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Ultracentrifugation of Single-Domain Magnetite Particles and the De Gennes—Pincus Approach to Ferromagnetic Colloids in the Dilute Regime†

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We report an analytical ultracentrifugation study on sedimentation in dilute stable dispersions of uniform, magnetic iron oxide (Fe₃O₄) colloids. On increase of the dipolar coupling constant, tuned by the average particle size, the linear concentration dependence of the sedimentation velocity shows an abrupt transition from the hindered sedimentation expected for hard spheres to a marked acceleration already for weak dipolar interactions. This transition is not reproduced by sedimentation theory derived from an effective, isotropic pair correlation function of the type proposed by De Gennes and Pincus, for reasons which are made clear. Accelerated settling, instead, follows a scaling based on the mass action law for dimer formation with dipoles in head-to-tail configuration. Our work illustrates that orientational averaging of dipole interactions of ferromagnetic colloids in the dilute regime is inapplicable, with an obvious implication for the possible existence of isotropic gas—liquid criticality for such colloids.

1. Introduction

Single-domain ferromagnetic colloids are Brownian particles with an embedded permanent magnetic dipole moment.2 The anisotropic magnetic interaction between such colloids, as discussed by De Gennes and Pincus in a classical paper,1 may induce spontaneous formation of dipolar structures such as chains, wormlike clusters, and flux-closure rings. These equilibrium structures, which form in absence of an external field, have since been widely studied theoretically and via computer simulations.3 More recently, direct experimental evidence for the existence of dipolar structures in dispersions of ferromagnetic colloids has been reported: first for the case of metallic iron particles4,5 and later also for monodisperse magnetite (Fe₃O₄) colloids.6,7 These experimental studies4–7 employed in situ imaging of colloids via cryogenic transmission electron microscopy (cryo-TEM, Figure 1), a method introduced earlier by Donselaar et al.8 for the study of ferrofluids. For the magnetite particles in ref 6, analysis of cryo-TEM images7 confirms that the dipolar colloids self-assemble to truly equilibrium structures, which validates the thermodynamic approach in ref 1 and later studies.3

De Gennes and Pincus1 also predicted that, despite the anisotropy of the dipolar interaction, the low density limit could favor a fluid with an isotropic structure. Their approach is essentially as follows. In the dilute limit ferromagnetic colloids (with diameter D) mainly experience the weak dipolar interactions that occur at large center-to-center distances r ≫ D. Averaging this anisotropic interaction over all Boltzmann-weighted dipole—dipole orientations (see also section 2) yields an effective isotropic attraction which scales as −1/r⁶, for r ≫ D. This attraction is the magnetic analogue of the (molecular) Van der Waals force, and consequently, according to De Gennes and Pincus,1 a gas—liquid phase transition may occur for magnetic colloids, just as for any other Van der Waals fluid. This prediction initiated extensive literature on liquid—vapor criticality and other phase transition scenarios8–16 in dipolar hard-sphere fluids.3,11–16 There is little doubt that an effective isotropic attraction is physically unrealistic for colloids with a very strong head-to-tail contact attraction: they will form chainlike structures, even in the very dilute limit. However, if the dipolar interaction is sufficiently weak at all distances r ⩾ D, one could argue that preaveraging the anisotropic interaction may be justified such that the pair correlation function (pcf) can be approximated by a hard sphere perturbed by an isotropic attraction.

Figure 1. Typical in situ cryo-TEM images6,7 of vitrified films, which are quasi-2-D systems, of magnetite dispersions D and E in zero external magnetic field. Effect of increasing dipolar attraction is manifested by the formation of dipolar structures. Note that particle concentrations are much higher than in sedimentation experiments.
De Gennes and Pincus\(^1\) restricted themselves to static properties, as is usually the case in theory and simulations on dipolar spheres. An experimental test for their approach to the dilute regime would be the measurement of osmotic pressures to verify, for example, whether the second virial coefficient agrees with calculations based on an isotropic pcf. A similar approach has been followed to test equations of state for charged colloids.\(^{17-19}\) For ferromagnetic colloids, to our knowledge, no equation of state has been measured yet, at least not for monodisperse, uncharged particles that sufficiently resemble the dipolar spheres from the theory.\(^1\) However, it is equally possible to probe the pcf via a dynamic property such as sedimentation of particles under gravity or in a centrifuge. The reason is that at sufficiently low concentrations sedimentation does not distort the equilibrium pcf.\(^{20,21}\) Thus, the concentration dependence of sedimentation in the dilute regime provides a test for the static pcf, analogous to the concentration dependence of the osmotic pressure. This insight has first been exploited by Vrij and co-workers\(^{22-24}\) to investigate the equilibrium pcf of hard spheres\(^2\) as well as attractive spheres\(^{23,24}\) via ultracentrifugation of model silica dispersions. The aim of the present work is to employ this strategy, but now for colloids with a magnetic moment, to test the De Gennes—Pincus approach to ferromagnetic colloids in the dilute regime.

