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Thermodynamics of the Screened Coulomb Pair Potential[†]

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The thermodynamics of a screened Coulomb potential of the Yukawa-type is examined in detail. It is shown that, as a consequence of the screening term, the Gibbs and Helmholtz free energies are not equal. Furthermore, the Gibbs form has an attractive tail. The well-known Derjaguin−Landau−Verwey−Overbeek (DLVO) and the Sogami−Ise theories are compared, and attempts to eliminate the attractive tail are discussed in detail. Parallels are found in the phase transitions in charged colloid systems and the van der Waals gas, with particular emphasis on the "internal pressures" and "excluded volumes". On the basis of computer simulations, it is concluded that the screened Coulomb interaction is inadequate for describing systems that have many-body interactions. A new interpretation of the stability of void regions within a charged colloid system is presented.

1. Introduction

On February 5, 1857, Michael Faraday gave his Bakerian lecture to the Royal Society in London on the relationship between light and suspended metallic particles. The focus of the lecture was on the properties of "ruby gold" and the wave nature of light. He concluded that the color resulted from dispersed gold particles that were too small to be seen by any optical device of his day. A testimony to the stability of colloidal gold is that one sample survived to the second World War, when it was accidently destroyed.

Charged colloidal systems are very complex in nature, both because of the variety of components and the long-range nature of electrical interactions. In general, the colloid system is composed of highly charged particles of size in the nanometer range, the neutralizing counterions, added electrolyte, and polar solvent. A step toward simplifying the characterization of such a complex system is the averaging of the effects of the microions and solvent, which provide a uniform milieu in which the macroions are suspended. Thus, a multicomponent system is reduced to an effective one-component system in which only the positions of the charged colloids are considered. Theories that use this approach generally incorporate a "screening parameter", κ, to reflect the bulk electrical properties of the milieu. The theoretical description of the system is further simplified in the infinite dilution limit in which only the interaction between a pair of colloidal particles is considered.

Such a model is described in the account of the DLVO (Derjaguin−Landau−Verwey−Overbeek) potential given by Verwey and Overbeek[1] in 1948. The DLVO potential is composed of a repulsive screened Coulomb interaction and an ad hoc introduction of a van der Waals attraction term. For the particles I and J separated by the center-to-center distance $r_{\mathrm{I,J}}$, the DLVO Helmholtz free energy is of the general form,

$$A_{\mathrm{I,J}}^{\mathrm{DLVO}}(r_{\mathrm{I,J}}, \kappa) = A_{\mathrm{I,J}}^{\mathrm{DLVO,elec}}(r_{\mathrm{I,J}}, \kappa) - A_{\mathrm{I,J}}^{\mathrm{vdW}}(r_{\mathrm{I,J}}) \quad (1.1)$$

where κ is the screening parameter.

In their derivation of the electrical interaction between pairs of charged particles, Verwey and Overbeek assumed that the electrical work and chemical work at the surface of the macroparticle exactly cancel each other, and in their own words,[1] the "very simple result is that we find the total free energy of the double layer if only we calculate the *electrical* work necessary to discharge stepwise all ions of the *solution*".

Thus, Verwey and Overbeek viewed the interaction between charged colloidal particles as acting solely through their respective counterion clouds or double layers. Their result for the Helmholtz free energy of the electrical double layer interaction for spherical particles takes on the simplified form,

$$A_{\mathrm{I,J}}^{\mathrm{DLVO,elec}}(r_{\mathrm{I,J}}, \kappa) = U_{\mathrm{I,J}}^{\mathrm{C}}(r_{\mathrm{I,J}}) B_{\mathrm{I,J}}(\kappa)^{\mathrm{DLVO}} \exp(-\kappa r_{\mathrm{I,J}}) \quad (1.2)$$

In eq 1.2 $U_{\mathrm{I,J}}^{\mathrm{C}}(r_{\mathrm{I,J}})$ is unscreened pairwise Coulomb interaction

$$U_{\mathrm{I,J}}^{\mathrm{C}}(r_{\mathrm{I,J}}) = \frac{Z_I Z_J e^2}{\varepsilon r_{\mathrm{I,J}}} \quad (1.3)$$

where e is the magnitude of the electron charge, ε is the bulk dielectric constant, a_{K} is the radius of the K-th particle, Z_{K} is the magnitude of the charge (with sign) of the K-th particle, and $B(\kappa)^{\mathrm{DLVO}}$ is the form factor for the DLVO potential,

$$B_{\mathrm{I,J}}(\kappa)^{\mathrm{DLVO}} = \left(\frac{\exp(\kappa a_{\mathrm{I}})}{1 + \kappa a_{\mathrm{I}}}\right)\left(\frac{\exp(\kappa a_{\mathrm{J}})}{1 + \kappa a_{\mathrm{J}}}\right) \quad (1.4)$$

Since they used the term "free energy", represented by F, without identifying it with either the Gibbs free energy (G) or the Helmholtz free energy (A), one may conclude Verwey and Overbeek assumed their equivalence in the DLVO theory. This conclusion is based on the assumption that the external pressure and total volume of the system remains constant, that is,

$$\Delta G - \Delta A = \Delta(PV) = 0 \quad (1.5)$$

Within the context of the DLVO potential, colloid stability is obtained as long as the screening parameter is sufficiently small such that $A_{\mathrm{I,J}}^{\mathrm{DLVO,elec}}(r_{\mathrm{I,J}},\kappa) > A_{\mathrm{I,J}}^{\mathrm{vdW}}(r_{\mathrm{I,J}})$. Phase instability is brought on when $A_{\mathrm{I,J}}^{\mathrm{DLVO,elec}}(r_{\mathrm{I,J}},\kappa) < A_{\mathrm{I,J}}^{\mathrm{vdW}}(r_{\mathrm{I,J}})$. It is emphasized that the

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van der Waals interaction $A_{I,J}^{vdW}(r_{I,J})$ is very short ranged; thus, the instability corresponds to a flocculation transition in which the particles are in physical contact.

