

# On the electrostatic interaction in macroionic solutions and suspensions

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It is shown that the theory of Sogami and Ise leading to an attraction between particles with charges of the same sign contains errors. When the errors are corrected the calculated attraction disappears.

## INTRODUCTION

Ise and co-workers<sup>1-7</sup> have been pointing out over many years that suspended particles with high charge in aqueous solutions, such as polyelectrolytes, latex particles, and micelles, may form ordered structures and they have argued that this order is caused by attraction between the like charged particles through the intermediate of counterions.

In two papers by Sogami<sup>8</sup> and Sogami and Ise<sup>9</sup> a theory for this attraction has been given. The theory was based on the calculation of the electrical contribution to the free energy of the whole suspension. The calculations were performed using the linearized Poisson-Boltzmann equation, assuming constant charge on each particle and using the so-called "primitive model," in which the solvent is treated as a continuum with dielectric constant,  $\epsilon$ .

The free energy contained terms related to the self-energy, to the ionic atmospheres around individual particles, and to the electrical interaction between pairs of particles. In the Helmholtz free energy  $F$  the pair interaction was a pure repulsion with an  $[\exp(-\kappa R_{mn})]/R_{mn}$  dependence on the distance  $R_{mn}$  between the centers of the spherical particles  $m$  and  $n$ .  $\kappa$  is the reciprocal Debye length. Then, rather surprisingly, the Gibbs free energy  $G$  as calculated from the Helmholtz free energy showed a minimum in the pair interaction with an attraction for large distances and a repulsion for short distances.

Since one is dealing with excess quantities, due to electrical effects, it is quite unexpected that such a large, qualitative difference between  $F$  and  $G$  is found in a condensed virtually incompressible system. This made it worth while to check again whether the theory was correct.

## BRIEF DESCRIPTION OF SOGAMI AND ISE'S THEORY

In Sogami and Ise's paper<sup>9</sup> the Helmholtz free energy of the suspension with the particles assumed to be in fixed positions is written

$$F = F' + F^{\text{el}} = F' + E_{\text{self}} + \sum_n V_n^F + \frac{1}{2} \sum_{m \neq n} U_{mn}^F, \quad (1)$$

where  $F'$  is the free energy with all particles and small ions discharged and  $F^{\text{el}}$  is due to the charging process. For spherical particles,

$$E_{\text{self}} = \sum_n \frac{(Z_n e)^2}{2\epsilon a_n}, \quad (2)$$

$$V_n^F = \frac{(Z_n e)^2}{4\epsilon \kappa a_n^2} (1 - e^{-2\kappa a_n} - 2\kappa a_n), \quad (3)$$

$$U_{mn}^F = Z_m Z_n e^2 \frac{\sinh \kappa a_n \sinh \kappa a_m \exp(-\kappa R_{mn})}{\kappa^2 a_n a_m \epsilon R_{mn}}, \quad (4)$$

$Z_n e$  is the uniformly distributed surface charge of the  $n$ th particle with radius  $a_n$ .  $\kappa$  is the inverse Debye length based on the average concentrations of the small ions ( $n_{i0}$ ) with charge numbers  $z_i$ , that compensate the charges on the particles:

$$\kappa^2 = \frac{4\pi e^2}{\epsilon k T} \sum_i n_{i0} z_i^2 \quad \text{and} \quad \sum_i n_{i0} z_i + \frac{1}{V} \sum Z_n = 0, \quad (5)$$

where  $V$  is the volume of the solution.

For what follows the precise form of Eqs. (2), (3), and (4) is not important, but it is important that  $E_{\text{self}}$  and  $V_n^F$  are independent of the positions of the particles, whereas  $U_{mn}^F$  contains the relative positions of the particles explicitly. In all terms the composition of the solution only manifests itself through the Debye length  $1/\kappa$ .

