

# Scattering of Disklike Particle Suspensions: Evidence for Repulsive Interactions and Large Length Scale Structure from Static Light Scattering and Ultra-Small-Angle Neutron Scattering

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Received September 18, 2002. In Final Form: November 24, 2002

We present static light scattering results for Laponite suspensions. Analyzing our data using the Zimm technique, we measure a second virial coefficient of  $6.0 \times 10^{-23} \text{ m}^3$  at an ionic strength of  $10^{-4} \text{ M}$ . Both results agree well with recent theories and computations for the thermodynamics of hard disks. Our data support the conclusion that the classical Onsager result underestimates the repulsive contribution in discotic systems. We also present neutron scattering results at very low  $q$  which conclusively confirm the existence of large-scale structure in Laponite gels above the isotropic–nematic transition.

## Introduction

Laponite is a synthetic hectorite clay that is often used as a model anisotropic colloid to study phase behavior of disklike particles. Several papers have been devoted to the structure and rheological properties of Laponite solutions.<sup>1–22</sup> The particles bear a negative charge on their

face, which is balanced by  $\text{Na}^+$  in the ionic double layer. The edges can carry either positive or negative charges due to surface acids, depending on the pH.<sup>1</sup> Aqueous Laponite solutions form strong gels at low concentrations. The nature of this gel and the underlying interparticle interactions have been the cause of considerable debate in the literature. Some authors favor gel formation by an attractive association process, driven by either van der Waals forces or electrostatic interactions between the edges and faces of the particles. The latter gives rise to the so-called “house of cards” structure,<sup>2</sup> where the gel would presumably consist of T-shaped units. Monte Carlo simulations<sup>3</sup> have shown aggregates with edge–face interactions at higher volume fractions. However, the main problem with the “attractive gel” picture is that no direct experimental evidence has been found for T-shaped aggregates in Laponite solutions. Small-angle X-ray scattering (SAXS),<sup>1,4–6</sup> small-angle neutron scattering (SANS),<sup>7</sup> and transmission electron microscopy (TEM)<sup>4</sup> suggest that aggregation and direct particle-to-particle contact do not occur in the gel, at least at low concentration. Thus, an alternate explanation is that electrostatic repulsion dominates the interparticle interaction and is responsible for gelation. This repulsion arises from overlapping double layers. Osmotic pressure experiments show that there is a net repulsion between particles, even in the gel state.<sup>1,8,9</sup> Moreover, the osmotic pressure decreases with ionic strength, which is consistent with the classical Derjaguin–Landau–Verwey–Overbeek (DLVO) theory.<sup>1</sup> These experimental results agree, at least qualitatively, with simulation results.<sup>10</sup> A recent analytical and numerical model was developed by Hansen and co-workers<sup>11</sup> for the osmotic pressure,  $P$ , that accounts for the particle orientation and contribution of counterions. However, this model was used to fit experimental data at high concentrations, where the systems are nematic.

To date, scattering experiments have shown conflicting results and have not served to elucidate the solution

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structure. Investigations of Pignon et al.<sup>12</sup> yield a fractal exponent that increases from 1 to 1.8 at the critical volume fraction. Moreover, they observe a characteristic length scale of 1  $\mu\text{m}$  in the gel. These results are consistent with a gel formed from an associative aggregation process. Kroon et al.<sup>13</sup> observed a fractal dimension that evolved from 2.8 to 2.1 during gel formation. However, no preferred length scale was observed during their experiments, leading the authors to believe that gel does not form through an aggregation process of larger and larger clusters. These measured fractal dimensions have been questioned by Bonn et al.,<sup>14</sup> who performed static light scattering (SLS) at pH 10. The authors show that if solutions are not filtered, an apparent fractal dimension of 2 can be observed. However, after solutions are passed through 0.8  $\mu\text{m}$  filters, the scattered intensity decreases and is nearly flat with  $q$ . They also show that the shape of the SLS spectra does not evolve upon aging up to 3 h after dispersion. The authors suggest that filtering removes or breaks up large, undispersed aggregates and that the solution structure can be described as a repulsive glass. This colloidal glass picture is supported by results from diffusing wave spectroscopy,<sup>15,16</sup> which demonstrate that the aging behavior and dynamics of Laponite gels follow scaling laws expected for glassy systems. Moreover, the nonlinear rheology qualitatively matches predictions for soft glasses.<sup>16</sup>

