

COMMENTARY

Paradoxes of the Repulsion-Only Assumption

It has been a widely accepted practice to treat the long-range interaction between charged colloidal particles as being purely repulsive.¹ This “repulsion-only assumption” at long range is inherent in the widely used DLVO (Derjaguin–Landau–Verwey–Overbeek) theory.^{1,2} However, recently introduced experimental techniques have begun to provide results that cannot be explained within this theoretical framework. These results clearly suggest the existence of a long-range attractive interaction between like-charged macroions in addition to the long-espoused repulsion. The inclusion of both attraction and repulsion at long range we refer to as the (long-range) attraction–repulsion assumption. The most conclusive of these findings have been obtained by scanning microscopic observation of void structures in highly purified dispersions. An example is shown in Figure 1.³ Figure 1a shows a random distribution pictured just after vigorous shaking of a latex dispersion, while Figure 1b shows huge void structures which developed in the dispersion after being left standing for 90 days at 23 °C. It should be noted that the dispersion in which such huge void structures were maintained was homogeneous on a macroscopic scale, forming a single phase. It would be fair to say that this type of microscopic structural inhomogeneity had not been previously anticipated from conventional analysis. However, structural inhomogeneities of various kinds have recently been observed, not only in colloidal dispersions but also in Langmuir–Blodgett films.^{4,5}

In this Commentary we restrict our consideration to colloidal systems and we address the recent controversy over the presence of long-range attraction between colloidal particles. To falsify the repulsion-only assumption (or demonstrate its incompatibility with experiments), we first consider two very clear cases.

The Effective-Sphere Concept and the Avogadro Number. Is Perrin's Sedimentation Experiment⁶ Wrong? In *Accounts* and also other journals, various phenomena in colloidal dispersions have been claimed to be explicable by introducing an enlarged-sphere concept, which is consistent with the repulsion-only assumption.^{7,8} For example, sedimentation equilibrium data on polymer latex particles were reported to be successfully described by assuming an “effective” radius (bare radius plus the Debye length $1/\kappa$) for the particles. Since Perrin obtained an Avogadro number (N_A) very close to 6.02×10^{23} by

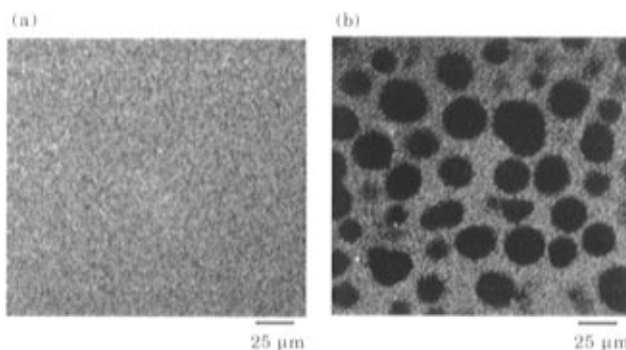


Figure 1. Laser scanning micrographs showing random distribution of latex particles (a) and void structures (b). The pictures were taken with an Ar laser (488 nm, 25 mW) and a $\times 63$ objective (N.A. 1.25) in a horizontal focus plane at a vertical distance of $22 \mu\text{m}$ inside from the coverslip–dispersion interface. Latex: N100 (polystyrene-based; diameter, $0.12 \mu\text{m}$; effective charge number, 1400/particle); latex concentration, 0.1%; dispersant, $\text{D}_2\text{O}-\text{H}_2\text{O}$ (1/1). The particles are shown as white dots, and the voids are seen as large black areas. Photograph a was taken just after shaking of the dispersion while b was photographed after it had been kept standing in a thermostated chamber (23 °C) for 90 days.

using the bare radius from his measurements, the use of the enlarged radius implies that (1) Perrin's analysis was wrong, (2) his experimental data were not correct, or (3) the recent measurements by Okubo were unacceptable, if N_A is to be 6.02×10^{23} . An independent check⁹ confirmed that, when the bare radius was employed, the correct value of N_A could be obtained from the sedimentation equilibrium experiments, ensuring that Perrin's analysis and experimental data are correct. This means that what was claimed to be a sedimentation equilibrium in Okubo's paper was something different. Although a separate paper¹⁰ has to be consulted for detail, it is judged from his paper that the particles “sedimented down” by an acceleration more than 10 times larger than 980 cm/s^2 . This is simply impossible.