The ferromagnetic colloids in this study (further characterized in section 3) were used previously in cryo-TEM investigations (Figure 1) on dipolar structure formation.\(^6,7\) These colloids are fairly uniform in size which is essential for comparison to theory. In earlier sedimentation studies\(^{25,26}\) this comparison was seriously hampered by polydispersity and lack of size control in the colloid synthesis. Tuning of the average particle size can now be achieved via a seeded-growth technique.\(^6,27\) Since the magnetic moment of a single-domain colloid is proportional to its volume, the particle size sets the amplitude of the dipolar interaction. Thus, by studying particles with different average size, we can assess the effect of an increasing dipole moment on the concentration-dependent sedimentation velocity.

Accurate measurements of this concentration dependence for small particles require analytical ultracentrifugation, a method described in detail elsewhere.\(^{28-30}\) The detection of settling particles is based on optical absorption. An advantage of magnetite colloids in this respect is their strong light absorption, allowing their detection even at the very low concentrations where colloids freely settle as noninteracting particles.

2. Sedimentation Theory

In what follows we will only consider the sedimentation velocity of colloids in absence of an external magnetic field; for settling in an external field see refs 21 and 31. The concentration dependence of the sedimentation coefficient \(s\) of Brownian spheres can be written as

\[
\frac{s}{s^\infty} = 1 - K_s \phi + O(\phi^2) \tag{1}
\]

where \(\phi\) is the total sphere volume fraction and \(s^\infty\) the sedimentation coefficient of freely settling spheres in the limit of infinite dilution. It is assumed here that the colloids are uncharged; in particular, for charged spheres at low ionic strength the concentration dependence is much steeper than the linear term in eq 1.\(^{21,32}\) \(K_s\) quantifies the effect of solvent backflow, which always accompanies particle settling in a closed vessel, and hydrodynamic interactions between sedimenting spheres. For a positive Batchelor coefficient \(K_s\) in eq 1 sphere—sphere interaction slows down the sedimentation velocity, a retardation also known as “hindered settling”. A negative \(K_s\) manifests an increase of \(s\) with concentration, which can be called “accelerated settling”. Batchelor\(^{20}\) has shown that \(K_s\) is completely determined by the isotropic equilibrium pair correlation function \(g(z)\) via

\[
K_s = \frac{1}{2} - 3 \int_{z=1}^\infty dz z [g(z) - 1] + \int_0^\infty dz z^2 [A(z) + 2B(z) + C(z)] \tag{2}
\]

The hydrodynamic mobility functions\(^{20,21,33}\) are up to order \(O(z^{-1})\) given by

\[
A(z) = -\frac{15}{4} z^{-4} + \frac{11}{2} z^{-6} + O(z^{-8})
\]

\[
B(z) = -\frac{17}{16} z^{-6} + O(z^{-8})
\]

\[
C(z) = \frac{75}{4} z^{-7} + O(z^{-9}) \tag{3}
\]

Here \(z = r/a\) is the center-to-center distance between the spheres, scaled on the sphere radius \(a\). For a pure hard-sphere potential the pcf is

\[
g_{HS}(z) = \begin{cases} 
0, & z < 2 \\
1, & z \geq 2
\end{cases} \tag{4}
\]

For this pcf one obtains from eq 2 the well-known value of \(K_s = 6.55\) for hard spheres without any additional repulsive or attractive interaction.\(^{20}\) This value corresponds to a modest hindered settling in a dilute dispersion of hard spheres, mainly caused by the retarding effect of solvent backflow. Batchelor\(^{20}\) already pointed out that any attractions will weaken the hindrance of sphere sedimentation. Qualitatively, this weakening is due to the enhanced probability for attractive spheres to shield each other against the backflow. Jansen et al.\(^{23}\) in their ultracentrifugal study of silica spheres, interacting via an isotropic attraction, indeed measured Batchelor coefficients that were significantly below the hard-sphere value of \(K_s = 6.55\). Nevertheless, \(K_s\) remained positive, implying that in the silica dispersions the isotropic attractions were not strong enough to achieve accelerated settling.