For several years, Ise and co-workers reported two-state structures in charged colloid systems in which the interparticle separation distance was less than that expected based on concentration but much larger than that for the van der Waals attraction.[2−4] In an attempt to account for these observations, Sogami and Ise[5] (SI) proposed a model in which the screened Coulomb term itself has both repulsion and attraction components. A crucial point in their model is that the Gibbs and Helmholtz free energies are not equal. They proposed that the relationship between the Gibbs free and Helmholtz free energies was, in their notation, of the form,

$$G = \left[\sum_{i} n_{i0}\left(\frac{\partial A}{\partial n_{i0}}\right)_{V,T,Z} + \sum_{n} Z_{n}\left(\frac{\partial A}{\partial Z_{n}}\right)_{V,T,n}\right]_{V=V(P,T)} \tag{1.6}$$

The first term was interpreted as the creation of counterions (subscript i) at a fixed charge of the colloid particle, and the second term as the creation of the charge on the colloidal particle (subscript n). The SI results for the Helmholtz free energy can be expressed in the general form of eq 1.2,

$$A_{I,J}^{SI,elec}(r_{I,J}, \kappa) = U_{I,J}^{C}(r_{I,J})B(\kappa)^{SI} \exp(-\kappa r_{I,J}) \tag{1.7}$$

where the SI form factor is

$$B_{I,J}(\kappa)^{SI} = \frac{\sinh(\kappa a_I)}{\kappa a_I}\frac{\sinh(\kappa a_J)}{\kappa a_J} \tag{1.8}$$

Sogami and Ise obtained the following relationship between the Helmholtz free energy form, $A_{I,J}^{SI,elec}(r_{I,J},\kappa)$, and the Gibbs free energy form, $G_{I,J}^{SI,elec}(r_{I,J},\kappa)$,

$$G_{I,J}^{SI,elec}(r_{I,J}, \kappa) = \left(2 + \kappa^2\frac{\partial}{\partial \kappa^2}\right)A_{I,J}^{SI,elec}(r_{I,J}, \kappa) = G_{op}^{SI}A_{I,J}^{SI,elec}(r_{I,J}, \kappa) \tag{1.9}$$

where we have introduced the notation G_{op}^{SI} as the "SI Gibbsian operator". In the case of spherical colloids, Sogami and Ise obtained the following expression for $G_{I,J}^{SI,elec}(r_{I,J},\kappa)$,

$$G_{I,J}^{SI,elec}(r_{I,J}, \kappa) = \frac{[2 + \kappa a_I \coth(\kappa a_I) + \kappa a_J \coth(\kappa a_J) - \kappa r_{I,J}]}{2}A_{I,J}^{SI,elec}(r_{I,J}, \kappa) \tag{1.10}$$

According to eq 1.10, $G_{I,J}^{SI,elec}(r_{I,J},\kappa)$ exhibits a minimum at the location

$$r_{min} = \frac{1 + C + \sqrt{(C + 1)(C + 3)}}{\kappa} \tag{1.11}$$

where

$$C = \frac{\kappa a_I \coth(\kappa a_I) + \kappa a_J \coth(\kappa a_J)}{2} \tag{1.12}$$

It goes without saying that those who have embraced the DLVO theory have strong objections to the SI theory.

Examined herein are the thermodynamic descriptions of a pairwise interaction using a screened Coulomb potential. It is shown that, by applying standard thermodynamics expressions, the Gibbs and Helmholtz free energies are indeed different for the screened Coulomb potential and that it is a mathematical certainty that there is an "attractive tail" for the Gibbs formulation. It is further argued, through use of the van der Waals gas expression, that the internal pressure of the system plays a major role in the determination of the thermodynamic properties of charged colloidal systems, leading to the formation of stable clusters, and even void regions, in response to the internal electrical stress imposed on the system. This interpretation is supported by Brownian dynamics simulations. It is further argued that the screened Coulomb potential is inadequate when many-body interactions and the disposition of the microions are prominent factors in the description of the thermodynamics of the system.

2. Alternative "Derivation" of the SI Gibbsian Operator

The SI relationship between the Gibbs free energy and Helmholtz free energy given by eq 1.6 does not exhibit symmetry in treatment of the microions and the macroions. Implicit in this expression are that the neutral macroions already exist in the absence of any microparticles (no derivative in the macroion concentration) and that the microions are created as charged particles (no derivative in the microion charge). Although this expression may be suspect, it is shown in this section that the SI operator is obtained when a symmetrized expression is employed.

The basis of eq 1.6 lies in two thermodynamic relationships involving the chemical potential, μ, of the system. The first is the expression for the Gibbs free energy,

$$G = \sum_{i} \mu_i n_i \tag{2.1}$$

The second is the relationship between the chemical potential and the Helmholtz free energy,

$$\mu_i = \left(\frac{\partial A}{\partial n_i}\right)_{V,T,n'} \tag{2.2}$$

where the subscript n′ indicates that the concentrations of all the other components are held constant.

