Equilibrium Sedimentation Profiles of Screened Charged Colloids: A Test of the Hard-Sphere Equation of State

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Equilibrium sedimentation profiles of concentrated suspensions of charged colliods are accurately determined by measuring the intensity of the depolarized light scattered by optically anisotropic particles. From the data we derive the osmotic pressure Π versus the particle volume fraction Φ. The $\Pi(\Phi)$ values obtained with strongly screened colloids are in excellent agreement with the predicted hard-sphere equation of state. The data show that, besides gravitation, there is an additional force acting on the particles, probably due to the buildup of an electrostatic sedimentation potential.

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Suspensions of model colloidal particles represent, besides their intrinsic interest, a very important system for the study of basic properties of liquids because they show length scales accessible to optical scattering techniques, and interparticle potentials simple enough to allow quantitative tests of liquid state theories [1]. The usual experimental approach is that of deriving the static structure factor from scattering experiments. However, it is known that the measurement of the equation of state would constitute a more stringent test of the properties of the system, because of the greater sensitivity to the details of the interparticle interaction potential [2]. It has been noted [3–5] that a single measurement of the particle density profile of a colloidal suspension at sedimentation equilibrium under the gravitational field can directly yield the full equation of state of the suspension, but sufficiently accurate data are not available, except for measurements of the osmotic pressure at melting in settling suspensions of polystyrene particles by Hachisu and Takano [4] and for the study of order-disorder transition in suspensions of colloidal silica performed by Davis, Russel, and Glantsching [6]. It is indeed very difficult to obtain accurate sedimentation profiles over a wide range of volume fractions by using standard colloidal suspensions. We present in this work a sedimentation experiment performed with model particles made of a fluorinated polymer, which present a unique combination of two extremely interesting features [7–9]: They have a partially crystalline internal structure yielding an appreciable intrinsic optical anisotropy, and they are composed of a material having an average index of refraction very close to that of suspending medium (water). While the latter feature allows us to study highly concentrated samples, the former ensures the presence of a strong depolarized component in the scattered light intensity which is strictly proportional to the particle number density and totally insensitive to interparticle interactions. The particles present a surface electric charge, but behave as hard spheres upon addition of an appropriate amount of salt [8]. The obtained sedimentation profiles allow a test of the theoretical predictions for the hard-sphere (HS) equation of state, including the crystallization transition. We find that the agreement with the Carnahan-Starling equation of state is very good. However, the experimental profiles give an effective reduced mass of the particles which is smaller than the true value. The mass renormalization factor depends simultaneously on the number of particles in the cell, and on the ionic strength. This new effect indicates that an electrostatic potential is created in the sedimentation cell, and suggests that sedimentation profiles of charged particles are not adequately described by one-component models even in the region of high screening.

We consider a suspension of particles having a reduced mass $m = V_P\Delta\rho$, where V_P is the particle volume and $\Delta\rho$ is the difference between the densities of particle and solvent, at sedimentation equilibrium in a cell of height h. Calling the local particle number density $n(z)$, where z is the vertical coordinate measured from the bottom of the sedimenting cell, and assuming that h is large enough to ensure a vanishing particle density $n(h)$ at the top of the cell, the osmotic pressure of the system $\Pi(z)$ can be written in a one-component model as [10]

$$\frac{\Pi(z)}{k_BT} = l_g^{-1}\int_z^h n(z)dz\,, \tag{1}$$

where $l_g = k_BT/mg$, called the gravitational length, is the only relevant length scale which determines the equilibrium profile. The osmotic compressibility factor $(nk_BT)^{-1}\Pi$ can be determined experimentally as a function of $n(z)$, according to Eq. (1), by a simple numerical integration of the measured concentration profile. By introducing the isothermal osmotic compressibility $\chi_T = k_BT(\partial\Pi/\partial n)_T^{-1}$, the equation for $n(z)$ can be written as

$$\frac{dn(z)}{dz} = -l_g^{-1}\chi_T n(z)\,. \tag{2}$$

Note that, in the dilute gas limit, we obtain from Eq. (2) the usual barometric law $n(z) = n_0\exp(-z/l_g)$.