More recently, both experiments and simulations have indicated that the gel microstructure and interparticle interactions are strongly dependent on pH and ionic strength. Kutter et al.<sup>17</sup> performed molecular-dynamics simulations on disks with a finite number of discrete charges, an improvement on the quadrupole model used by Dijkstra et al.<sup>3</sup> Two cases were considered: in the first, all sites carried negative charges, and in the second, edge sites were assigned positive charges. The second case presumably occurs at lower solution pH.<sup>1</sup> In both cases, a gel phase was formed at higher volume fractions. However, the T-shaped clusters were only found for particles with positive edge charges and conditions of strong screening.<sup>17</sup> The other type of gel phase is due to repulsive interactions and may be metastable.<sup>17</sup> Experimental evidence from SAXS, performed by Saunders et al.<sup>18</sup> on solutions in the range  $7.5 < \text{pH} < 9.2$ , suggests a similar picture. The spectra show a change from face-face to edge-face interactions as pH decreases, suggesting that different mechanisms may be responsible for gelation at low and high pH. Recent viscosity and transient electric birefringence measurements<sup>19</sup> on samples of varying ionic strength have yielded results that are consistent with aggregate formation; however, the authors note that their samples were neither stored in a manner that would prevent acidification from  $\text{CO}_2$  nor filtered,<sup>19</sup> which would both have a large impact on the process of gel formation and the gel structure.

The purpose of this article is to report scattering results for Laponite suspensions at pH 10, in the dilute regime and in the gel phase. These experiments yield the second virial coefficient,  $A_2$ , thus quantifying the interparticle interactions and the structure of the gels. We use our experimentally determined value of  $A_2$ , together with the analytic equation of Hansen and co-workers,<sup>11</sup> to compute  $P$  in the isotropic phase. This correction results in a much improved fit to the osmotic pressure data at low concentrations. In addition, our ultra-small-angle neutron scattering (USANS) experiments are the first to be obtained in the very low  $q$  range on the new perfect crystal diffractometer beamline at NIST. These experiments are also the first to strongly demonstrate that the scattered

intensity exhibits power-law behavior at very low  $q$ , indicating that the dispersions do have structure on large length scales. This is in contrast to the results reported by Bonn et al.<sup>14</sup> and others,<sup>20</sup> who have questioned the existence of a large-scale structure.

## Materials and Methods

Laponite RD was purchased from Laporte, Ltd., and used without further purification. The particles have a thickness,  $l$ , of 10 Å and an average diameter,  $d$ , of 300 Å. For SLS measurements, the clays were mixed with ultrapure water (Milli-Q-Plus) at pH 10 to avoid particle dissolution<sup>21,22</sup> and dispersed by means of an UltraTurrax high-speed stirrer for 10 min. The dilute solutions were filtered through 0.45  $\mu\text{m}$  Millipore filters and left to rest for 1 week prior to light scattering and differential refractometry. We verified that filtration does not change the concentration within experimental error. Samples were prepared with no added salt except NaOH, corresponding to an ionic strength of  $10^{-4}$  M (pH = 10), and with added NaCl to obtain an ionic strength of 0.005 M. The refractive index increment,  $dn/dc$ , was measured at 25 °C using a Chromatrix KMX-16 differential refractometer at a wavelength  $\lambda = 633$  nm, on samples in the concentration range 0.01–2.0 wt %. We find a  $dn/dc$  value of 0.084 mL/g, in good agreement with previously reported values of 0.09 mL/g.<sup>7</sup> SLS experiments were performed at 25 °C using an argon laser at a wavelength of 514.5 nm with a Brookhaven goniometer and photomultiplier tube. Samples were in the concentration range 0.01–0.4 wt %, corresponding to volume fractions,  $\phi$ , of  $4 \times 10^{-5}$  to  $1.6 \times 10^{-3}$ . Five runs were performed on each sample to ensure reproducibility.