In this alternative derivation of the SI Gibbsian operator, the simpler form of the screened Coulomb potential is used in which the form factors $B(\kappa)$ are set equal to unity, that is,

$$A_{I,J}^{elec}(r_{I,J}, \kappa) = \frac{Z_I Z_J e^2}{\varepsilon}\left[\frac{\exp(-\kappa r_{I,J})}{r_{I,J}}\right] \tag{2.3}$$

which is recognized as the Yukawa form of the potential. Since the SI theory focuses on systems in which there are no added electrolytes, the screening parameter for the SI theory only involves the neutralizing counterions,

$$\kappa_{\mathrm{SI}}{}^2 = 4\pi\lambda_{\mathrm{B}}\sum_{\mathrm{i}} z_{\mathrm{i}}{}^2 n_{\mathrm{i0}} \tag{2.4}$$

where z_{i} is the magnitude of charge on the counterion of concentration n_{i0} in particles per cm^3 and $\lambda_{\mathrm{B}} = e^2/\varepsilon k_{\mathrm{B}}T$ is the Bjerrum length.

All of the macroions are identical. Therefore, we are permitted to change the notation from individual macroions with subscripts I and J to simply the subscript "n" to distinguish the macroions from the microions. With this simplified notation, the Helmholtz free energy in the SI notation becomes,

$$A_{\mathrm{I,J}}^{\mathrm{SI,elec}}(r_{\mathrm{I,J}}, \kappa) = \frac{Z_{\mathrm{n}}{}^2 e^2}{\varepsilon}\left[\frac{\exp(-\kappa_{\mathrm{SI}} r_{\mathrm{I,J}})}{r_{\mathrm{I,J}}}\right] \tag{2.5}$$

Clearly, the only evidence of a contribution of the macroions is in the charge Z_{n}, whereas the contribution of the counterions is in the screening parameter κ_{SI}. This is perhaps the origin of the asymmetry of eq 1.6.

The concentration of the macroions in the pre-exponential factor can be introduced through an "averaged pairwise interaction" in a manner similar to that by Warren,[6] which we symbolically represent as

$$\bar{A}^{\mathrm{elec}}(\kappa) = \left(\frac{e^2}{2\varepsilon}\right)\sum_{\mathrm{I}}\sum_{\mathrm{J}\neq\mathrm{I}} Z_{\mathrm{I}} n_{\mathrm{I}} Z_{\mathrm{J}} n_{\mathrm{J}}\left\langle\frac{\exp(-\kappa r_{\mathrm{I,J}})}{r_{\mathrm{I,J}}}\right\rangle \tag{2.6}$$

where $\bar{A}^{\mathrm{elec}}$ is the Helmholtz free energy per unit volume and the brackets $\langle\rangle$ represent an average using a pair correlation function. Also, the screening parameter is defined in the more general form,

$$\kappa^2 = 4\pi\lambda_{\mathrm{B}}\sum_{\mathrm{J}} z_{\mathrm{J}}{}^2 n_{\mathrm{J}} \tag{2.7}$$

where the summation is over all of the "free" microions in the system, regardless of source. Note is taken that the concentration and charge of the macroions appear as a product in eq 2.6, so the following relationship holds,

$$Z_{\mathrm{J}}\left(\frac{\partial \bar{A}^{\mathrm{elec}}(\kappa)}{\partial Z_{\mathrm{J}}}\right)_{V,T} = n_{\mathrm{J}}\left(\frac{\partial \bar{A}^{\mathrm{elec}}(\kappa)}{\partial n_{\mathrm{J}}}\right)_{V,T} \tag{2.8}$$

Thus, symmetrization of eq 1.6 is obtained upon substitution of the identity of eq 2.8, with a subsequent change to the summations over all of the macroion concentrations as well as the microion concentrations.

To be technically correct, however, if one were to calculate directly the interaction between two specific macroions I and J separated by the distance $r_{\mathrm{I,J}}$, the concentration parameters n_{I} and n_{J} should be replaced by unity, giving rise to eq 2.3 for the pair Helmholtz free energy. We can represent the concentration in the double summation by use of the delta function $\delta(\mathrm{I} - \mathrm{I}')$ to select the specific macroion I of interest. Let I′ represent all of the macroions in the pool, including the macroion I. If we randomly select a macroion I′ in the system while being interested only in macroion I, then $\delta(\mathrm{I} - \mathrm{I}') = 0$ if the random pick is the wrong macroion, whereas $\delta(\mathrm{I} - \mathrm{I}') = 1$ if I′ is the correct macroion I. The total Helmholtz free energy is therefore,

$$\begin{aligned}\bar{A}^{\mathrm{elec}}(\kappa) &= \left(\frac{e^2}{2\varepsilon}\right)\sum_{\mathrm{I}}\sum_{\mathrm{J}\neq\mathrm{I}}\frac{\delta(\mathrm{I}-\mathrm{I}')\delta(\mathrm{J}-\mathrm{J}')}{V^2}\left(\frac{Z_{\mathrm{I}}Z_{\mathrm{J}}\exp(-\kappa r_{\mathrm{I,J}})}{r_{\mathrm{I,J}}}\right)\\ &= \left(\frac{1}{2}\right)\sum_{\mathrm{I}}\sum_{\mathrm{J}\neq\mathrm{I}}\bar{A}_{\mathrm{I,J}}^{\mathrm{elec}}(r_{\mathrm{I,J}}, \kappa)\end{aligned} \tag{2.9}$$