The magnetic part of the pair potential for two spheres each carrying a permanent magnetic moment \(\mu\) is

\[
\beta U_{1,2} = \lambda \left( \frac{D}{r} \right)^3 [\hat{\mu}_1 \cdot \hat{\mu}_2 - 3(\hat{\mu}_1 \cdot \hat{r})(\hat{\mu}_2 \cdot \hat{r})] \tag{5}
\]

Here \(\hat{\mu}_{1,2}\) and \(\hat{r}\) are unit vectors for respectively the orientations and the center-to-center separation of dipole moments 1 and 2, \(\beta = 1/k_B T\), and \(\lambda\) is the coupling constant, which reads for two identical contacting dipolar spheres with a center-to-center distance \(D\):
\[ \lambda = \frac{\mu_0^2 \mu_0}{4\pi k_B T d^2} \]  

where \( \mu_0 \) is the vacuum permeability. Note that \( \beta U_{1,2} = -2\lambda \) is the maximal attraction for two contacting spheres with their dipoles in a head-to-tail configuration. Dhont\textsuperscript{21} argues that for the case of dipolar spheres calculation of \( K_s \) via eq 2 still applies under the following conditions. First, sedimenting spheres should experience no torque due to their dipolar interaction, implying that a sphere can rotate freely around its embedded dipole. In other words, the colloids exhibit Neél relaxation\textsuperscript{2,34} in which dipole orientations fluctuate rapidly relative to the particle’s crystal lattice. Since the evaluation of \( K_s \) via eq 2 is only valid for an isotropic pcf, the second condition is that the anisotropic pcf of the dipolar spheres is replaced by its average over all dipole orientations. This average is evaluated in the low-density limit via

\[ \langle g(z) \rangle = \langle \exp(-\beta U_{1,2}) \rangle \]

in which the brackets denote an average over all orientations. Chan et al.\textsuperscript{35} found an analytic expression for the average pcf in eq 7, valid for arbitrary values of the coupling constant. For small values of \( \lambda \) this expression can be expanded to find the isotropic pcf for weakly interacting particles:

\[ \langle g(z) \rangle = 1 + \frac{64\lambda^2}{3z^6} + \frac{4096\lambda^4}{25z^{12}} + \ldots, \quad z \geq 2 \]

\[ = 0, \quad z < 2 \]

In this expansion only even powers of the coupling constant appear. Note that the leading 1/z\(^6\) term is actually the one in the De Gennes–Pincus approach.\textsuperscript{1} On substitution of eq 8 in eq 2 we find

\[ K_s = 6.44 - \lambda^2 - \frac{6}{125}\lambda^4 \]

This adds a term of order \( \lambda^2 \) to the result first found by Dhont:\textsuperscript{21}

\[ K_s = 6.44 - 0.97\lambda^2 \]

Using more accurate hydrodynamic mobility functions\textsuperscript{20,21} yields a numerical coefficient of 6.55 instead of 6.44, such that \( K_s \) reduces to the correct value for hard spheres in the limit \( \lambda \rightarrow 0 \).

3. Sedimentation Experiments

3.1. Magnetic Colloids and Sample Preparation. Single-domain magnetite (Fe\(_3\)O\(_4\)) colloids were synthesized via the thermal decomposition of iron(III) acetylacetonate in a solution of 1,2-hexanediol, oleic acid, and oleylamine in phenyl ether. The method is described in detail elsewhere,\textsuperscript{6,22} including the seeded-growth technique to control the average particle size.\textsuperscript{6} For ultracentrifuge experiments the magnetite particles, covered with an oleic acid layer, were eventually dispersed to a stable dispersion in cis-trans-decalin, to which 15.6 mM oleic acid was added, which ensures dispersion stability.\textsuperscript{28} We verified that free oleic acid did not induce any depletion attraction, as discussed further in ref 28.

### Table 1: Colloid Characterization

<table>
<thead>
<tr>
<th>Sample</th>
<th>cis-Trans</th>
<th>cis-Trans</th>
<th>cis-Trans</th>
<th>cis-Trans</th>
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<tbody>
<tr>
<td>A</td>
<td>2.4</td>
<td>5.5</td>
<td>0.024</td>
<td>0.002</td>
<td>2.3</td>
</tr>
<tr>
<td>B</td>
<td>3.8</td>
<td>7.0</td>
<td>0.114</td>
<td>0.014</td>
<td>3.8</td>
</tr>
<tr>
<td>C</td>
<td>4.6</td>
<td>9.2</td>
<td>0.168</td>
<td>0.017</td>
<td>4.4</td>
</tr>
<tr>
<td>D</td>
<td>4.8</td>
<td>10.1</td>
<td>0.183</td>
<td>0.018</td>
<td>4.5</td>
</tr>
<tr>
<td>E</td>
<td>7.1</td>
<td>11.3</td>
<td>0.658</td>
<td>0.067</td>
<td>6.9</td>
</tr>
</tbody>
</table>

\(^a\) Average radius from TEM micrographs as in Figure 2.
\(^b\) Relative polydispersities in TEM radii. \(^c\) Magnetic moments determined from magnetization curves. \(^d\) Magnetic radii calculated from magnetic moments using eq 11. \(^e\) Maximum contact attraction for two dipoles in head-to-tail configuration, calculated from \( \mu \), \( a_{\text{TEM}} \), and center-to-center contact distance of 2\( a_{\text{TEM}} + 2\Delta \), where \( \Delta = 2 \text{ nm} \) is the oleic acid layer thickness.