Apart from the fundamental problem discussed above, as one of the reviewers pointed out, the effective-sphere concept has another paradoxical feature: when the particle concentration is lowered, the effective radius must increase, which should lead to packing transition. In real hard-sphere systems, however, this transition takes place due to an increase (not a decrease) in the sphere concentration.

Dialectical Error and Selective Choice of Evidence in the Previous Arguments in Favor of the Repulsion-Only Assumption. In the previous section, the repulsion-only assumption was demonstrated to be not generally correct. A similar kind of falsification would also be intrinsically possible for other phenomena that were claimed to be explicable by the repulsion-only assumption, but it appears rather difficult because of various adjustable parameters introduced into the theory

(1) Derjaguin, B. V.; Landau, L. *Acta Physicochim.* **1941**, *14*, 633. Verwey, E. J. W.; Overbeek, J. Th. G. *Theory of the Stability of Lyophobic Colloids*; Elsevier: Amsterdam, 1948.

(2) In the sense that two macroions or particles experience only repulsion electrostatically, the DLVO theory and the interpretation based thereupon are conveniently called the repulsion-only assumption.

(3) Void structures can be easily observed by ordinary microscopy and laser scanning microscope in highly purified latex dispersions. For microscopic pictures, see: (a) Ito, K.; Yoshida, H.; Ise, N. *Chem. Lett.* **1992**, 2081. (b) Doshio, S.; et al. *Langmuir*, **1993**, *9*, 394. (c) Ito, K.; Yoshida, H.; Ise, N. *Science* **1994**, *263*, 66. (d) Yoshida, H.; Ise, N.; Hashimoto, T. *J. Chem. Phys.*, in press.

(4) Uyeda, N.; et al. *Nature* **1987**, *327*, 319.

(5) Ringsdorf, H.; et al. *Science* **1993**, *259*, 213.

(6) Perrin, J. *Les Atomes*; Librairie Felix Alcan: Paris, 1913.

(7) Okubo, T. *J. Chem. Phys.* **1987**, *86*, 5182.

(8) Okubo, T. *Acc. Chem. Res.* **1988**, *21*, 281.

(9) Ito, K.; Ieki, T.; Ise, N. *Langmuir* **1992**, *8*, 2952.

(10) Yamanaka, J.; Matsuoka, H.; Kitano, H.; Ise, N. *J. Colloid Interface Sci.* **1990**, *134*, 92.

or interpretation, since "you cannot prove a vague theory wrong".¹¹ Although we would not follow the definition of Popper¹² to claim immediately that the interpretation in terms of the repulsion-only assumption cannot be judged as scientific, we would like to demonstrate that some of these arguments contain a dialectical (logical) error. In previous arguments, the structure factor,¹³ the elastic modulus,¹⁴ and the thermal compression¹⁵ of colloidal crystals were reported to be satisfactorily explained by the purely repulsive DLVO (or Yukawa) potential. However, it was later discovered¹⁶⁻¹⁸ that these properties can likewise be satisfactorily accounted for by the Sogami potential,¹⁹ which contains not only an (electrostatic) repulsive part but also an (electrostatic) attractive tail. It is thus logically impossible and also wrong to conclude that the Yukawa potential (and hence the repulsion-only assumption) is the only correct one. It is a dialectical error to claim, without disproving its opposite interpretation, that the repulsion-only assumption is correct.