Keeping in mind the order of appearance of I and J, each of which runs over all of the macroions in the system, one may write eq 2.9 in a more transparent form,

$$\left(\frac{1}{2}\right)\sum_{\mathrm{I}}\sum_{\mathrm{J}\neq\mathrm{I}}\left(\delta(\mathrm{I}-\mathrm{I}')\frac{\partial}{\partial\delta(\mathrm{I}-\mathrm{I}')} + \delta(\mathrm{J}-\mathrm{J}')\frac{\partial}{\partial\delta(\mathrm{J}-\mathrm{J}')}\right)(\bar{A}_{\mathrm{I,J}}^{\mathrm{elec}}(r_{\mathrm{I,J}}, \kappa)) = 2\bar{A}^{\mathrm{elec}}(\kappa) \tag{2.10}$$

Since the microions appear only in the definition of the screening parameter, we can expression the microion contribution in simplified form,

$$\sum_{\mathrm{J}} n_{\mathrm{J}}\left(\frac{\partial}{\partial n_{\mathrm{J}}}\right)_{V,T} = \left(\sum_{\mathrm{J}} n_{\mathrm{J}}\left(\frac{\partial\kappa^2}{\partial n_{\mathrm{J}}}\right)_{V,T}\right)\left(\frac{\partial}{\partial\kappa^2}\right)_{V,T} = \kappa^2\left(\frac{\partial}{\partial\kappa^2}\right)_{V,T} \tag{2.11}$$

Since eq 2.11 placed no restrictions on the source of the microions, the combination of eqs 2.11 and 2.10 results in a general expression for the Gibbsian operator $G_{\mathrm{op}}^{\mathrm{gen}}$

$$G_{\mathrm{op}}^{\mathrm{gen}} = 2 + \kappa^2\left(\frac{\partial}{\partial\kappa^2}\right) \tag{2.12}$$

It is noted that $G_{\mathrm{op}}^{\mathrm{gen}}$ is the same form as $G_{\mathrm{op}}^{\mathrm{SI}}$ derived by Sogami and Ise as given in eq 1.9, except now all of the microions are included.

We now apply $G_{\mathrm{op}}^{\mathrm{gen}}$ to $\bar{A}_{\mathrm{I,J}}^{\mathrm{elec}}(r_{\mathrm{I,J}},\kappa)$ defined in eq 2.7, with the result

$$\bar{G}_{\mathrm{I,J}}^{\mathrm{elec}}(r_{\mathrm{I,J}}, \kappa) = G_{\mathrm{op}}^{\mathrm{gen}}\bar{A}_{\mathrm{I,J}}^{\mathrm{elec}}(r_{\mathrm{I,J}}, \kappa) = \left(2 - \frac{\kappa r_{\mathrm{I,J}}}{2}\right)\bar{A}_{\mathrm{I,J}}^{\mathrm{elec}}(r_{\mathrm{I,J}}, \kappa) \tag{2.13}$$

One can draw the general conclusion that in the conversion from the Helmholtz free energy to the Gibbs free energy an attractive tail is obtained for a screened Coulomb interaction.

3. Objections of Overbeek to the SI Theory

The response of Overbeek[7] to the SI paper is viewed by many as the final nail in the coffin to the SI theory. The intent of Overbeek was to cancel the source of the attraction term in the SI theory, which arises from the derivative with respect to κ.

Overbeek was aware of the fact that the attractive term in the Gibbsian potential was due to the microion number in the numerator of the screening parameter. The most obvious way to cancel this contribution was to introduce a parameter in the denominator of the screening parameter which would give a derivative of equal but of opposite sign to the microion contribution. The logical choice to accomplish this cancellation was to introduce the number of solvent particles N_{solv} to give the number ratio $N_{\mathrm{j}}/N_{\mathrm{solv}}$, where N_{j} is the number of microions of type j. Overbeek thus defined the volume of the system as the volume of only the solvent particles, $V = N_{\mathrm{solv}}\bar{v}_{\mathrm{solv}}$, where $\bar{v}_{\mathrm{solv}}$ is the volume of one solvent particle. In other words, Overbeek was treating the macroions as if they were point particles. This was, ironically, one of the criticisms he had of Langmuir's treatment of macroions in the Debye−Hückel limit. With this assumption, the screening parameter now has the form,

$$\kappa^2 = 4\pi\lambda_{\mathrm{B}} \sum_{\mathrm{j}} \frac{z_{\mathrm{j}}^{\,2} N_{\mathrm{j}}}{N_{\mathrm{solv}}\bar{v}_{\mathrm{solv}}} \tag{3.1}$$

where the summation is over all of the microions in the system. The corresponding derivative for the solvent is

$$N_{\mathrm{solv}}\left(\frac{\partial}{\partial N_{\mathrm{solv}}}\right)_{V,T} = N_{\mathrm{solv,j}}\left(\frac{\partial \kappa^2}{\partial N_{\mathrm{solv}}}\right)_{V,T}\left(\frac{\partial}{\partial \kappa^2}\right)_{V,T} = -\kappa^2\left(\frac{\partial}{\partial \kappa^2}\right)_{V,T} \tag{3.2}$$

Clearly, the introduction of eq 3.2 into eq 1.9 results in the cancellation of the attractive contribution of the microions, which was the main goal of Overbeek. However, introduction of the solvent into only the screening parameter is a selective application of the introduction of the solvent contribution. This selective application was by design because the objective was to cancel the attractive part due to the counterions in the screening parameter. To have an objective introduction of the solvent particles, one must be consistent and include the solvent not only in the concentration term in the screening parameter but also in the pre-exponential factor involving the macroion concentrations.