Magnetization curves were for all dispersions recorded at 25 °C with an alternating gradient magnetometer (AGM, Micromag 2900, Princeton Measurements Corp.). The curves could in all cases be fitted very well with a modified Langevin equation,\textsuperscript{28,36} yielding the magnetic particle moments in Table 1, from which magnetic particle radii were calculated using

\[ a_{\text{mag}} = \left( \frac{3\mu_{\text{mag}}}{4\pi m_s} \right)^{1/3} \]

Here we substituted the bulk volume magnetization of magnetite \( m_s = 4.84 \times 10^3 \text{ A m}^{-1} \) at 298 K.\textsuperscript{36} Note that the magnetic radius and the TEM radius \( a_{\text{TEM}} \) do not include the oleic acid layer of the particles, with thickness \( \Delta = 2 \text{ nm} \). Thus, in the calculation of the coupling constant from eq 6 (see Table 1) the center-to-center distance at contact equals \( D = 2(a_{\text{TEM}} + \Delta) \).

For all dispersions A–E (see Table 1 and Figure 2) centrifugation samples were prepared by diluting stock dispersions of known particle weight concentration \( c \) with a standard solution of 15.6 mM oleic acid in cis-trans-decalin. Since the oleic acid concentration varies upon dilution of magnetite stock dispersions, viscosities and densities of oleic acid cis-trans-decalin solutions (5–50 mM) were determined using an Ubbelohde capillary viscometer and an Anton Paar DMA 5000 density meter. All apparent sedimentation coefficients were corrected for solvent viscosity \( \eta_s \) and mass density \( \rho_s \) to obtain sedimentation coefficients for particles in cis-trans-decalin at 20.0 °C using

\[ s = s_{\text{app}} \left( \frac{\eta_s}{\eta_a} \right) \left( \frac{1 + \frac{3}{2} \frac{\rho_a}{\rho_s}}{1 + \frac{3}{2} \frac{\rho_a}{\rho_s}} \right) \]

The same solutions were used to determine oleic acid in cis-trans-decalin extinction coefficients at 228, 229, and 230 nm (Varian Cary 1E UV–vis spectrophotometer) required for the free oleic acid concentration determination.

The particle volume fraction \( \phi \) was calculated from \( \phi = c/\rho_p \), where \( \rho_p \) is the size-dependent mass density of the oleic acid-coated magnetite particles.\textsuperscript{28} Here \( \rho_p \) was calculated via

\[ \rho_p = \frac{\rho_{\text{TEM}} a_{\text{mag}}^3 + (a_{\text{TEM}}^3 - a_{\text{TEM}}^3) \rho_{oa}}{a_{\text{TEM}}^3} \]

substituting an iron oxide core radius, \( a_{\text{TEM}} \), as obtained from TEM images and density \( \rho_{\text{mag}} = 5.17 \text{ g cm}^{-3} \).\textsuperscript{37} The layer
thickness\textsuperscript{7} and density\textsuperscript{38} of the reversibly adsorbed oleic acid are respectively 2 nm and $\rho_{oa} = 0.891 \text{ g cm}^{-3}$.

3.2. Analytical Ultracentrifugation. The sedimentation velocity (SV) measurements were performed with an analytical ultracentrifuge (AUC, Beckman Coulter Optima XL-A) equipped with absorbance optics to monitor sedimenting particles with a high spatial resolution of about 20 µm. The AUC experiments and subsequent data analysis are described in detail in ref 28. Here we merely mention some items that are important to achieve the accuracy of the primary velocity profiles in Figure 3 and the final SV data collected in Figure 4.

Double sector Epon charcoal-filled centerpieces of 3 and 12 mm were used to cover a large concentration range. For each sample a wavelength spectrum was recorded, in addition to the xenon flash lamp emission, through an empty hole in the An-50 Ti rotor. Using these spectra, we maximized the signal-to-noise ratio by matching the wavelength of a local emission maximum with an attenuance in the optical density range 0.6–0.9 OD.

We note here that for the analysis of velocity profiles as in Figure 3 an appropriate and model-independent analysis should be used to obtain diffusion deconvoluted sedimentation coefficients (Figure 4), since the settling of particles is partly counteracted by diffusion, which results in the broadening of the solvent–dispersion interface. Therefore, data collected during SV experiments containing at least 35 scans were analyzed using the second moment analysis (SM)\textsuperscript{40} and the enhanced van Holde–Weischet analysis (vHW),\textsuperscript{41,42} both imple-
tributions

G

agree quite well with values for similar single-domain magnetite

is twice the thickness of the oleic acid layer on the particles.

The smallest surface-to-surface distance is about 4 nm, which

2 that the magnetite particles generally do not touch each other.

mentioned in UltraScan.29 Integral sedimentation coefficient dis-

tributions $G(s)$ and differential sedimentation coefficient dis-

tributions (envelope of histogram) obtained from the vHW

analysis equal the results from the SM analysis. The corrected

weight-average sedimentation coefficients were computed from

the apparent weight-average sedimentation coefficients via eq

12.

