surface (dimensionless height $z' = 2\sigma = 0$, $\sigma = 2a$ is particle diameter) without crystal formation (consistent with previous work). The equation of state in equilibrium shows significant deviation from the Carnahan–Starling hard-sphere equation of state. Sedimentation profiles at three distinct ionic strengths were obtained—no salt added ("no salt"): screening length $\kappa^{-1} = 53 \pm 2$ nm, as well as with (KCl) salt added ("salt 1"): $\kappa^{-1} = 50 \pm 2$ nm, and "salt 2": $\kappa^{-1} = 10 \pm 2$ nm. Given that $k\sigma > 10$ for all samples, they are expected to be indistinguishable and to exhibit hard-sphere-like behaviour. The equation of state was then calculated (Fig. 1(b)). All experimental equations of state in Fig. 1(b) are indeed indistinguishable, but at significant deviation from the hard-sphere equation of state (dashed line in Fig. 1(b)).

As shown in Fig. 1(b), there is a steep rise in osmotic pressure at a packing fraction close to 0.2, and at higher pressures the curve oscillates back and forth in $a$ function of applied voltage. The dipolar interaction energy (scaled with respect to $k_BT$) has the form

$$\frac{u_{\text{dipolar}}}{k_BT} = \frac{\Lambda}{(R/\sigma)^2} \left( \frac{3\cos^2 \theta - 1}{2} \right)$$

where $a$ is the particle radius, $\sigma = 2a$, $R$ is the interparticle distance, $E_o = V/d$ is the zero-peak electric field amplitude, $\beta = (\epsilon_p - \epsilon_f)(\epsilon_f + 2\epsilon_p)$, with $\epsilon_f$ and $\epsilon_p$ being the fluid and particle dielectric constant and $\Lambda$ is the dipolar strength parameter $\Lambda = \pi\epsilon_o\alpha^2\alpha^3 E_o^2/2k_BT$. The angle $\theta$ is the angle between the line joining particle centres and the field direction. $\Lambda$ represents the magnitude of the scaled dipolar energy for two touching particles $R = 2a$ and $\theta = 0$ and can be calculated from the applied zero-peak potential difference $V_o$, the electrode gap of 2 mm, and the particle and solvent properties. The particle volume fraction as a function of height $z'$ from the bottom was obtained at varying dipolar strengths $\Lambda$. Fig. 2(a) shows the volume fraction as a function of $z'$ for different $V_o$. It is immediately apparent that the tail of the sedimentation profile becomes steeper and less extended with increasing voltage. From these sedimentation profiles and using eqn (1) we obtain next the equation of state as a function of increasing voltage (Fig. 2(b)). Only curves for $V_o = 0, 100$ V, $200$ V and $300$ V are shown, for clarity. At low $\phi$, the applied field induces interactions that reduce both the pressure $(T/\sigma)^2$ was chosen to match the experimental value. In addition, we carried out simulations of sedimenting hard spheres of fixed mass and buoyant force but varying $\sigma_{\text{eff}}$. We approximated the discontinuous hard-sphere potential with a Lennard-Jones potential cut at the minimum of the potential $2^{1/6}\sigma$ and shifted up to zero, with $k_BT\epsilon_{\text{LJ}} = 1$, ensuring that the bulk equation of state matches the Carnahan–Starling model.† Fig. 1(c) shows that both the Yuwaka system with $\kappa = 60$ (the dependence on $\kappa$ is logarithmic) and hard spheres with $\sigma_{\text{eff}} = 1.25$ match fairly well the experimental profile. If we stopped here, we could conclude that a sufficiently large surface charge could produce a hard-sphere-like profile with $\sigma_{\text{eff}} > \sigma$ even when the screening length is short.

However, if we assume that surface charge will not increase when more salt is added, we can test the above. Plotting the hard-sphere-plus-Yukawa potential for $\epsilon = 60$ and $k\sigma = 80$, we find that $\sigma_{\text{eff}} \approx 1r$ (Fig. 1(c) inset). Therefore, the experiments done with "salt 2" ($k\sigma = 80$) should return the profiles to true hard-sphere profiles. However, experimentally the "salt 2" profiles are indistinguishable from the "salt 1" profiles.

The upshot of this detailed analysis is that we cannot explain the extended sedimentation profiles (i.e. $\sigma_{\text{eff}} > \sigma$) observed in this study with a simple electrostatic repulsion model. One reason sometimes invoked for such discrepancies is the breakdown of the one-component fluid approach in a sedimented (and therefore spatially heterogeneous) colloidal dispersion; that is, while the colloids (the macro-ions) are sedimented, the counterions are dispersed throughout the solvent, giving rise to poorer charge screening than in the unsedimented dispersion. This explanation too seems less likely in the presence of added salt. The main point to be noted is that the equation of state at zero field is robust and can be fit to an effective hard-sphere density profile.

The next experiment was to obtain sedimentation profiles as a function of applied voltage. The dipolar potential $u_{\text{dipolar}}(r)$ is given by