An objective introduction of the solvent introduces the ratio $\delta(\mathrm{I} - \mathrm{I}')\delta(\mathrm{J} - \mathrm{J}')/N_{\mathrm{solv}}^{\,2}$ in the pre-exponential factor in eq 2.9. Since we have already considered the colloid particles and the microions, we focus solely on the solvent contribution. The solvent, however, can be represented in many different ways, depending upon the particular model. Overbeek, for example, treated all of the particles as point particles except for the solvent. Let us define "x" as a particular component of the solvent and $y(x)$ as a specific representation of the solvent contribution. We now rewrite eq 2.9 in the generalized form,

$$\begin{aligned} A^{\mathrm{elec}}(\kappa) &= \left(\frac{1}{2}\right)\sum_{\mathrm{I}}\sum_{\mathrm{J}\neq\mathrm{I}}\left(\frac{e^2}{\varepsilon}\right)\frac{\delta(\mathrm{I} - \mathrm{I}')\delta(\mathrm{J} - \mathrm{J}')}{(N_{\mathrm{solv}}\bar{v}_{\mathrm{solv}})^2}\left(\frac{Z_{\mathrm{I}}Z_{\mathrm{J}}}{r_{\mathrm{I,J}}}\right)\exp(-\kappa r_{\mathrm{I,J}}) \\ &= \left(\frac{1}{2}\right)\sum_{\mathrm{I}}\sum_{\mathrm{J}\neq\mathrm{I}}\frac{P_{\mathrm{I,J}}}{y(x)^2}\exp\left(-\frac{Q_{\mathrm{I,J}}}{y(x)^{1/2}}\right) \end{aligned} \tag{3.3}$$

where the terms $P_{\mathrm{I,J}}$ and $Q_{\mathrm{I,J}}$ are collections of all of the terms that are not of interest. The desired solvent correction expression for the derivative of $A_{\mathrm{I,J}}^{\mathrm{elec}}(r_{\mathrm{I,J}},\kappa)$ with respect to the generalized concentration variable x is,

$$A_{\mathrm{I,J}}^{\mathrm{corr}}(r_{\mathrm{I,J}},\kappa) = x\left(\frac{\partial A_{\mathrm{I,J}}^{\mathrm{elec}}(r_{\mathrm{I,J}},\kappa)}{\partial x}\right) = \left[-2 + \frac{\kappa r_{\mathrm{I,J}}}{2}\right]A_{\mathrm{I,J}}^{\mathrm{elec}}(r_{\mathrm{I,J}},\kappa)\left(\frac{x}{y(x)}\right)\left(\frac{\partial y(x)}{\partial x}\right) \tag{3.4}$$

As an example, let us use the Overbeek expression for the solvent and set $x = N_{\mathrm{solv}}$ and $y(x) = x = N_{\mathrm{solv}}$. It therefore follows that $P_{\mathrm{I,J}} = \delta(\mathrm{I} - \mathrm{J}')\delta(\mathrm{J} - \mathrm{J}')\ Z_{\mathrm{I}}Z_{\mathrm{J}}e^2/(\varepsilon r_{\mathrm{I,J}}\bar{v}_{\mathrm{solv}}^{\,2})$ with a corresponding expression for $Q_{\mathrm{I,J}}$. Substitution of these expressions for x and $y(x)$ into eq 3.4 results in the Overbeek solvent correction,

$$A_{\mathrm{I,J}}^{\mathrm{corr}}(r_{\mathrm{I,J}},\kappa) = N_{\mathrm{solv}}\left(\frac{\partial A_{\mathrm{I,J}}^{\mathrm{elec}}(r_{\mathrm{I,J}},\kappa)}{\partial N_{\mathrm{solv}}}\right) = \left(\frac{\kappa r_{\mathrm{I,J}}}{2} - 2\right)A_{\mathrm{I,J}}^{\mathrm{elec}}(r_{\mathrm{I,J}},\kappa) \tag{3.5}$$

Notice that, by including the solvent concentration in the prefactor, we pick up the additional "correction term" of −2. Adding eqs 3.2 and 3.5 to the Gibbsian operator defined by eq 2.12, we have

$$G_{\mathrm{I,J}}^{\mathrm{SI,elec}}(r_{\mathrm{I,J}},\kappa) = \left(2 - \frac{\kappa r_{\mathrm{i,j}}}{2}\right)A_{\mathrm{I,J}}^{\mathrm{SI,elec}}(r_{\mathrm{I,J}},\kappa) + \left(\frac{\kappa r_{\mathrm{i,j}}}{2} - 2\right)A_{\mathrm{I,J}}^{\mathrm{SI,elec}}(r_{\mathrm{I,J}},\kappa) = 0 \tag{3.6}$$

In other words, objective application of the solvent in both the pre-exponential term and the exponential argument results in a cancellation of all electrical interactions in the Gibbs free energy even though the electrical interactions are present in the Helmholtz free energy.