In none of the AUC experiments, or in any other experiments

for that matter, did we find indications for colloidal instability

of particles. Dispersion stability is also evident from the ob-

servation that D particles, after being packed by ultracen-

trifugation on the bottom of a cell, could be easily redispersed.

Centrifugation of the redispersed particles yielded the same

settling velocity as previously.

4. Results and Discussion

4.1. Magnetic Colloids. The seeded-growth method yields

single-domain magnetite particles that are quite uniform in size,

as illustrated by Figures 1 and 2. Polydispersity of particles is

small enough for them to crystallize to an ordered lattice when

dispersions dry on a TEM grid. In particular, for particles A,

B, and C (Figure 2) hexagonal ordering can be clearly observed.

For comparison, Figure 2 (panel X) also shows a typical image

of magnetite colloids from the conventional coprecipitation in

aqueous solution,39 which lack such ordering. Note also in Figure

2 that the magnetite particles generally do not touch each other.

The smallest surface-to-surface distance is about 4 nm, which

is twice the thickness of the oleic acid layer on the particles.

Dipole moments from magnetization experiments (Table 1)

agree quite well with values for similar single-domain magnetite

particles determined independently elsewhere7 and correspond

to coupling constants in the range $\lambda \approx 0.02–2$. This means

that, except possibly for the smallest particles A, interparticle

attraction is dominated by the magnetic dipoles. Despite the

oleic acid layer on their surface, particles may also experience a

residual Van der Waals attraction at contact. However, as

shown in detail elsewhere,29 this residue is a marginal effect

that has no bearing on the comparison between theory and

experiments discussed below. Radii calculated from magnetic

moments (Table 1) agree very well with radii from electron

microscopy, which also demonstrates that the values for $\lambda$

in Table 1 accurately quantify the dipolar interaction in the various

dispersions.

4.2. Sedimentation Experiments. Typical examples of time-

resolved concentration profiles in the sector-shaped sedimenta-

tion cells as recorded by the analytical ultracentrifuge are shown

in Figure 3. We briefly discuss here some salient points, refer-

ring for a detailed analysis of the profiles to ref 28. The profiles in

Figure 3 are obtained at rotor speeds of 13 400 rpm (E) and

42 000 rpm (A), corresponding to an acceleration of 13 047g

to 128 174g at a radial distance $r = 6.5$ cm from the center of

rotation. This implies a stationary settling velocity of $v = s\omega^2r$

$\approx 1.8$ $\mu$m $s^{-1}$ for the A-particles and $v = s\omega^2r \approx 2.0$

$\mu$m $s^{-1}$ for the E-particles. Thus, per second an E-particle

traverses $280$ times its own radius. This is a substantial rate, but

nevertheless the particles experience a low Reynolds number of order $Re \sim 10^{-3}$, which is clearly small enough for making a comparison to sedimentation theory (section 2) that is valid only for purely

viscous Stokes flow. The theory, incidentally, also assumes that the Pécelt number is small enough such that the particles are

Brownian spheres. For our experiments this number is in the

range $Pe \sim 10^{-3}–10^{-2}$ so this assumption is satisfied. For

sedimentation of non-Brownian spheres see ref 43.

The profiles in Figure 3 for the highest concentration of the

smallest particles A are quite steep, which is indicative for

hindered settling of repulsive colloids. Self-sharpening of

concentration profiles, well-known for repulsive interactions,44

occurs because particles in the tail of the profile move faster

than those in the leading part where sedimentation is more

hindered. The profiles for the largest particles E show the

opposite trend: here boundary broadening takes place that

TABLE 2: Batchelor Coefficients

<table>
<thead>
<tr>
<th>dispersion</th>
<th>$\lambda^a$</th>
<th>$K^b$</th>
<th>$K^c$</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>0.020 ± 0.003</td>
<td>12 ± 2</td>
<td>6.55</td>
</tr>
<tr>
<td>B</td>
<td>0.208 ± 0.044</td>
<td>-48 ± 3</td>
<td>6.51</td>
</tr>
<tr>
<td>C</td>
<td>0.302 ± 0.065</td>
<td>-56 ± 4</td>
<td>6.46</td>
</tr>
<tr>
<td>D</td>
<td>0.329 ± 0.073</td>
<td>-61 ± 4</td>
<td>6.44</td>
</tr>
<tr>
<td>E</td>
<td>1.773 ± 0.428</td>
<td>-242 ± 33</td>
<td>2.93</td>
</tr>
</tbody>
</table>

$^a$ Coupling constant from magnetization measurements.

$^b$ Experimental Batchelor coefficients from linear fits in Figure 4.

$^c$ From substitution of $\lambda$ in eq 9 using 6.55 instead of 6.44.
Figure 5. Sedimentation coefficient at infinite dilution, $s^o$, versus iron oxide core radius $a_{ox}$ from TEM micrographs. Experimental data (O) are fitted linearly (−) with the constraint $s(x = 0) = 0$.