We interpreted our SLS data using the classical Zimm plot. The intensity is corrected for reflection and then plotted in terms of the Rayleigh ratio, defined as

$$\Delta R = R_{\text{toluene}} \sin \theta \frac{(I_{\text{lap}} - I_{\text{solvent}})}{I_{\text{toluene},90}} \quad (1)$$

where  $R_{\text{toluene}}$  is the Rayleigh ratio of toluene,  $\theta$  is the scattering angle,  $I_{\text{lap}}$  ( $I_{\text{solvent}}$ ) is the scattered intensity of the Laponite solution (solvent) at the specified angle, and  $I_{\text{toluene},90}$  is the measured intensity for toluene at 90°. The data are then plotted according to the equation

$$\frac{Kc}{\Delta R} = \frac{1}{M} \left[ 1 + \frac{R_g^2}{3} \left( \frac{4\pi}{\lambda} \sin \frac{\theta}{2} \right)^2 + 2A_2c + \dots \right] \quad (2)$$

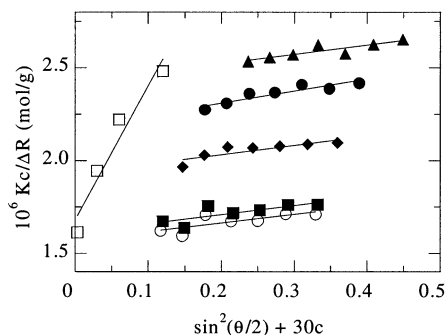
where  $R_g$  is the radius of gyration,  $M$  is the molecular weight, and  $K$  is an optical constant given by

$$K = \frac{4\pi^2 n^2 (dn/dc)^2}{N_A \lambda^4} \quad (3)$$

where  $N_A$  is Avogadro's constant. According to eq 2, extrapolating the data to zero concentration will yield the molecular weight and the radius of gyration, while an extrapolation to zero angle will yield the molecular weight and the second virial coefficient.

The concentrated suspensions for SANS and USANS ( $2 < c < 6$  wt %) were dispersed in  $\text{D}_2\text{O}$  at pH 10, stirred for 10 min, and filtered through 0.8  $\mu\text{m}$  Millipore filters. The solutions were left to rest for 1 week, and all experiments were performed at ambient temperature. USANS and SANS experiments were performed at NIST, NCNR, in Gaithersburg, MD. SANS measurements were taken on the NG3 beamline with an incident wavelength of 6 Å and two sample to 2D-detector distances: 13.1 and 2.1 m, giving scattering vectors  $q$  ranging from 0.003 to 0.2 Å<sup>-1</sup>. USANS measurements were collected on the new thermal-neutron double-crystal diffractometer (BT5).<sup>23</sup> The experimental instrument includes a premonochromator and a pair of multiple reflection channel-cut crystals. The setup specifications lead to a neutron wavelength of  $\lambda = 2.4$  Å and reliable measurements

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**Figure 1.** Zimm plot at pH 10 with no added salt. The filled triangles, circles, diamonds, and squares correspond to concentrations of 0.4, 0.2, 0.1, and 0.01 wt %, respectively. The open squares and circles are the zero-angle and zero-concentration extrapolation.

from 0.000 03 to 0.001 Å<sup>-1</sup>. The direct noniterative method proposed by Singh et al.<sup>24</sup> was used to desmear experimental spectra. All spectra were corrected and obtained in absolute scale (cm<sup>-1</sup>) and then normalized by the contrast factor  $K_f$  (= 400 φ cm<sup>-1</sup>).

### Results and Discussion

Results from SLS on the sample with no added salt ( $I = 10^{-4}$  M) are shown in Figure 1. The nearly parallel, linear fits of the data indicate that the concentrations and angles are low enough that eq 2 can be used to interpret the data. The molecular weights we obtain from our zero-angle and zero-concentration extrapolation are  $600 \pm 30$  kg/mol and  $640 \pm 20$  kg/mol, respectively. These results are in good agreement with the value obtained by Lécolier,<sup>9</sup> 670 kg/mol, from osmotic pressure measurements, and the result of Avery and Ramsay,<sup>7</sup> 710 kg/mol, obtained from SLS measurements.

