

Elastic properties of colloidal crystals

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The shear modulus of colloidal dispersions was calculated by assuming the purely repulsive Derjaguin-Landau-Verwey-Overbeek (DLVO) potential and the Sogami potential containing a short-range repulsion and long-range attraction. These two potentials gave practically the same shear moduli, which were in a good agreement with the observed values. This agreement indicates that the DLVO potential (and hence Yukawa potential) need not always be considered the only correct one in contrast to the widely accepted view. Attention was drawn to recent experimental data obtained by metallurgical microscope, laser scanning microscope, and dynamic light scattering, which showed a definite contribution of a long-range attractive interparticle interaction.

Recently, various authors have carried out computer simulations to calculate the structure factor $S(q)$ of colloidal dispersions.¹⁻³ The unique aspect was that these authors took into consideration both the widely accepted Derjaguin-Landau-Verwey-Overbeek (DLVO) (or Yukawa) potential (purely repulsive) and the Sogami potential (repulsive *plus* attractive).⁴ The results showed that these two potentials provide practically the same $S(q)$ except in a very low q range, where q is the scattering vector. This was in good agreement with the observed one. We began to wonder whether other physicochemical quantities of colloidal systems might also be satisfactorily described by these potentials. In the present work, we calculated the shear modulus (G) of colloidal dispersions by assuming the DLVO potential [Eq. (1)] and the Sogami potential [Eq. (2)], which are given as follows:

$$V_{\text{DLVO}} = [\exp(\kappa a)/(1 + \kappa a)]^2 [Z^2 e^2 / 4\pi\epsilon R] \exp(-\kappa R), \quad (1)$$

$$V_{\text{Sogami}} = [\sinh(\kappa a)/\kappa a]^2 [1 + \kappa a \coth(\kappa a) - \kappa R / 2] \times (Z^2 e^2 / 4\pi\epsilon R) \exp(-\kappa R), \quad (2)$$

where κ is the reciprocal Debye length, a the radius of the particle, Z the valency of the particle, e the elementary charge, ϵ the dielectric constant of the solvent, and R the interparticle spacing. Provided that an fcc structure covers the entire dispersion, the shear modulus G is given as follows:

$$G = (0.833/R)(\partial^2 V / \partial R^2), \quad (3)$$

where V is the interparticle potential. Putting V_{DLVO} or V_{Sogami} into Eq. (3), the shear modulus was calculated and compared with the observed values.⁵

As was the case in the previous paper,⁵ Z was assumed to be an adjustable parameter, since no experimental determination was carried out for their latex particles. Z was determined at the volume fraction 0.1 for a sample without added electrolyte and assumed to be independent of the concentrations of the latex and electrolyte. Figure 1 shows the shear moduli, G_{DLVO} and G_{Sogami} , which

were obtained from V_{DLVO} and V_{Sogami} , respectively.

From Fig. 1 it is difficult to conclude which of the potentials is more appropriate to represent the observed behavior: the overall qualitative behavior is well represented almost equally by these two potentials. The deviation of G_{Sogami} at very low concentrations of the added electrolyte might be due to structural inhomogeneity (such as void formation) observed under such a condition, which invalidates the use of Eq. (3).⁶ While its experimental evaluation should be carried out by transference measurements,⁷ we point out that the two Z values adopted are not far from that expected for latex particles having an

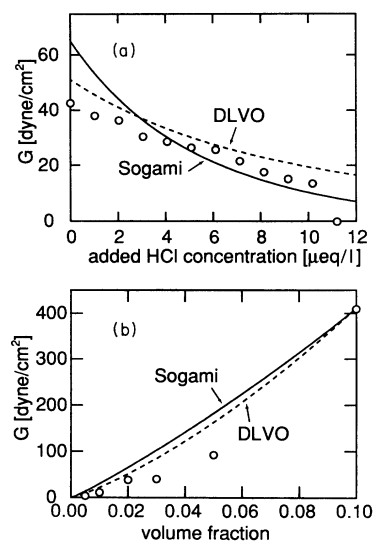


FIG. 1. Shear moduli obtained from the DLVO potential and from the Sogami potential for dispersions of latex particles of a diameter of $0.109 \mu\text{m}$. (a) Electrolyte concentration dependence at a latex concentration of 2%. (b) Latex concentration dependence with no added electrolyte. The circles are observed values reported in Ref. 5 for a latex with a particle diameter of $0.109 \mu\text{m}$ and an analytical charge number of 600 ± 100 . The Z values adopted were 180 and 170 for the DLVO and Sogami potentials, respectively.

analytical charge number of 600 ± 100 .⁸

Instead of Eq. (3), it was assumed⁵ that

$$G = (4/9)cV(\kappa R)^2 \quad (4)$$

with concentration c for a bcc structure. Equation (4) is valid for exponentially decreasing potentials such as the DLVO potential. Thus, in the present paper, which aims at comparison of the DLVO and (non-DLVO-type) Sogami potentials, Eq. (4) was not considered.

We note that a similar agreement between G_{DLVO} and G_{Sogami} has also been confirmed for a $0.22\text{-}\mu\text{m}$ latex. From the present study as well as from the simulation works,¹⁻³ it is clear that the DLVO potential is not the only correct answer, in contrast to the majority opinion in the colloid field. The same statement holds also for the Yukawa potential, which differs from the DLVO form only by a geometric factor. Agreement between theory and experiment is necessary but not sufficient. *The frequent claim, that (colloidal) crystals are stabilized from purely repulsive Coulombic interactions, need not always be considered true, at least as far as the structure factor and shear modulus are concerned.*

On the other hand, the inappropriateness of the DLVO theory is clear, because the theory predicts the deeper secondary minimum with increasing ionic strength whereas experiments show the opposite trend. One of the rationales for the DLVO potential (more generally, repulsion-only assumption) was the famous computer simulation by Alder,^{10,11} which showed clearly the phase transition phenomena at a very high volume fraction (about 0.50) for hard-sphere systems. As was most carefully commented by Alder, a simple repulsive potential was chosen to save computation time; it was not claimed to be a realistic potential. Furthermore, the coexistence of ordered and disordered structures in latex dispersions (to be mentioned below) was observed at much lower concentrations (for example, below 0.02) than the above prediction. Thus it seems difficult to account for the observed phase transition and to rationalize the repulsion-only assumption in terms of the Alder transition.