In arguments in favor of the repulsion-only assumption, experimental data that do not support this assumption are not infrequently ignored. As an example, we mention here the work on thermal compression.¹⁵ In this work, the latex concentration was given to be 2%, and the nearest-neighbor distance in the ordered (bcc) structure was determined by the Kossel line analysis (2450 Å). Knowing the particle radius (415 Å), the particle concentration in the ordered region was calculated to be 2.64%. Simple arithmetic shows that the ordered structures at a higher latex concentration (2.64%) must coexist with regions of concentrations smaller than 2% (disordered regions or voids). This fact was completely ignored by Rundquist et al.,¹⁵ although such a structural inhomogeneity, or two-state structure, is one of the key phenomena indicative of an attractive interaction. It should be emphasized that our recent study²⁰ using ultra-small-angle X-ray scattering (USAXS) gave 5 orders of sharp Bragg diffraction for a colloidal silica dispersion (3.76 vol %), providing a nearest-neighbor interparticle spacing of 2600 Å compared with an average spacing of 2900 Å obtained from the particle concentration. In light of the fact that the former spacing was obtained from 5 orders of diffraction (not from a single peak or micrographic pictures of local structures as was usually the case in our previous studies), the USAXS data is most conclusive evidence for the two-state structure.

The Overbeek Correction and the Gibbs–Duhem Relation. As mentioned above, Sogami's pair potential contains repulsive and attractive parts, at variance with the DLVO potential. Overbeek criticized the Sogami theory and claimed that the attractive part disappears *exactly* if the contribution of the solvent is duly taken

into account.²¹ However, Overbeek's argument is thermodynamically incorrect, as pointed out by us,^{3b,22} because it violates the Gibbs–Duhem relation. It should be noted that this violation resulted from ignoring the contribution (to the chemical potential) of macroions (latex particles) in comparison with the small-ion contribution. According to Smalley,²³ inclusion of the solvent to account for the "error" in the Sogami theory leads to the unacceptable conclusion that there is no free energy associated with the electrical double layers.²⁴ In other words, as one of the reviewers pointed out, Overbeek was considering an entirely different model, and his argument is not a satisfactory refutation of the Sogami theory.

Even though it is unacceptable thermodynamically, Overbeek's criticism has surprisingly often^{25,26} been taken as having disproved the Sogami theory. Furthermore, in conferences we have often come across the assertion that Overbeek's violation of the Gibbs–Duhem relation is justifiable because the motion of macroions is assumed to be adiabatically cut off from that of counterions in the Sogami theory. This argument is also basically wrong. The Gibbs–Duhem relation refers to the relative change of the chemical potentials of components at constant pressure and temperature and has nothing to do with the adiabatic condition. If this claim *were* correct, we are led to the curious situation in which the Gibbs–Duhem relation need not be valid for atoms and molecules, since they are described on the basis of the Born–Oppenheimer (adiabatic) approximation.

Recent Measurements of Interparticle Potential.

It would be most desirable if the interparticle potential could be measured directly or independently. Recent technical developments have made it possible to measure the surface force between two surfaces. For example, a repulsive interaction was detected between mica surfaces in salt solution using the surface force apparatus (SFA).²⁷ Using an atomic force microscope (AFM), repulsive forces were detected between silica particles and a silica plate,²⁸ between spherical latex particles,²⁹ and also between a sphere and a plate of titanium dioxide.³⁰ A common characteristic of these studies is the fact that the distance investigated is relatively short. The original authors pointed out that the repulsive forces were more or less in agreement with the DLVO theory, leaving an impression that the DLVO theory is the only correct one and these direct measurements disproved the presence of an attraction. This impression is wrong, since the Sogami theory also predicts a repulsive interaction at such short distances. The attractions which have been observed and discussed in terms of the Sogami theory appear at much longer distances (about 1 μm for particles studied microscopically). In this regard, it has to be pointed out that direct measurements by SFA and AFM were carried out up to, at most, 1000 Å. Clearly these direct measure-

(11) Feynman, R. *The Character of Physical Law*; MIT Press: Cambridge, MA: 1965; Chapter 7.

(12) Popper, K. *The Logic of Scientific Discovery*; Hutchinson: London, 1959; Chapter 1, Section 6. Sir Popper states, "I shall certainly admit a system as empirical or scientific only if it is capable of being tested by experience. These considerations suggest that not the verifiability but the falsifiability of a system is to be taken as a criterion of demarcation. It must be possible for an empirical scientific system to be refuted by experience."