Figure 6. Schematic illustration of a dilute magnetite dispersion in which weakly bounded “dimers” form due to the dipolar attraction (magnetic dipole moments are represented by black arrows). As indicated by the vectors that represent the sedimentation rates of the monomers and dimers, the larger mass of a dimer is not fully compensated by the increase of the viscous drag force.

Figure 7. Retardation of the rotational mobility of a dipole moment inside a magnetite particle versus particle volume $V_{mag}$ according to eq 14. A and E represent respectively the smallest and largest magnetic colloids.

manifests a net interparticle attraction increasing the settling rate of particles in the leading edge. Diffusion, of course, also broadens the dispersion–solvent interface which can be corrected for as mentioned in section 3.2, to finally obtain the sedimentation coefficients in Figure 4.

For all magnetite dispersions these coefficients are clearly a linear function of concentration (Figure 4), in accordance with eq 1. Extrapolation to zero concentration should yield sedimentation coefficients $s^o$ of noninteracting particles, scaling with the particle radius $a$ as $s^o \sim a^2$. The settling at infinite dilution indeed precisely follows this scaling as shown in Figure 5. The scaling also confirms that the ultracentrifuge really monitors sedimentation in the dilute regime, with a linear first-order correction to ideal behavior of the particles. Moreover, the particles settle as a stable dispersion because irreversible particle aggregation would invalidate the scaling in Figure 5 as well as the linear dependence in Figure 4. This dependence manifests a reversible effect of attractions that vanishes upon extrapolation to infinite dilution. These attractions apparently do not induce any kind of phase instability. Nucleation of a liquid phase, for example, would lead to rapidly sedimenting droplets that certainly would have been detected in the velocity profiles (Figure 3).

What the interparticle attractions do cause is an abrupt transition from weakly hindered to pronounced accelerated settling as soon as the particles have a noticeable magnetic moment (particles B in Table 1). Only the smallest particles A in this study exhibit hindered settling, with a Batchelor coefficient $K_c = 12 \pm 2$. The difference with the value of 6.55 for hard spheres can easily be explained by a slight underestimation of the volume fraction $\phi$. If we supplement the radius of the effective hard sphere with 1 nm due to, for example, surface roughness or a solvation layer, the Batchelor coefficient already reduces to $K_c \approx 6$. Quite striking in Figure 4 is not only the abrupt emergence of accelerated sedimentation but also the large, negative values of the Batchelor coefficient, down to $K_c = -242$ for the E-colloids. These features are not reproduced by eq 1, if we substitute the Batchelor coefficient calculated from eq 9. As depicted in Figure 4, eq 9 only predicts a modest decrease of the Batchelor coefficient with respect to the hard-sphere value. Moreover, the calculated coefficient does not change sign, not even for particles E, which have the highest coupling constant.

To explain the discrepancy between experiments and theory in Figure 2, let us first recapitulate the assumptions in the theory. The calculation of the Batchelor coefficient as represented by eq 2 requires that (1) the magnetic colloids are torque-free and that (2) their pcf is preaveraged over all orientations. Next eq 9 is obtained with the additional assumption that (3) this average isotropic attraction is sufficiently weak. How weak? Our derivation of the $O(\lambda^4)$ term in eq 9 indicates that eq 8 is applicable up to $\lambda \approx 2$, confirming numerical calculations\textsuperscript{21} based on the preaveraged pcf without assumption (3). The experimental coupling constants (Table 1) do not exceed $\lambda \approx 2$ and, consequently, are within the range of applicability of the weak-interaction result eq 9. Nevertheless, this result clearly does not account for the trend in Figure 4, implying that the discrepancy is due to assumption (1) or (2).

With respect to the orientational averaging of the dipolar pcf in assumption (1) it should be noted that the maximal contact attraction is $-2\lambda$ (head-to-tail dipoles), whereas the maximal repulsion equals $2\lambda$ (tail-to-tail or head-to-head). Thus, two dipoles in a contacting pair of spheres experience energy barriers of $4\lambda$ when sampling orientation space. This implies for our particles barrier heights ranging from about $1k_BT$ (B-particles) to about $8k_BT$ (E-particles) which are significant values. Of course, as also noted in the De Gennes–Pincus approach,\textsuperscript{1} at center-to-center distances $r \gg D$ these barriers become unimportant and dipoles will sample all orientations with comparable probability. However, sedimentation by attractive colloids is largely determined by events at distances of order $r = D$ where,
diffusing in a force field. Even for the E-particles with the largest dipole moment this time is of order of milliseconds, which is very short on the experimental time scale. Thus, we may assume that the ultracentrifuge monitors settling of a mixture of monomers and dimers that is in equilibrium at any radial position. This assumption entails an exponential dependence of the Batchelor coefficient on the dipolar coupling constant $\lambda$ as can be shown as follows.