Another way to represent the "solvent correction term" is to acknowledge the finite size of the microions and macroions and write the total volume of the system in terms of partial volumes,

$$V = N_{\mathrm{p}}\bar{v}_{\mathrm{p}} + N_{\mathrm{mic}}\bar{v}_{\mathrm{mic}} + N_{\mathrm{solv}}\bar{v}_{\mathrm{solv}} \tag{3.7}$$

where "p" denotes the macroions and "mic" collectively represents all of the microions. The volume of the solvent may then be expressed in terms of the volume fractions of the other components,

$$N_{\mathrm{solv}}\bar{v}_{\mathrm{solv}} = V - N_{\mathrm{p}}\bar{v}_{\mathrm{p}} - N_{\mathrm{mic}}\bar{v}_{\mathrm{mic}} = V(1 - \phi_{\mathrm{p}} - \phi_{\mathrm{mic}}) \tag{3.8}$$

where $\phi_{\mathrm{b}} = N_{\mathrm{b}}\bar{v}_{\mathrm{b}}/V$ is a volume fraction of the b-th component. Now we have a different representation of the solvent volume, which is recognized as the standard form of the "free volume" of the system. For the purpose of illustration, the particular component of interest is taken to be the macroion, and set $x = N_{\mathrm{p}}$, the collective number of macroions, and the specific form representing the solvent is $y(x) = (1 - \phi_{\mathrm{p}} - \phi_{\mathrm{mic}})$. We now evaluate eq 3.4 with these expressions,

$$\begin{aligned} A_{\mathrm{I,J}}^{\mathrm{corr}}(r_{\mathrm{I,J}},\kappa) &= N_{\mathrm{p}}\left(\frac{\partial A_{\mathrm{I,J}}^{\mathrm{elec}}(r_{\mathrm{I,J}},\kappa)}{\partial N_{\mathrm{p}}}\right) \\ &= \left[\frac{\kappa r_{\mathrm{I,J}}}{2} - 2\right]\left(\frac{N_{\mathrm{p}}}{1 - \phi_{\mathrm{p}} - \phi_{\mathrm{mic}}}\right)\left(\frac{\partial \phi_{\mathrm{p}}}{\partial N_{\mathrm{p}}}\right)A_{\mathrm{I,J}}^{\mathrm{elec}}(r_{\mathrm{I,J}},\kappa) \\ &= \left[\frac{\kappa r_{\mathrm{I,J}}}{2} - 2\right]\left(\frac{\phi_{\mathrm{p}}}{1 - \phi_{\mathrm{p}} - \phi_{\mathrm{mic}}}\right)A_{\mathrm{I,J}}^{\mathrm{elec}}(r_{\mathrm{I,J}},\kappa) \end{aligned} \tag{3.9}$$

A similar expression is obtained for the microion correction. Clearly these correction terms are small, on the order of the respective volume fractions. The effect of the finite size of the particles making up the solvent is to retain electrical properties of the Gibbs form of the free energy, but with a value slightly less than that of eq 2.13. This is more acceptable than the

Overbeek treatment of the macroions and microions as point particles resulting in eq 3.6.

The second attempt by Overbeek to eliminate the attraction part of the Gibbsian operator is to "simplify" the above argument through the use of the Gibbs−Duhem relationship, as manifested in the "charging process" given by eq 15 in the Overbeek paper,[7]

$$N_{\text{solv}}\mu_{\text{solv}}^{\text{elec}} + \sum_{\text{ions}} N_j\mu_j^{\text{elec}} = \int_{e=0}^{e=e} (N_{\text{solv}} d\mu_{\text{solv}}^{\text{elec}} + \sum_{\text{ions}} N_j d\mu_j^{\text{elec}}) \tag{3.10}$$

where Overbeek interprets the integration as the Debye−Hückel charging process (e is the charging parameter). Overbeek[7] remarked on eq 3.10, "This remarkable result shows that the solvent and the small ions together just give a zero contribution to G^{el} (and incidentally also to F^{el})".

One has to view this conclusion, especially the reference to F^{el}, in the context of the DLVO theory in regards to the electrical contribution to the free energy as stated by Verwey and Overbeek:[1] "The very simple result is that we find the total free energy of the double layer if only we calculate the *electrical* work necessary to discharge stepwise all ions of the *solution*".

As first pointed out by Smalley,[8] if Overbeek correctly applied the Gibbs−Duhem expression such that the inclusion of the solvent canceled the contribution of the small ions in solution then there were no electrical contributions in the DLVO model as well!

By improperly using the Gibbs−Duhem relationship, Overbeek failed to recognize its significance. The Gibbs free energy in terms of the chemical potential is given by eq 2.1. Changing the notation to the current situation, the differentiation of eq 2.1 gives the following expression,

$$dG = (d\mu_{\text{solv}})N_{\text{solv}} + \sum_j (d\mu_j)N_j + \mu_{\text{solv}}(dN_{\text{solv}}) + \sum_j \mu_j(dN_j) \tag{3.11}$$

We now compare this with the thermodynamic expression for the Gibbs free energy change upon the introduction of particles,

$$dG = \mu_{\text{solv}}(dN_{\text{solv}}) + \sum_j \mu_j(dN_j) \tag{3.12}$$

To reconcile eqs 3.11 and 3.12, we must have the relationship,

$$(d\mu_{\text{solv}})N_{\text{solv}} + \sum_j (d\mu_j)N_j = 0 \tag{3.13}$$

It is noted that eq 3.13 is the Gibbs−Duhem relationship. What the Gibbs−Duhem relationship tells us is that all of the components in a system are related. The correct interpretation of eq 3.13 is that the activity of the solvent changes with a change in the chemical potential of any or all of the other components. A classic example of the application of the Gibbs−Duhem expression is that the boiling temperature of a solvent changes when a solute is present. Perhaps the basis of Overbeek's incorrect interpretation of the Gibbs−Duhem relationship has, in addition to his attempt to eliminate the attraction part in the Gibbsian operator, a foundation in the assumption that the chemical and electrical work on the surface of the macroion exactly cancels, thus leading to the double layer interaction theory.