$$u_{\text{dipolar}}(r) = \frac{e}{r/\sigma} \exp[-k(r-\sigma)]$$

for $r > \sigma$. For $k\sigma = 16$ (as in "salt 1") this potential has a steep rise at $r/k\sigma_{\text{eff}} = 1$, with an effective hard-sphere diameter $\sigma_{\text{eff}} > \sigma$ that varies roughly as $\log e$. Indeed, we obtain a better fit to the solid part of the sedimentation profile by carrying out simulations of a system of particles under gravity interacting through eqn (3), with $k\sigma = 16$ and varying $e$. We use molecular dynamics simulation of 4000 particles in a $20.2a \times 20.2a \times 122a$ cell that is periodic in the $xy$ plane with gravity along the $z$ axis. The areal density ($=9.8/\sigma^2$) was chosen to match the experimental value. In addition, we carried out simulations of sedimenting hard spheres of fixed mass and buoyant force but varying $\sigma_{\text{eff}}$. We approximated the discontinuous hard-sphere potential with a Lennard-Jones potential cut at the minimum of the potential $2^{1/6}\sigma$ and shifted up to zero, with $k_BT\epsilon_{\text{LJ}} = 1$, ensuring that the bulk equation of state matches the Carnahan–Starling model.† Fig. 1(c) shows that both the Yuwaka system with $\kappa = 60$ (the dependence on $\kappa$ is logarithmic) and hard spheres with $\sigma_{\text{eff}} = 1.25$ match fairly well the experimental profile. If we stopped here, we could conclude that a sufficiently large surface charge could produce a hard-sphere-like profile with $\sigma_{\text{eff}} > \sigma$ even when the screening length is short.

† Continuous potentials are used to approximate hard spheres; see, e.g. Voigtmann et al. where the authors use a simple power law potential with exponent 36. In our simulations, we confirm that our potential is sufficiently hard-sphere-like by checking that doubling the exponents in our potential results in no significant change in our simulated profiles.
favorable to take a particle from the barometric regime and place it in the denser sediment in the presence of increasing attractions.

For anisotropic interactions, it is clear that even in the limit of weak interactions, the equation of state will not tell the full story, because no information about anisotropy is built into it. Thus we looked next at orientational order parameters.

4 Orientational order parameters

On increasing the electric field, angular correlations between particles increase. This is seen qualitatively in Fig. 3 where increasing field (applied along the vertical direction) gives rise to the increase in orientational order in confocal snapshots at a fixed height. From the 3-dimensional datastacks, two-particle bonds were defined when the distance between two spheres was less than 1.2\(\sigma\). The bond angular order parameter \(\langle \cos^2 \theta \rangle\) was then obtained as a function of local volume fraction \(\varphi\). To improve statistics, several images at a given depth \(z\) were averaged. The \(\langle \cos^2 \theta \rangle\) vs. \(\varphi\) profile for 0.77 \(\mu\)m colloids is presented in Fig. 4(a).

For each value of potential, \(\langle \cos^2 \theta \rangle\) was roughly constant for \(\varphi > 0.02\) (for \(\varphi < 0.02\) there are very few bonds and hence the data there is noisy). For an isotropic system in 2 dimensions, one expects \(\langle \cos^2 \theta \rangle = 0.5\), while for perfectly ordered chains along the field direction, one would obtain \(\langle \cos^2 \theta \rangle = 1\). In our experiments, for different potentials, the higher potential corresponded to a higher average value of \(\langle \cos^2 \theta \rangle\), i.e. particles are more likely to form chains parallel to the field.
were generally linear for all experiments, we adopted as our anisotropies in colloidal interactions. Colloids in electric fields even for relatively small fields.

Fig. 5 shows a clear difference between linear and rotating fields strength has been obtained: the apparent compressibility is a state for tunable dipolar colloids as a function of dipolar sphere diameter larger than the bare diameter. In the presence of an external electric field, the dependence of the equations of behaviour in the sediment corresponds to an effective hard-fluid.

Here, were consistent with those in the simpler field geometry (S2 lin vs. S1 in Fig. 4(b)). We then applied a rotating electric field. The electric field experiment was repeated in a sample where the electrode geometry allowed the application of either a linear or a rotating electric field (by controlling the relative phase of the electrode pairs). We first tested that the linear electric field results or a rotating electric field (by controlling the relative phase of electro. Here, stayed almost steady over the whole range of applied field energy. This is expected because no direction in the x–y plane is preferred in a rotating field. The plot of vs. (not shown) the curves for 1.14 μm spheres (“L1”) do not overlay with those for 0.77 μm spheres (“S1” and “S2 lin”).

The electric field experiment was repeated in a sample where the electrode geometry allowed the application of either a linear or a rotating electric field (by controlling the relative phase of electrode pairs). We first tested that the linear electric field results vs. (E). For a perfect particle chain parallel to the linear field, α₀ = 1. In our experiments α₀ increased from 0.5 to 0.8 over the range of dipolar strengths probed. For both particle sizes, all data falls on one master curve. Thus the particle-size dependence of the field response scales exactly as one would expect for the dipolar interaction (Δ ≈ a²E₀²). When α₀ is plotted against E₀ (not shown) the curves for 1.14 μm spheres (“L1”) do not overlay with those for 0.77 μm spheres (“S1” and “S2 lin”).

Colloid sediments with external forces thus display non-trivial behaviour. While there is weaker ordering near the wall than expected from molecular dynamics simulations, the fluid regime can be captured within a hard-sphere-plus-Yukawa (or an effective hard-sphere) model. In spite of the fact that in all cases kₐ ≫ 1 for the bulk solution, the observed zero-field behaviour in the sediment corresponds to an effective hard-sphere diameter larger than the bare diameter. In the presence of an external electric field, the dependence of the equations of state for tunable dipolar colloids as a function of dipolar strength has been obtained: the apparent compressibility is found to increase with the dipolar strength parameter Δ. Orientational order parameters prove to be a sensitive probe of anisotropies in colloidal interactions. Colloids in electric fields show dependencies that are indeed quantitatively consistent with dipolar interactions.

Acknowledgements

We acknowledge advice on colloid synthesis from Carlos van Kats, assistance on initial electric field design from Joseph Fitzgerald, and discussions with Amit Agarwal. This work was supported by the Natural Sciences and Engineering Research Council of Canada, the Canada Foundation for Innovation, and ACEnet, with computational support provided by SHARCNET and ACEnet.

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