The Gibbs free energy  $G$  is now written as

$$G = \left[ \sum_i n_{i0} \left( \frac{\partial F}{\partial n_{i0}} \right)_{V,T} \right]_{V=V(T,P)}, \quad (6)$$

and it is said that "the contribution from macroions is included in this expression through the charge balance equation." For  $N_{\text{part}}$  identical macroions, each with charge number  $Z_n$ ,  $G$  is then transformed into

$$G = \left[ \sum_i n_{i0} \left( \frac{\partial F}{\partial n_{i0}} \right)_{V,T,Z_n} + N_{\text{part}} Z_n \left( \frac{\partial F}{\partial Z_n} \right)_{V,T,N_{\text{part}}} \right]_{V(P,T)}. \quad (7)$$

Straightforward algebra then leads to

$$G = G' + 2E_{\text{self}} + \sum_n V_n^G + \frac{1}{2} \sum_{m \neq n} U_{mn}^G, \quad (8)$$

with

$$U_{mn}^G = U_{mn}^F \times \left( \frac{2 + \kappa a_m \coth \kappa a_m + \kappa a_n \coth \kappa a_n - \kappa R_{mn}}{2} \right), \quad (9)$$

which thus is negative above a certain value of  $R_{mn}$ , implying attraction between the particles.

In principle the thermodynamic properties of the suspension can now be found, leaving the position of the particles and thus  $R_{mn}$  free, by using statistical thermodynamics with  $U_{mn}^G$  as the pair interaction potential.

## CRITICISM AND CORRECTION

Unfortunately Eqs. (6) and (7) are not correct. If one wants to calculate  $G$  as

$$G = \sum_j N_j \tilde{\mu}_j = \sum_j N_j \left( \frac{\partial F}{\partial N_j} \right)_{V,T,N_{i \neq j}}, \quad (10)$$

where  $\tilde{\mu}_j$  and  $N_j$  are the electrochemical potential and the number of molecules (or ions) of component  $j$ , one has to sum over *all* components of the system. It is all right to calculate  $F$  in the first place using the "primitive model" and treat the solvent as a dielectric continuum. But, nevertheless, the solvent molecules carry part of the electrical free energy due to the existence of a Gibbs–Duhem relation between  $d\mu_{\text{solvent}}$  and the variation of the electrochemical potentials of the ions. Therefore, the solvent is one of the components  $j$ . As soon as the contribution of the solvent is included in Eq. (10), which replaces Eq. (7), the attractive branch and the minimum in  $U_{mn}^G$  disappear. The various kinds of small ions,  $i$ , are further components, as already recognized in Eq. (7).

Finally the particles with their surface charges contribute to the Gibbs free energy. Sogami and Ise<sup>9</sup> assumed that the " $Z_n$  univalent immobile charges" on the  $n$ th particle should be treated as a component and that their chemical potential is given by  $(\partial F / \partial Z_n)_{V,T,n}$ . This is not correct, since, in the original equations for  $F$ , the particles are assumed to have a constant charge and *no mechanism* is in-

cluded for charge variation by adsorption or dissociation with the concomitant changes in nonelectrical free energy. One may add or subtract a whole particle, charge and all, but the charge number  $Z_n$  should not be changed.

However, so long as the individual particle positions are considered to be fixed (at  $R_n$  for the  $n$ th particle) changing the number,  $N_{\text{part}}$ , of particles is not a meaningful process. One therefore cannot separate the contribution of the particles to the free energy into contributions of individual particles and thus one must write

$$G = N_{\text{solv}} \mu_{\text{solv}} + \sum_i N_i \tilde{\mu}_i + G_{\text{part}} = F + PV, \quad (11)$$

where  $G_{\text{part}}$  is the contribution of all the particles to  $G$ .

## CALCULATIONS

Instead of using as in Eq. (10)

$$\tilde{\mu}_j = \left( \frac{\partial F}{\partial N_j} \right)_{V,T,N_{i \neq j}} \quad (12)$$

which is somewhat awkward on account of the requirement  $V = \text{const}$ , we use

$$\tilde{\mu}_j = \left( \frac{\partial F}{\partial N_j} \right)_{P,T} + P \left( \frac{\partial V}{\partial N_j} \right)_{P,T}. \quad (13)$$

We shall first deal with the contributions of the solvent and the small ions.