The recorded signal in the Beckman Coulter Optima XL-A AUC is the total optical attenuation determined by the weight concentration of sedimenting species. Thus, the average sedimentation coefficient for a mixture of monomers $m$ and dimers $d$ is the weight average:

$$s = \frac{c_m s_m^2 + c_d s_d^2}{c}$$  \hspace{1cm} (16)

Here $s_m$ and $s_d$ are the sedimentation coefficients of respectively monomers and dimers at infinite dilution; $c = c_m + c_d$ is the total weight concentration. In terms of the sedimentation ratio $\chi = s_d/s_m$ we have

$$\frac{s}{s_m} = \chi + (1 - \chi) \frac{c_m}{c}$$  \hspace{1cm} (17)

The equilibrium constant for a reversible dimerization is

$$K_c = \frac{c_d}{c_m^2} = \frac{c - c_m}{c_m^2}$$  \hspace{1cm} (18)

Solving this quadratic equation, we find for the monomer concentration $c_m$ up to second order in particle concentration $c$:

$$c_m = c - K_c c^2 + O(c^3)$$  \hspace{1cm} (19)

which on substitution in eq 17 yields

$$\frac{s}{s_m} = 1 - (1 - \chi)K_c c + O(c^2)$$  \hspace{1cm} (20)

The accelerated settling predicted by eq 20 is completely due to the ratio of dimers to monomers that shifts to higher values with concentration due to the mass action law eq 18. The concentration dependence in eq 20 indeed would disappear for $\chi = 1$ because then monomers and dimers settle at equal rates. For an upper estimate of $\chi$ we note that a dumbbell is twice as heavy as a monomer sphere, whereas its Stokes friction is only by 1.33 times as large. Thus $\chi = s_d/s_m \sim 2/1.33 \sim 1.5$.

It should be noted that eq 20 neglects correlations between monomers and dimers. The contribution of these correlations to the Batchelor coefficient, however, is not significant since it is comparable to that of nonmagnetic hard spheres. This contribution is a small effect compared to dimerization caused by magnetic attraction.

For the equilibrium constant $K_c$ we apply a scaling based on an earlier image analysis of dipolar structure formation in concentrated magnetite dispersions. In this analysis the number of doublets, triplets, etc., were counted on cryo-TEM images, qualitatively speaking, most of the shielding against solvent backflow takes place. In other words, sedimentation mainly samples the short-range part of the pair correlation function where the replacement of the dipolar anisotropy by its isotropic average is difficult to justify.

If assumption (2) is at least doubtful, assumption (1) is almost certainly invalid. When magnetic particles can freely rotate around their internal moment, the dipoles indeed cannot mediate a torque. However, the energy barrier for this rotation strongly increases with the particle volume. In fact, it appears that as soon as the particle volume is large enough for dipolar interactions to become significant, then simultaneously the assumption of torque-free interactions breaks down. To demonstrate this, we calculate the rotational diffusion coefficient $D_\tau$ of a magnetic moment relative to its host crystal via

$$D_\tau = D_0 \exp[-\gamma V_{mag}/k_B T]; \quad V_{mag} = \mu m_s$$  \hspace{1cm} (14)

Here $\gamma \sim 41$ kJ m$^{-3}$ is the anisotropy constant of magnetite, $V_{mag}$ is the magnetic particle volume determined according to eq 11 by the magnetic moment $\mu$, and the magnetite volume magnetization $m_s = 4.84 \times 10^5$ A m$^{-1}$. Further, $D_0$ is the free diffusion coefficient of the dipole moment for the case the energy barrier $\gamma V_{mag}$ is zero. Figure 4 shows that the rotational mobility $D_\tau/D_0$ indeed drastically decreases with particle volume: already the small increase in particle size from A to B virtually immobilizes the dipole orientation in the particles. This indicates that theory for torque-free colloids must fail quite abruptly when the particle radius exceeds $a = 2.4$ nm.

In most practical magnetite ferrofluids, incidently, the average particle radius is around 5 nm, with a typical polydispersity of 40% (see also panel X in Figure 2). If particles are much larger, fluids may aggregate, and if they are much smaller, the magnetization of the fluid is too weak for practical applications.2

Thus, for the large majority of particles in magnetite ferrofluids the assumption of torque-free interactions is highly questionable.

When sedimenting colloids exert torques on each other that are mediated by their dipoles, the applicability of an isotropic, preaveraged pcf is no longer an issue. For dipolar spheres with fixed dipoles the full anisotropic pcf must be used in the calculation of hydrodynamic mobility functions for the Batchelor coefficient from the beginning, just as for colloidal rods.