The importance of the attractive component in macroionic solutions and colloidal dispersions has been pointed out on the basis of the following recent experimental findings:^{6,12,13} (1) the fact that the observed interparticle or intermacroionic spacing ($2D_{\text{expt}}$) is smaller at relatively low polymer or latex concentrations than the average spacing ($2D_0$) to be calculated from the concentration of the particles or macroions, (2) the coexistence of ordered regions with a higher particle density with disordered regions with a lower density (the two-state structure), (3) the presence of void structure,¹⁴ and (4) the Ostwald ripening mechanism in colloidal crystal growth.¹⁵ The above experimental findings have been obtained at much lower concentrations, as mentioned above, than 0.50. They have been feared to be due to a dispersion-glass interface (wall) effect since only particles near ($1\text{--}2\ \mu\text{m}$ and at most $10\ \mu\text{m}$ away from) the glass wall could be observed. Thus we recently adopted a confocal laser scanning microscope (LSM), with which the "inside" structure ($50\ \mu\text{m}$ away from the interface) can be

studied.¹⁶ The study has demonstrated that the interparticle distance does not depend on the distance from the glass wall, confirming the previously obtained agreement^{17,18} of the spacings determined by the dynamic light scattering method and by the microscopic method. The LSM study also showed that void structures exist even inside the dispersion, and their cross section may be larger inside than near the interface.¹⁹ Considering also that Perrin's experiment on sedimentation equilibrium²⁰ was carried out by using a microscope and an acceptable value for the Avogadro number was obtained from the particle distribution determined on four focal planes at distances of 5 and $35\ \mu\text{m}$ away from the glass wall,²¹ the concern about the wall effect has considerably diminished.

These findings are easily interpreted if we accept the existence of a long-range attraction in addition to the widely accepted repulsion. In other words, the Sogami-type potential is preferred. The very reason why the DLVO potential and the Sogami potential led us to practically the same shear modulus and structure factor lies in the fact that the potential minimum between colloidal particles is very shallow (about kT in Sood's simulation²).

It is reminded that the non-space-filling localized ordered structure (the two-state structure) cannot be detected by the conventional scattering technique, since it manifests itself in a very low q range. This means that previous scattering experiments neither disprove the existence of the attraction nor prove the repulsion. In this respect, the scattering study in the low- q range is certainly interesting: Our most recent small-angle neutron-scattering experiments²³ show a sharp upturn of the scattering intensity between 0.01 and $0.001\ \text{\AA}^{-1}$ for polystyrene-sulfonate- D_2O solutions.²⁴ From the upturn, the radius of gyration of localized ordered domain for this ionic polymer was found to be, for example, $686\ \text{\AA}$ at $0.04\ \text{g/ml}$. By independent DLS measurements, Sedlak and Amis²⁶ found two relaxation processes for the same polymer in water, and they obtained therefrom the radius of gyration of the domain to be about $600\ \text{\AA}$ at $0.0456\ \text{g/ml}$. Agreement between the two groups is most satisfactory. The recent ultra-small-angle x-ray-scattering (USAXS) study^{27,28} appears to point to the upturn below about $10^{-3}\ \text{\AA}^{-1}$ for dispersions of a latex particle of $0.3\ \mu\text{m}$ diameter, in which a much larger localized structure than in the linear polymer solutions might be expected. Detailed quantitative analysis is in progress.

It would be of interest to make an additional remark of the Sogami potential being more realistic than the Yukawa potential. We note that the salt concentration dependencies of these potentials are different. As the salt concentration is increased, the Yukawa potential is simply lowered. When combined with van der Waals attractive component, as is conventionally done by colloid scientists, the so-called secondary minimum created by the Yukawa potential becomes deeper and deeper with salt concentration, as mentioned above briefly. This means that ordering of colloidal particles is more and more stabilized with increasing salt concentration. This is in complete contradiction to the widely recognized fact that the ordered structure is destroyed in the presence of

a large amount of salt. On the other hand, the potential minimum of the Sogami potential becomes first deeper with salt concentration and, after passing a minimum, it becomes shallower (see Figs. 2 and 3 of Ref. 4). This tendency is at least qualitatively in agreement with the observation and shows an advantage of the Sogami potential over the Yukawawa potential. Second, attention is drawn to the "reentrant phase transition" observed by Arora *et al.*²⁹ They found that latex dispersions "phase separate" into dense and rare phases only for a restricted range of salt concentration. Although it has been found in binary liquids,³⁰ this phase separation cannot be accounted for in terms of the Yukawa potential; the salt concentration dependence of the Sogami potential provides a reasonable explanation, as pointed out by Arora *et al.*

The Sogami potential has been a topic of considerable

debate.³¹ In our present argument, its accuracy is not important. The points we stress are the facts that (1) only repulsive interactions were considered by previous authors, (2) the contribution of an attractive component was not assessed at all, except by those referred to in Refs. 1–3, and (3) the attraction was nonetheless regarded to be unimportant. If the interparticle interaction was to be handled in a logical way, it would have been necessary to test an empirical (Sogami-like) potential containing repulsive *plus* attractive components. The claim that the attraction is unnecessary is obviously in contradiction to the recent experimental data.

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