We have used nearly monodisperse latex spheres of a polytetrafluorethylene copolymer (PFA) obtained by Au-

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simont S.p.A, Milano (Italy), with an average refractive index $n_P = 1.352$, and an intrinsic optical anisotropy $\Delta n \approx 0.005$. The particle surface is electrically charged: According to titration data the number of ionizable sites is about 2000. For the specific application of sedimentation studies fluorinated polymer particles present an important feature, namely, a very high density, $\rho_P = 2.14 \pm 0.04$ g/cm^3. Indeed the typical sedimentation time for an initially homogeneous solution of height h is of the order of few Stokes times t_S, where $t_S = h/V_S$ is the time taken by a free particle of radius R to settle over a distance h at the Stokes velocity $V_S = mg/6\pi\eta R$. The feasibility of the experiment requires a not too long equilibration time, and a not too sharp sedimentation profile. If, for instance, we want to get equilibrium in a 3 cm cell within 1 month, having l_g larger than 100 μm, the density difference $\Delta\rho$ between particles and solvent has to be at least 0.3 g/cm^3.

To minimize the coherent polarized scattered intensity, we matched the solvent refractive index to n_P by adding 18% urea to water. The sedimentation cell consisted of a 1 cm optical path cuvette, inserted in a thermostatting unit and mounted on a vertical translator with a spatial resolution of 20 μm. The incident vertically polarized He-Ne laser beam is focused in the cell center to a spot size of about 50 μm. The horizontal component of the intensity I_{VH} scattered at 90° is measured as a function of z, and the value of the particle volume fraction $\Phi(z) = V_P n(z)$ is calibrated by comparison with the depolarized scattering from a homogeneous suspension at known volume fraction. The absolute volume fraction of the reference homogeneous suspension was determined both by density measurements and by weighing the residual solid content after drying a known sample mass [8]. The combination of these two independent procedures gives the absolute calibration of ϕ with a fractional accuracy of about 3%, setting at the same time a limit to the uncertainty for ρ_P. Incident and transmitted intensities are also monitored to correct data for the turbidity of the suspension, which was in any case reasonably low due to the index-matching condition.

Figure 1 shows the steady-state sedimentation profile obtained after 100 d for an initially homogeneous 3 cm high suspension at $\Phi_0 = 0.12$ of PFA spheres with $R = 90$ nm and very low polidispersity ($\leq 5\%$). About 100 mM NaCl were added to the solution to screen the Coulombic repulsion and effectively mimic a hard-sphere suspension. In order to avoid any coagulation a small concentration of nonionic surfactant (Triton×100) almost isopicnic with the solvent has been added to the suspension. The volume fractions in Fig. 1 are evaluated, taking into account the adsorbed surfactant layer. It should be noted that the thickness of the layer (≈ 2 nm) is larger than the Debye-Hückel length at the used salt concentration [9].

The full time evolution of the profile was followed, and no appreciable changes were observed after 100 d. The two main features of the profile are the existence at the top of the sediment of a barometric region that extends for about three decades in volume fraction, and the presence of a discontinuity in the profile followed by an almost constant concentration in the lower part of the cell. This latter feature is visually confirmed by the observation of a meniscus separating the upper sediment from the nearly homogeneous bottom layer. The optical distortions due to the presence of the discontinuity prevented measurements in a range of ±100 μm around the meniscus. From the slope of the profile in the barometric region we derive the experimental value of the gravitational length, $l_g^* = 0.0188$ cm. The equilibrium concentration profile has been numerically integrated according to Eq. (1) and the results are reported in Fig. 2. The inset shows the barometric region where the osmotic pressure conforms to Van't Hoff's law, being linear in Φ. The

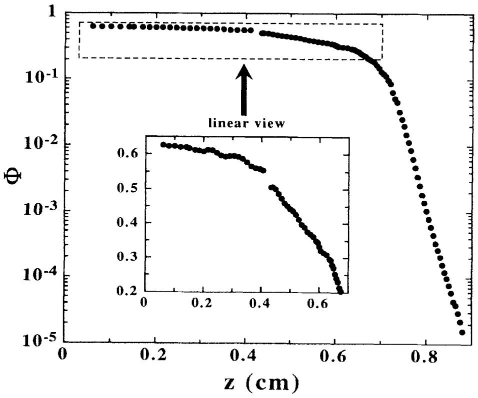

FIG. 1. Particle volume fraction Φ at equilibrium as a function of the distance z from the bottom of the sedimentation cell for a suspension of highly screened 90 nm PFA spheres. The linear inset evidences the high-Φ region showing the discontinuity which corresponds to the visual meniscus.