4.3. Dimer Model. In want of a calculation of $K_c$ in which the dipolar anisotropy is fully taken into account, we restrict ourselves here to a simplified treatment. This approach almost suggests itself on inspection of the cryo-TEM image of the E-particles in Figure 1, showing single particles as well as colloids that are associated to doublets, triplets, and larger structures. Elsewhere,7 we have shown that this structure formation is reversible. Thus, if we decrease the particle concentration in Figure 1 to the much lower values as in the sedimentation experiments, virtually only association to dimers occurs. This is consistent with the linearity of the concentration-dependent settling in Figure 4 that manifests interactions between two particles only. The lifetime $\tau$ of dimers is approximately

$$\tau = \frac{a_{tot}^3}{D_{eff}} = \frac{3a_{tot}^3 \eta_s}{k_B T} \exp(-\beta U_{mag})$$  \hspace{1cm} (15)

where $k_B$ is the Boltzmann constant, $T$ is the absolute temperature, and $D_{eff}$ is an effective diffusion coefficient for a sphere...
which showed that the formation of short dipolar chains obeys a mass action law of the type

$$x_q = x_1^q \exp[-(q - 1)\beta U_{\text{mag}}]$$

(21)

Here $x_1$ is the monomer mole fraction and $x_q$ is the mole fraction of a linear $q$-mer of contacting spheres, clicked together by the maximal attraction $U_{\text{mag}}$. Now in this image analysis $^5$ only two particles in direct contact are counted as a doublet. For sedimentation, however, this is too restrictive: the dimers are two spheres that are close enough to significantly enhance each other's settling velocity. Thus, the attractive energy of these two spheres that are close enough to significantly enhance each other’s settling velocity. The attractive energy of these dimers will on average be lower than $U_{\text{mag}}$. Therefore, we obtain from eq 21 for the monomer–dimer equilibrium

$$\frac{x_2}{x_1} = \exp(-\alpha \beta U_{\text{mag}})$$

(22)

$\alpha = 1$ denotes two contacting spheres with dipoles precisely in head-to-tail configuration; $\alpha < 1$ accounts for any weakening of the attraction for sedimenting dimers. The equilibrium constant in eq 18 must be proportional to the thermodynamic equilibrium constant in eq 22 which implies for eq 20

$$\frac{C_s}{C_m} = 1 - (1 - \chi) \exp(-\alpha \beta U_{\text{mag}}) + O(\phi^2)$$

(23)

According to this result, the Batchelor coefficient should scale as $\ln K_s \sim -\alpha \beta U_{\text{mag}} + \text{constant}$. Figure 5 shows that the experimental coefficients follow this scaling quite well, with a value of $\alpha = 0.5 \pm 0.02$. The reduction of $\alpha = 1$ to $\alpha = 0.5$ corresponds, according to eq 5, on average to $(d/h)^2 \approx 0.5$, i.e., two spheres with head-to-tail dipoles at a center-to-center distance of $r \approx 1.25D$. This is certainly a distance at which particles will accelerate each other’s sedimentation velocity.

5. Conclusions

The uniform and controlled size of the magnetite particles in this study makes them very suitable for investigating the effect of dipolar interactions on the concentration-dependent sedimentation of ferromagnetic colloids. The analytical ultracentrifuge monitors the magnetite particles, due to their light absorption, almost down to infinite dilution, allowing accurate measurements of the linear concentration dependence of sedimentation in the dilute regime.

We have investigated five well-characterized dispersions with increasing average particle size and, consequently, increasing dipolar coupling constant $\lambda$ as determined from magnetization curves. From the comparison with theory for an effective isotropic particle correlation function (pcf), a comparison that has no adjustable parameters, we conclude that this pcf is unable to reproduce the marked accelerated sedimentation observed in the experiments: the effective pcf predicts for the Batchelor coefficient in eq 1 the scaling $K_s \sim \lambda^2$ whereas the experimental data obey $K_s \sim \exp(\lambda)$. The latter scaling also follows from our dimerization model which does not presuppose an isotropic contact attraction. The considerable energy barrier against dipole reorientation inside the particles for particle radii $r > 4 \text{ nm}$ also invalidates the assumption that magnetite particles are torque-free. For the dynamics of ferromagnetic colloids, theory therefore should address the sedimentation of spheres with a fixed dipole moment, taking the anisotropy of the dipolar interaction fully into account. Since $K_s$ is determined by the equilibrium pcf only, and since $K_s$ is not reproduced by an effective, isotropic pcf, this effective pcf will neither apply to static properties such as the osmotic pressure in the same dilute concentration regime.

The final conclusion from our ultracentrifugation experiments appears to be that, for any significant value of colloidal magnetic moments, preaveraging of the dipolar anisotropy is inapplicable. This also makes the existence of an isotropic Van der Waals instability for ferromagnetic colloids highly unlikely. The possibility for phase equilibria involving dipolar structures$^9$ is, of course, not affected by the outcome of our experiments. How the experimental phase equilibria actually look like for magnetite or any other magnetic colloids is currently being investigated.

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References and Notes


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