(13) For example: Härtl, W.; Versmold, H.; Wittig, U. *Ber. Bunsenges. Phys. Chem.* **1984**, *81*, 1063.

(14) Lindsay, M.; Chaikin, P. M. *J. Chem. Phys.* **1982**, *76*, 3774.

(15) Rundquist, P. A.; Jagannathan, S.; Kesavamoorthy, R.; Brnardic, C.; Xu, S.; Asher, A. S. *J. Chem. Phys.* **1991**, *94*, 711.

(16) Sood, A. K. In *Solid State Physics*; Ehrenreich, H., Turnbull, D., Eds.; Academic Press: New York, 1991; Vol. 45, p 1.

(17) Ito, K.; Sumaru, K.; Ise, N. *Phys. Rev. B* **1992**, *46*, 3105.

(18) Ise, N.; Smalley, M. V. *Phys. Rev. B* **1994**, *50*, 16722.

(19) Sogami, I.; Ise, N. *J. Chem. Phys.* **1984**, *81*, 6320.

(20) Konishi, T.; Ise, N.; Matsuoka, H.; Yamaoka, H.; Sogami, I. S.; Yoshiyama, T. *Phys. Rev. B* **1995**, *51*, 3914.

(21) Overbeek, J. Th. G. *J. Chem. Phys.* **1987**, *87*, 4406.

(22) Ise, N.; Matsuoka, H.; Ito, K.; Yoshida, H.; Yamanaka, J. *Langmuir* **1990**, *6*, 296, footnote 32.

(23) Smalley, M. V. *Mol. Phys.* **1990**, *71*, 1251.

(24) For further detailed discussion, see: Schmitz, K. S. *Macroions in Solution and Colloidal Suspensions*; VCH Publishers: New York, 1993; Chapter 4.

(25) Wang, L.; Bloomfield, V. A. *Macromolecules* **1991**, *24*, 5791; **1992**, *25*, 5266. Weil, G. J. *Phys. (Paris)* **1988**, *49*, 1049. Okubo, T. Reference 8; *Polymer Applications* **1988**, *14*, 223 (in Japanese); *J. Chem. Phys.* **1988**, *88*, 6581. Badirkhan, Z.; Tosi, M. P. *Phys. Chem. Liq.* **1990**, *21*, 177.

(26) Vondermassen, K.; et al. **1994**, *10*, 1351.

(27) Pashley, P. M.; Israelachvili, J. N. *J. Colloid Interface Sci.* **1984**, *101*, 511.

(28) Ducker, W. A.; Senden, T. J.; Pashley, R. M. *Nature* **1991**, *353* 239; *Langmuir* **1992**, *8*, 1831.

(29) Li, Y. Q.; Tao, N. J.; Pan, J.; Garcia, A. A.; Lindsay, S. M. *Langmuir* **1993**, *9*, 1831.

(30) Larson, I.; Drummond, C. J.; Chan, D. Y. C.; Grieser, F. J. *Am. Chem. Soc.* **1993**, *115*, 11885.

ments do not disprove either the attraction or the Sogami theory, nor do they prove the DLVO theory.

An independent method to find the interparticle potential is the determination of the pair correlation function²⁶ for colloidal particles. Kepler and Fraden detected both the repulsive component and the attractive tail for latex particles confined between two glass plates.³¹ They compared the potential curve with the DLVO theory including the van der Waals attraction and found that the attraction was so strong that the Hamaker constant had to be adjusted to $1-33 \times 10^{-19}$ J, several orders of magnitude larger than the previously found value. When Tata and Arora analyzed these results,³² they rejected the idea of the original authors that the observed attraction arose from the electrostatic influence of the confining glass plates, and they demonstrated that the curve (the position of the potential minimum and its depth) could be satisfactorily reproduced by the Sogami theory, as seen from Figure 2, which gives the potential-distance curve observed and that (dashed curve) calculated by Tata and Arora. Although they did not interpret it in this way, the work of Kepler and Fraden is the first direct experimental demonstration of the existence of a long-range attraction in colloidal dispersions.³³

We have shown above some of the imperfections of the repulsion-only assumption that can be demonstrated in

(31) Kepler, G. M.; Fraden, S. A. *Phys. Rev. Lett.* **1994**, *73*, 356.