$$\begin{aligned} N_{\text{solv}} \mu_{\text{solv}} + \sum_i N_i \tilde{\mu}_i &= N_{\text{solv}} \left( \frac{\partial F'}{\partial N_{\text{solv}}} \right)_{P,T} + \sum_i N_i \left( \frac{\partial F'}{\partial N_i} \right)_{P,T} \\ &+ PN_{\text{solv}} V_{\text{solv}} + P \sum_i N_i V_i + N_{\text{solv}} \left( \frac{\partial F^{\text{el}}}{\partial N_{\text{solv}}} \right)_{P,T} + \sum_i N_i \left( \frac{\partial F^{\text{el}}}{\partial N_i} \right)_{P,T} = F'_{\text{solution}} + PV_{\text{solution}} \\ &+ \frac{\partial F^{\text{el}}}{\partial(\kappa^2)} \left\{ N_{\text{solv}} V_{\text{solv}} \frac{\partial(\kappa^2)}{\partial V_{\text{solution}}} + \sum_i N_i \left( V_i \frac{\partial(\kappa^2)}{\partial V_{\text{solution}}} + \frac{\partial(\kappa^2)}{\partial N_i} \right) \right\} \\ &= G'_{\text{solution}} + \frac{\partial F^{\text{el}}}{\partial(\kappa^2)} \left\{ -V_{\text{solution}} \frac{\kappa^2}{V_{\text{solution}}} + \kappa^2 \right\} = G'_{\text{solution}}, \end{aligned} \quad (14)$$

where the subscript solution includes all solvent and small ions, but not the particles with their charges.  $V_j$  represents the molecular volume of  $j$ . Note that  $F^{\text{el}} \neq 0$ , but  $V^{\text{el}} = 0$ , since  $V^{\text{el}}$  means the change in volume during the charging process conducted at constant numbers of ions and solvent molecules, with all particles at fixed positions,  $R_n$ .

This remarkable result shows that the solvent and the small ions together just give a zero contribution to  $G^{\text{el}}$  (and incidentally also to  $F^{\text{el}}$ ). The same result can be obtained in a more simple way, which also shows that the result is quite general, independent of the specific form of  $F^{\text{el}}$ .

$$\begin{aligned} N_{\text{solv}} \mu_{\text{solv}}^{\text{el}} + \sum_i N_i \tilde{\mu}_i^{\text{el}} \\ = \int_{e=0}^{e=e} \left( N_{\text{solv}} d\mu_{\text{solv}}^{\text{el}} + \sum_i N_i d\tilde{\mu}_i^{\text{el}} \right)_{P,T} = 0. \end{aligned} \quad (15)$$

The integral describes the Debye–Hückel type charging process, which has also been used in the calculations of  $F^{\text{el}}$  and

the integrand is zero on account of the Gibbs–Duhem relation in the solution.

The term  $-\kappa R_{mn}$  in Eq. (9), which resulted in the attraction between the particles had its origin in the term  $\kappa^2$  ( $\partial F^{\text{el}} / \partial \kappa^2$ ), derived from  $\sum N_i \tilde{\mu}_i$  in Eq. (11). Now this term is exactly canceled by the corresponding term derived from the contribution of the solvent as shown in Eqs. (14) and (15) and that is why the attraction in  $G$  disappears.

Now we have to add the contribution of the particles to  $G$ :

$$\begin{aligned} G_{\text{total}} &= G'_{\text{solution}} + G'_{\text{part}} + G^{\text{el}}_{\text{part}} \\ &= F' + PV_{\text{solution}} + PV_{\text{part}} + F^{\text{el}} = G'_{\text{total}} + F^{\text{el}}, \end{aligned} \quad (16)$$

and thus

$$G^{\text{el}}_{\text{part}} (= G^{\text{el}}_{\text{total}}) = F^{\text{el}},$$

and in particular,

$$U_{mn}^G = U_{mn}^F, \quad (17)$$

showing that the interaction between the particles is the same at constant  $T$  and  $P$  as it is at constant  $T$  and  $V$  and thus the interaction is a pure repulsion according to Eq. (4).

It is with some irony that we now point to a remark made by Fowler and Guggenheim.<sup>10</sup> They state that if the volume is unaffected by pressure and by the charge of the ions the Debye-Hückel charging process [which was also used to derive Eq. (1)] leads to the electrical contribution  $F^{\text{el}}$  to the Helmholtz free energy, which is then indistinguishable from  $G^{\text{el}}$ . But if the charging process entails a change in volume and is carried out at constant pressure  $G^{\text{el}}$  rather than  $F^{\text{el}}$  is the electrical free energy found. Thus we might have used this argument to state that Eqs. (1)–(4) already represent Gibbs rather than Helmholtz free energies. That, however, would not have clarified, how Refs. 8 and 9 arrived at an incorrect expression for  $G^{\text{el}}$ .

## CONCLUSION

The claim in Sogami's and Ise's papers<sup>8,9</sup> that  $G^{\text{el}}$  leads to an attraction between particles is incorrect. The experimental data presented in papers 1 through 7 and in other similar publications will have to be explained in a different way.

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