As a point in passing, the solvent molecules are not charged. Hence, the integration of the solvent from charge $e = 0$ to $e = e$ in eq 3.10 has no physical meaning.

It is concluded that Overbeek was not successful in his attempt to eliminate the attractive part of the SI Gibbsian expression. Had his arguments been successful, then the correction would have also eliminated all electrical interactions in the DLVO theory, with the inescapable conclusion that charged colloidal systems behave in an identical manner as neutral particles. Furthermore, introducing a "solvent correction" in the form of the derivative N_{solv} $(\partial/\partial N_{\text{solv}})$ means that the amount of solvent changes, which is contrary to the usual assumption that the solvent acts as a "background" for the other components in the system. By using instead the "free volume", the transformation is made from solvent change to adjustable concentrations of the other particles in the system, which is consistent with the use of their derivatives of the Helmholtz free energy.

4. DLVO Potential and Phase Transitions

One of the apparent arguments in the SI camp to favor the SI potential over the DLVO potential is the existence of two phases, along with the statement that the spacing of particles in the "crystalline phase" is less than that expected for uniform distribution of particles. This situation is the source of the argument that some type of "attraction" must be present to explain the smaller separation distances. Ise et al.,[9] for example, recorded the trajectories of latex particles monitored with an Olympus microscope. Clearly shown in their Figure 2 are two states: a crystalline region in which the particles hardly move in the time window examined, and a highly kinetics phase in which the trajectories appear as car headlights in a long exposure photograph. The question arises if these two coexisting phases can likewise be explained in terms of the "purely repulsive" DLVO potential.

Molecular Dynamics Simulations of Robbins, Kremer, and Grest. Robbins et al.[10] used molecular dynamics methods for a fixed volume and number of particles to examined the phase diagram and dynamic properties of a system of particles. These particles interacted through a Yukawa potential, namely,

$$U_a = U_0 \exp(-\lambda) \tag{4.1}$$

where $a = \rho^{-1/3}$ is the average separation distance between particles, ρ is the density of particles of "effective" charge Z^*, $\lambda = \kappa a$ is the rate of fall off in the interaction, and the screening parameter κ depends upon the concentration $n_i = \rho Z^*$ of neutralizing screening ions of unit charge,

$$\kappa^2 = \frac{4\pi n_i e^2}{\varepsilon k_B T} \tag{4.2}$$

and

$$U_0 = \frac{(Z^* e)^2}{\varepsilon a} \tag{4.3}$$

Another parameter to characterize the molecular dynamics results is the temperature $\tilde{T}$,

$$\tilde{T} = \frac{k_B T}{m a^2 \omega_E{}^2} \qquad (4.4)$$

where m is the mass of the particle and ω_E is the Einstein frequency of the crystalline structures. The temperature $\tilde{T}$ is a measure of the transition temperature for the crystalline structure.

The Yukawa potential used in these simulations was per particle,

$$U_t = \frac{1}{2N} U_0 \sum_{I,J=1;I \neq J}^{N} \frac{\exp(-\lambda r_{I,J}/a)}{(r_{I,J}/a)} \qquad (4.5)$$

As noted by these authors, the parameter λ controls the shape of the potential. For finite temperatures, the free energy was minimized, where the parameters $\Gamma = U_0/k_B T$ and λ are the variables.

Of particular interest is their Figure 3 in which $k_B T/U_a$ and λ are the coordinates. In general, a liquid phase obtains for all λ at sufficiently high values of $k_B T/U_a$. The interpretation of this observation is that the kinetic energy of the system overcomes the repulsive interactions that tend to “force” particles in a crystalline structure, since the particles want to get as far away from each other as possible. Coexisting with the liquid state are the *bcc* crystalline structure (low values of λ) or the *fcc* crystalline structure (high values of λ). In regards to the liquid phase near the melting temperature, these authors note: “Although the bcc phase is not stable at any temperature for $\lambda > 5$, we find a coordination number of 14 near the melting temperature in liquid systems at all values of λ. This is evidence for bcc-like local order in the liquid phase.”

It is therefore possible, within the context of the DLVO potential, to have a crystalline structure in equilibrium with the liquid phase.