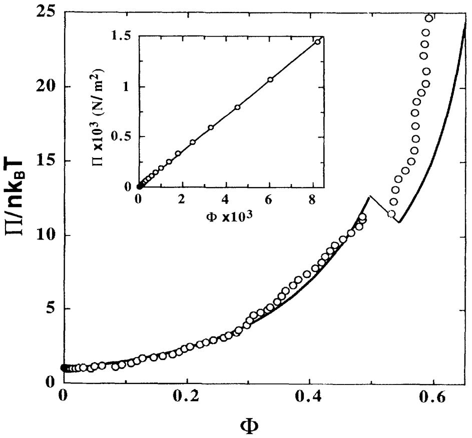

FIG. 2. Compressibility factor obtained from the sedimentation profile in Fig. 1. Full line is the theoretical expectation for a HS system. Inset: "Ideal gas" region at low Φ.

main body of the figure shows the full equation of state in terms of the compressibility factor Π/nk_BT. The discontinuity in volume fraction from $\Phi_F \approx 0.50$ to $\Phi_C \approx 0.55$ for a value of $\Pi/nk_BT \approx 12$ clearly indicates the phase transition of the HS fluid to a crystalline phase.

Our data represent, to our knowledge, the first direct measurement of the HS equation of state in an extended range of volume fractions [11]. The full curve in the fluid branch follows the Carnahan-Starling (CS) equation of state for hard spheres [12]. The agreement both with the CS equation and with the expected values for the volume fraction jump and for the absolute compressibility at the transition is remarkable. The full curve in the solid branch is the Hall empirical fit to molecular dynamics data [13], while the segment joining the two curves is the coexistence line determined by equating the chemical potential and the osmotic pressure of the two phases. The experimental data clearly deviate from the ideal crystal behavior: The weaker compressibility of the bottom layer suggests that the solid might be partly disordered.

A very puzzling aspect of the data is that the experimental value for the gravitational length is *considerably larger* than the value $l_g = 0.0128 \pm 0.0006$ cm which can be calculated using the known particle parameters. It should be stressed that the discrepancy influences the full equation of state and not simply the low volume fraction region: Assuming the calculated value for l_g, the measured equation of state, though still preserving the shape, would give absolute values for the compressibility factor which are systematically 30% lower than the theoretical ones. In other words, the particles behave as hard spheres, but subjected to an "effective" force $(mg)^*$ which is 30% weaker than the gravitational forces.

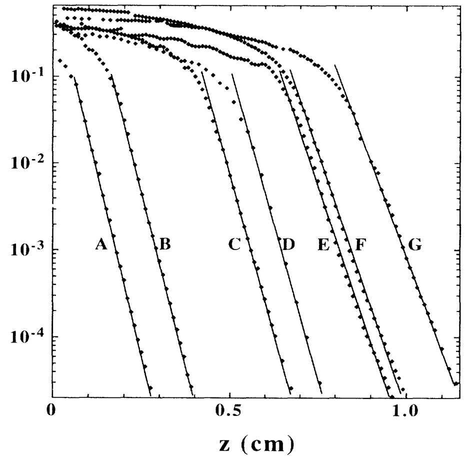

FIG. 3. Equilibrium sedimentation profiles for suspensions of 73 nm PFA spheres at different overall volume fraction Φ_0, cell height h, and added salt I. Describing each profile P as $P[\Phi_0(\%), h\ (\text{cm}), I\ (\text{m}M\ \text{NaCl})]$ we have $A[1, 1, 50]$; $B[1, 4, 50]$; $C[4.5, 3, 20]$; $D[4.5, 3, 0.2]$; $E[10, 1.7, 0]$; $F[9, 3, 50]$; $G[9, 3, 0.2]$.