The second virial coefficient for hard disks has been derived by Onsager as<sup>25</sup>

$$A_2 = \frac{\pi d^2 l}{4} \left( \frac{\pi}{4} \frac{d}{l} + \frac{3 + \pi}{2} + \frac{l}{d} \right) \quad (4)$$

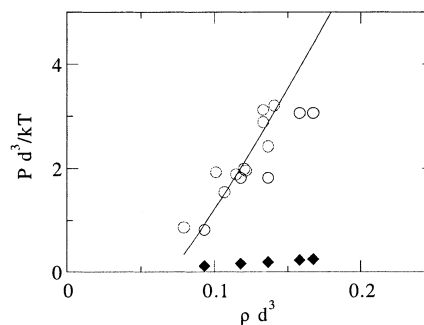
For Laponite, this yields a theoretical  $A_2 = 1.9 \times 10^{-23}$  m<sup>3</sup>. To compare this result to experimentally determined values for the osmotic pressure and the compressibility, we must estimate the energetic contribution to the compressibility. A straightforward way to evaluate this contribution consists of using the analytical equation obtained by solving the Ornstein–Zernike relation.<sup>11</sup> Following this method, the electrostatic contribution to osmotic pressure,  $P$ , has the form

$$\frac{P_{\text{charge}}}{kT} = (\rho Zp - 2\rho_s \ln[2\rho_s + \rho Zp] + 2\rho_s \ln[\rho_s]) \quad (5)$$

where  $\rho$  ( $\rho_s$ ) is the number density of particles (added salt), and  $Zp$  is the effective number of charges per particle. From the above expression, we can derive the total osmotic compressibility as

$$\frac{1}{kT} \frac{dP}{d\rho} = 1 + 2A_2\rho + Zp \left( 1 - \frac{2\rho_s}{2\rho_s + \rho Zp} \right) + \dots \quad (6)$$

In the dilute regime, the third term is negligible, and the



**Figure 2.** Osmotic pressure of isotropic solutions. The diamonds are the calculation of the hard core contribution based on the experimentally derived  $A_2$  value. The solid line is total pressure based on the model of Harnau et al. [4], using the experimentally measured value of  $A_2$ .

main contribution to the compressibility is from the hard core repulsion.

Harnau et al.<sup>11</sup> showed that  $P$  can be computed adequately if one takes into account the orientation parameter of the plates. They deduced a value of  $Zp = 50$ , well below the actual value for Laponite. They correctly computed  $P$  for high particle concentrations ( $c > 1\%$ ) and low ionic strength ( $I = 0.0001$  M) where the suspension is nematic.

Using the data in Figure 1, the value we obtain for  $A_2$  at  $I = 10^{-4}$  M is  $6.0 \times 10^{-23} \pm 1.2 \times 10^{-23}$  m<sup>3</sup>. Results from the sample at  $I = 0.005$  M yield a value of  $4.7 \times 10^{-23} \pm 0.9 \times 10^{-23}$  m<sup>3</sup>. Both of these are higher than predicted by eq 4. However, this is not unexpected. Numerical results on uncharged, infinitely thin disks have shown that eq 4 underestimates the value of  $A_2$ ;<sup>26</sup> analytical corrections to Onsager's expression (using the PRISM approach of Hansen and co-workers<sup>11</sup>) also yield a higher value of  $A_2$ . When our experimentally determined value of  $A_2$  is used to calculate the hard core contribution to  $P$ , we obtain results that are in good agreement with both analytical and numerical results.<sup>11,26</sup>

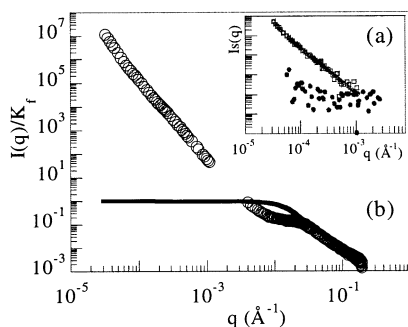
Thus, we used eq 5 in addition to the hard core contribution to fit our experimental data of  $P$  of the isotropic phase ( $0.6 < c < 1.4$  wt % and  $I = 0.0001$  M). The expansion of the hard core contribution to the second-order term is sufficient in this concentration regime. The result shown in Figure 2 using the effective charge/particle deduced by Harnau et al. fits  $P$  adequately. The osmotic pressure does not depend heavily on the value of  $A_2$ , because the hard disk repulsion contributes only about 10% to the total value of  $P$  as shown in Figure 2. However, the osmotic compressibility depends strongly on  $A_2$  and is less sensitive to  $Zp$  at very low concentration.