(32) Tata, B. V. R.; Arora, A. K. *Phys. Rev. Lett.* **1995**, *75*, 3200.

(33) By using a similar principle as Kepler and Fraden, Crocker and Grier observed only repulsion (ref 34). They stated that the "qualitative agreement between our measurement and the DLVO theory is excellent with no statistically significant evidence of a long-range attraction." However, Tata and Arora (ref 35) demonstrated using the parameter values charge number = 320, particle concentration = 2×10^{11} mL⁻¹, salt concentration = $0.4 \mu\text{M}$ that the Sogami theory predicts a repulsion and a very shallow potential minimum ($-0.09k_B T$) at a distance of 7.15 radii, which cannot be detected experimentally. This implies that the results reported by Crocker and Grier are in accordance with the Sogami theory. Vondermassen et al. (ref 26) carried out a similar experiment and stated that the results do not indicate an attraction. According to the Sogami theory, the attraction is weak when the charge number of particles is small, it becomes stronger with increasing charge number, and, passing a maximum, it becomes again weak. The particles of Vondermassen had only $190e$ (e : electronic charge), so that they could not detect the attraction. Thus their results are also predictable by the Sogami theory.

(34) Crocker, J. C.; Grier, D. G. *Phys. Rev. Lett.* **1994**, *73*, 352.

(35) Tata, B. V. R.; Arora, A. K. To be published.

(36) Ito, K.; Okumura, H.; Yoshida, H.; Ise, N. *Phys. Rev. B* **1990**, *41*, 5403. Yoshida, H.; Ito, K.; Ise, N. *J. Chem. Soc., Faraday Trans.* **1991**, *87*, 371.

(37) Arora, A. K.; Tata, B. V. R.; Sood, A. K.; Kesavamoorthy, R. *Phys. Rev. Lett.* **1988**, *60*, 2438.

(38) Tata, B. V. R.; Rajalakshmi, M.; Arora, A. K. *Phys. Rev. Lett.* **1992**, *69*, 3778.

(39) Compare parts a, b, and c of Figure 14 and see Remarks 4 in ref 1b. Thomas, R.; et al. *J. Phys. Chem.* **1993**, *97*, 13907. Ito, K.; Kuramoto, T.; Kitano, H. *J. Am. Chem. Soc.* **1995**, *117*, 5005.

(40) Langmuir, I. *J. Chem. Phys.* **1938**, *6*, 873.

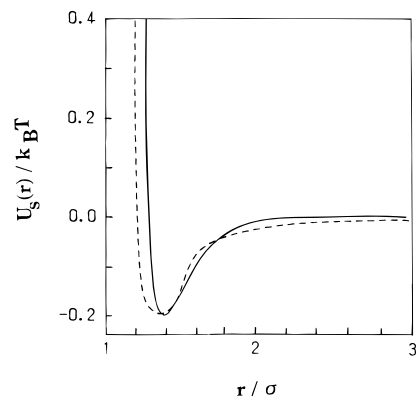


Figure 2. Comparison of the potential curve at a particle density of $3.8 \times 10^{-3}/\mu\text{m}^2$ found by Kepler and Fraden,³¹ with the Sogami potential (dashed curve) calculated by Tata and Arora (salt concentration = $2.9 \mu\text{M}$).

the light of fundamental factual knowledge and logical criteria. More and more experimental evidence is being accumulated which is in disagreement with this assumption. Besides the void formation, the Ostwald ripening mechanism in colloidal crystal growth,³⁶ re-entrant phase separation,³⁷ vapor-liquid condensation,³⁸ and positive adsorption of ionic species near a like-charged interface³⁹ can be understood without additional *ad hoc* assumptions if we accept the attraction-repulsion assumption. Finally, it should be mentioned that the attraction-repulsion assumption corrects "one of three fallacies in the theories of colloidal structure" pointed out by Langmuir.⁴⁰

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