In order to gain more insight about the discovered effect, we performed an extensive set of measurements on suspensions of smaller PFA particles, with $R = 73$ nm, which present a larger, and therefore more accurately measurable, gravitational length. The calculated value for these particles is $l_g = 0.0235 \pm 0.0012$ cm. Figure 3 reports a series of equilibrium profiles obtained starting from different initial conditions, as specified in the caption. We note from Fig. 3 that the thickness of the sedimented layer increases monotonically going from curve A to G. The value of l_g^*, as derived from the slope of the plots of Fig. 3, also increases monotonically going from A to G. Note, in particular, that curves E and F refer to suspensions which, despite the strongly different value of the ionic strength I, present a similar sediment thickness (due to different values of Φ_0 and h). Though the overall profiles are quite different, the values of l_g^* almost coincide. We also made the following test: After equilibration of cell B, most of the clear solvent over the sedimented layer was gently sucked out, yielding a much higher average Φ. No changes in l_g^* were observed after the cell was shaken and successively allowed to equilibrate again. Since Fig. 3 suggests an apparent correlation between l_g^* and the sediment thickness, we have plotted in Fig. 4 $(l_g^*)^{-1}$ as a function of the quantity s which is defined as the first moment of the mass distribution:

$$s = \left(\int z\Phi\, dz\right) \Big/ \left(\int \Phi\, dz\right). \qquad (3)$$

The plot suggests an almost linear dependence of $(l_g^*)^{-1}$ on s which extrapolates, for vanishing sediment thickness, to a value coincident, within uncertainty, with l_g^{-1}.

In order to rule out possible effects connected with the use of the mixed water-urea solvent, we have also studied some suspensions in pure water, where the concentration region below 1% is still transparent enough to be measured without turbidity problems, and we have found the

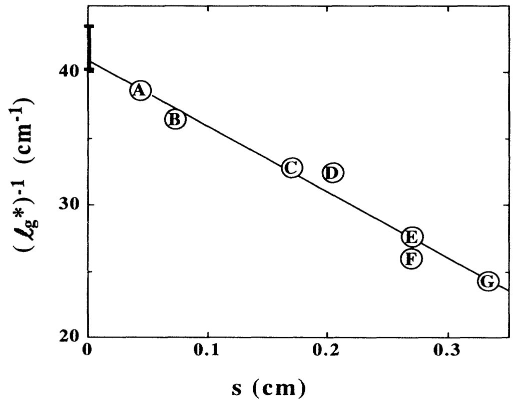

FIG. 4. Measured inverse gravitational length $(l_g^*)^{-1}$ as a function of the average sediment height s. Letters within the circles correspond to the profiles in Fig. 3. The bar on the vertical axis gives the calculated value for l_g with its uncertainty.

same discrepancy between l_g^* and l_g.

We have also measured directly the particle size in the barometric region of cells A and G by performing depolarized dynamic light scattering measurements. We found almost identical values for the decay rate Γ_{VH} of the correlation function, notwithstanding a difference of almost 50% in l_g^* for the two suspensions. This observation allows us to exclude the existence of some segregration mechanism which could squeeze the smallest particles out of the sedimented layer.

The origin of the discrepancy is probably related to a partial failure of the one-component fluid approach to suspensions of charged colloids. Indeed, such suspensions are multicomponent systems containing macroions, counterions, and salt ions. It is known that a sedimenting uniform column of charged macroions gives rise to a sedimentation potential, that is, to an electric potential difference between points at different levels, which is analogous to the streaming potential in a pressure flow and represents the reciprocal effect of electrophoresis [14]. It is reasonable to assume that an electric field E can still exist in the solution at equilibrium due to a nonuniform distribution of the various charged species along the cell. The physical origin of E might be seen considering that the counterions, though bound to follow the macroions to maintain charge neutrality, are "reluctant" to be segregated in the sedimented layer because of entropic reasons. Changes of the electromotive force of galvanic cells at sedimentation equilibrium in a centrifuge have indeed been observed [15]. At steady state the total chemical potential of each component must be uniform throughout the cell, so that the equilibrium condition for each charged species bearing a charge z_i will be given by

$$(\mathrm{grad}\mu_i)_{T,P} = -m_i g + z_i E \,. \tag{4}$$

If we limit our consideration to a suspension of colloids (having charge Z) with no added salt, and specialize Eq. (4) to both particles (P) and monovalent counterions (C), we obtain

$$\mathrm{grad}\mu_P + Z\mathrm{grad}\mu_C = -(m_P + Z m_C) g \,, \tag{5}$$

which suggests that the equilibrium condition will directly depend on the spatial distribution of the counterions. It is, however, not clear whether this approach could predict an effective particle mass which is z independent, implying a constant electric field in the cell, and which is only related to the thickness of the sediment. We regard the observed gravitational length "anomaly" as an interesting subject for further theoretical investigations.

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