The smeared neutron scattering results at low  $q$  are shown in Figure 3a for an isotropic and a birefringent gel. It was not possible to desmear the data for the isotropic gel ( $c = 2.5$  wt %) since the signal was very weak and almost flat. Data on the birefringent sample show a dramatic increase at low  $q$ . The corrected, desmeared data on this sample are shown in Figure 3b, normalized by  $K_f$ , along with SANS data and the theoretical form factor for disks with  $d = 280$  Å and  $l = 10$  Å. The scattering spectrum has three regimes. At high  $q$ , the experimental data overlap with the theoretical form factor for disks. In the middle regime, where  $q$  is roughly equal to  $1/d$ , the scattered intensity starts to decrease due to excluded volume interactions.<sup>1,6</sup> At low  $q$ , the data diverge with a slope that is close to  $q^{-3}$ .

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**Figure 3.** (a) USANS data, prior to desmearing, for an isotropic gel ( $c = 2.5$  wt %, filled circles) and a nematic gel ( $c = 6$  wt %, open squares). The open diamonds are fit to the smeared data at 6 wt %. (b) Normalized and corrected USANS and SANS data for  $c = 6$  wt %, with the form factor for disks (solid line).

This behavior is clearly related to the occurrence of an isotropic–nematic phase transition in concentration. At an ionic strength of  $10^{-4}$  M, this transition occurs at 3 wt %.<sup>5,8</sup> Below the isotropic–nematic transition, the sample is a gel, but the normalized scattered intensity can be fit with the form factor for hard disks.<sup>1,27</sup> Above this transition, the scattered data begin to decrease in the mid- $q$  range and diverge at low  $q$ . Our USANS data conclusively demonstrate that this divergence is real and persists to very low  $q$ , and it is not due to artifacts of the sample preparation procedure. Previously published SLS results that do not show this behavior at low  $q$  may conflict with our USANS results for several reasons. First, authors have reported scattering spectra taken as soon as 3 h after sample preparation;<sup>14</sup> however, the structure of Laponite dispersions is known to age slowly over time, requiring days for equilibration.<sup>13,15,28</sup> Second, some published results may have been taken in the isotropic gel regime. As discussed above, a divergence at low  $q$  is not expected in this regime, even though the sample is a gel. The

increase in the data at low  $q$  in the nematic case can be understood if we consider the invariant of the scattered intensity.<sup>29</sup> The appearance of a decrease in  $I(q)$  in the mid- $q$  range must be accompanied by a corresponding increase in  $I(q)$  at low  $q$ . Indeed, analysis of our data shows that the upturn in  $I(q)$  at low  $q$  is balanced by the undercorrelation at moderate values of  $q$  in the invariant integral.

### Conclusions

In summary, we have used static light scattering to quantify interparticle interactions for Laponite particles at pH 10. Our data for  $A_2$  provide the first experimental verification for recent theories of the thermodynamics of hard disks and support the assertion that the Onsager result underestimates the repulsive interaction in discotic systems. This result allows us to extend the model of Harnau et al.<sup>11</sup> to provide a much improved fit for the equation of state of disklike particles at low concentrations. The experimental values of  $A_2$  also support the picture of a repulsive gel or glassy structure for Laponite, rather than gelation through an attractive aggregation process. USANS measurements prove the existence of large-scale structure in concentrated gels above the isotropic–nematic transition. This structural behavior and scattering spectrum are not unexpected, given the fact that the Onsager transition is driven by hard core interactions.

**Acknowledgment.** The SANS data are based upon activities supported by the National Science Foundation under Agreement No. DMR-9986442. The identification of any commercial product or trade name does not imply endorsement or recommendation by the National Institute of Standards and Technology. The authors also acknowledge A. Al-kahwaji for assistance with the USANS measurements and P. Levitz for helpful discussions. This work was supported by the CNRS/Rhodia Complex Fluids Laboratory.

LA0265732

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