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# Repulsion-Only Assumption or the Long-Range Attraction–Repulsion Assumption?

**Norio Ise**[*,†] **and Hideki Matsuoka**[‡]

*Fukui Research Laboratory, Rengo Company, Ltd., 10-8-1 Jiyugaoka, Kanazu-cho, Sakai-gun, Fukui 919-06, Japan, and Department of Polymer Chemistry, Kyoto University, Kyoto 606-01, Japan*

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The interaction between macroions or between colloidal particles has often been discussed in terms of the repulsion-only assumption (the DLVO[1] or Yukawa potential), and actually fairly satisfactory agreement with experiments has been obtained. However, recently introduced experimental techniques started to provide results that cannot be explained with this assumption.[2] These results positively indicate the presence of a long-range attractive interaction in addition to the widely accepted repulsion, as shown in the Sogami potential.[3] (Let us call it the long-range attraction–repulsion assumption.) The presence of the long-range attraction has been criticized on various grounds by those who take the repulsion-only assumption for granted. We pointed out basic errors involved in these criticisms and also in the traditional analysis in terms of the repulsion-only assumption.

The errors are divided into two categories, factual and logical. In this paper, we point out one of the factual errors found in recent publication. Ferrari and Bloomfield[4] stated that "a model in which purely repulsive electrostatic interactions lead to clustering was proposed by Ise et al." and referred to one of our previous publications on small-angle X-ray scattering (SAXS) experiments of sodium polyacrylates.[5] The statement cited above is totally untrue. In this paper we claimed ordering of polyacrylate ions and found that the Bragg spacing between the macroions ($2D_{\mathrm{exp}}$) was smaller than the average inter-macroion spacing ($2D_0$) obtained from the concentration. From this fact, we pointed out that a two-state structure was maintained in the solutions and that the $2D_{\mathrm{exp}} < 2D_0$ relation reflects the *importance of the attractive interaction between macroions through the intermediary of their gegenions.* As the italicized statement (taken from the abstract of ref 5) shows clearly, we have *never* invoked a purely repulsive interaction to account for the observed structure formation of macroions and colloidal particles.

Ferrari and Bloomfield reported further that "the model (supposedly proposed by Ise et al.) has been shown by Overbeek[6] to be invalid". This is again untrue and incredible for two reasons. First, Overbeek criticized, not the SAXS paper, but a theoretical paper by Sogami and Ise,[3] in which a long-range, electrostatic attractive interaction, in addition to widely accepted repulsive interaction, was demonstrated to exist. Overbeek tried to disprove the existence of the attraction (not repulsion), though in a thermodynamically unacceptable way. This fact was not correctly understood by Ferrari and Bloomfield. As pointed out by one of the reviewers, if indeed Overbeek showed that the "repulsion-only assumption" was wrong, the comment of Ferrari and Bloomfield would be more confusing, since the electric part of the DLVO potential (or Yukawa potential) itself is "purely repulsive". Second, these authors again failed to realize Overbeek's violation of the Gibbs–Duhem relation, as was the case in another paper from the group.[7] Overbeek professed that the attractive tail in the Sogami potential exactly disappears, if the role of solvent is taken into account. This blunder was pointed out by us in a footnote of a review article.[8] Smalley further made clear that Overbeek's omission of the macroion contribution led to the implausible conclusion that "there is no energy associated with the electrical double layers".[9] Since such a situation is physically implausible, Overbeek's criticism must be unacceptable, as Schmitz pointed out recently.[10]

This violation of a thermodynamic axiom for multi-component systems is an example of the logical errors made in criticisms of the attraction–repulsion assumption. It is reminded here that, if Overbeek's argument *were* correct and if the attractive term really exactly disappears by introducing the solvent correction, the remaining repulsive terms, which Overbeek would probably accept, do not satisfy the Gibbs–Duhem relation. Although the detail should be referred to the monograph by Schmitz,[10] furthermore, Smalley's argument indicates that Overbeek's position should not be applied to the Sogami theory without losing the self-consistency, in other words, unless one accepts an implausible situation in the Overbeek–Verwey theoretical framework.[1] Since it is experimentally unacceptable that no electric energy is associated with electrical double layers, Overbeek's criticism lacks logical consistency.

For the readers' convenience, some other logical errors are worth considering here. First, the enlarged sphere concept, which is in line with the repulsion-only assumption and had been invoked by so many authors to account for colloidal phenomena, has been pointed out to lead to the indisputably unacceptable conclusion that Avogadro's number may not be $6.02 \times 10^{23}$.[11] Second, the computer-simulation work by Sood et al.[12] and the analysis by Ito et al.[13] have shown that both the DLVO potential and Sogami potential give almost equally satisfactory agreement with the observed structure factor and elastic modulus of colloidal dispersions. This means that previous arguments in favor of the DLVO potential cannot be justified, since the Sogami potential was not disproved experimentally. We will discuss a similar dialectical error in more recent publications shortly, for example, for photothermal compression of colloidal crystals.[14]

Since it is a part of the whole picture, though it concerns another paper, we mention another recent criticism by Overbeek[15] against a treatment of the interaction of electric double layers given by Sogami, Shinohara, and Smalley (SSS).[16] It was stressed by SSS that an attractive tail exists between two charged parallel plates immersed in an electrolyte solution, at variance with the DLVO theory. Overbeek claimed that SSS missed two nonelectric terms and, if these terms were tacked on to the SSS theory, the (purely repulsive) DLVO theory is recovered. Sogami and Smalley, however, demonstrated in a recent paper that including either or both of the two terms led to the system not being at thermal equilibrium[17] and pointed out that the equilibrium swelling of *n*-butylammonium vermiculite gels (best characterized one-dimensional colloid systems) is governed by the SSS concept with the Dirichlet boundary condition but not by the DLVO theory.

In conclusion, it is reemphasized that, without additional ad hoc assumptions, the long-range attractive interaction between like-charged ionic species through the intermediary of counterions, and hence the attraction–repulsion assumption, can account for the following recent experimental findings: (1) the two-state structure, namely,

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[†] Fukui Research Laboratory, Rengo Co., Ltd. Telephone: 776-73-7032. Fax: 776-73-7041.

[‡] Kyoto University.

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coexistence of localized ordered structures with disordered solutes,[2,5,18] (2) the interparticle spacing smaller than the average spacing,[2,5,18] (3) Ostwald ripening,[19] (4) reentrant phase separation,[20] (5) vapor–liquid phase equilibrium,[21] (6) void structures,[2,22,23] and (7) the positive adsorption of ionic solutes near a like-charged layer.[2,24-26] While the repulsion-only assumption would be apparently valid in limited cases such as highly concentrated solutions or dispersions, the attraction–repulsion assumption is correct in general cases.

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