Theory of Van Roij, Dijkstra, and Hansen. In response to the SI theory, van Roij et al.[11] (RDH) attempted to show that a phase separation from the “liquid state” to the heterogeneous “liquid-ordered” coexistence state does result from the DLVO “repulsive only” pairwise interaction. Their model involved N_p macroions of charge $-Ze$, $N_c = ZN_p$ counterions of charge $+e$, and N_s fully dissociated pairs of monovalent salt ions of charge $\pm e$. The total number of positively charged microions was $N_+ = N_c + N_s$ and negatively charged microions $N_- = N_s$, with number densities $n_\pm = N_\pm/V$. The microscopic distribution of the microions was characterized by equilibrium density profiles $\rho_\pm(\mathbf{r})$, the fundamental quantities in a density-functional theory. The Debye screening parameter was defined as

$$\kappa^2 = 4\pi\lambda_B(n_+ + n_-) = 4\pi\lambda_B n \qquad (4.6)$$

The effective one-component Hamiltonian for the macroions was of the form

$$V_p^{\text{eff}}(\{\mathbf{R}_J\}) = \Phi_0 + \sum_{I<J}^{N_p} \nu_{\text{eff}}(R_{I,J}) \qquad (4.7)$$

where $\nu_{\text{eff}}(R_{I,J})$ is the screened Coulomb potential acting between the macroions and Φ_0 is the so-called volume term that does not depend upon the position of the macroions and includes the ideal kinetics terms for the microions, hard-core contributions, a correction term for the neutralizing background, and a “self energy” term associated with the double layer of the macroions. The “volume term” results from mapping the multicomponent system into a “one-component” system.

In accordance with equilibrium conditions, the chemical potentials for the two phases must be equal for each species in the system,

$$\begin{aligned} \mu_p(n_p^{(1)}, n_s^{(1)}) &= \mu_p(n_p^{(2)}, n_s^{(2)}) \\ \mu_s(n_p^{(1)}, n_s^{(1)}) &= \mu_s(n_p^{(2)}, n_s^{(2)}) \end{aligned} \qquad (4.8)$$

where the subscripts “p” and “s” represent, respectively, the macroions and salt (added electrolyte), and the superscripts (1) and (2) identify the two phases. The pressure in the two phases must also be equal,

$$P(n_p^{(1)}, n_s^{(1)}) = P(n_p^{(2)}, n_s^{(2)}) \qquad (4.9)$$

The relationships between the chemical potential and the Helmholtz free energies employed in these simulations were,

$$\begin{aligned} \mu_p &= \left(\frac{\partial \bar{A}(n_p, n_s)}{\partial n_p}\right)_{n_s} \\ \mu_s &= \left(\frac{\partial \bar{A}(n_p, n_s)}{\partial n_s}\right)_{n_p} \end{aligned} \qquad (4.10)$$

where $\bar{A}(n_p, n_s) = A/V$ is the volume Helmholtz free energy. The pressure was given as

$$P = n_p\mu_p + n_s\mu_s - \bar{A}(n_p, n_s) \qquad (4.11)$$

Calculations were carried out with $T = 300$ K and a solvent dielectric constant $\varepsilon = 78$ to mimic experimental conditions. The phase diagrams were represented by the added electrolyte concentration n_s and the colloid packing fraction η, defined as

$$\eta = \frac{4\pi R^3}{3} n_p \qquad (4.12)$$

where R is the radius of the colloid particle. Three phases were identified: gas (G), fluid (F), and crystalline (FCC).

Of significance is the observed broadening of the fluid−solid phase transition as the concentration of added electrolyte is lowered below 20 μM. This represents the coexistence of a “dense” *fcc* solid with a “very low density” fluid phase, in regard to the macroion concentration. It is also of interest to note that as the added electrolyte concentration goes to zero, the system appears to revert to a one-phase *fcc* crystalline structure.

The underlying mechanism of the coexistence of phases is that the microions themselves are responsible for the phase separation. That is, the instability of the colloidal system reflects the instability of the microion system. Because of electrical neutrality, the macroions are “drawn in” to follow their counterions, which is why the added salt parameter n_s is used to represent the phase diagrams. In an attempt to maintain equal osmotic pressures in the two phases, the concentration of added electrolyte in the “fluid” phase is greater than the concentration of added electrolyte in the “crystalline” phase. From the point of view of the macroions, phase separation is a result of the "tail wagging the dog".

There is another point to be made in this study. The authors contend that coexistence of phases obtains even though the repulsive-only screened Coulomb interaction between macroions was employed. However, the chemical potential calculated in these studies, that is, eq 4.10, is identical to the application of eq 2.2 which generated the generalized Gibbsian operator defined in eq 2.12. By carrying out the differentiation via computer, the apparent "attraction" part may have been missed. Also, the pressure defined in the RDH theory manifested in eq 4.11 clearly requires that the Gibbs and Helmholtz free energies are in fact not locally equal.

Warren Theory. Warren[6] acknowledged the importance of the theory of Langmuir[12] for micelle stability. In his development, Warren incorporated the first two of the three criticisms of Langmuir[12] regarding the DLVO theory. These three criticisms, quoted from Langmuir, are the following.

(A) "No direct account is taken of the thermal agitation which by itself would tend to cause the colloid particles and the ions to be displaced throughout the liquid giving an osmotic pressure $p = \sum nkT$."

(B) "The attraction between the charged micelles and the ion atmosphere of opposite sign which extends throughout the intervening liquid is ignored or neglected although it exceeds the repulsive force between micelles."

(C) "The electric charges on the micelles are assumed to be constant, whereas they must be, in general, dependent on the concentration of the micelles."

Warren's rejection of the third criticism was based on Verwey and Overbeek's criticism of the Langmuir model regarding the calculation of the screening parameter as being far from the colloid particle. While embracing several points in the Langmuir view, the program of Warren followed very closely the program of van Roij, Dijkstra, and Hansen. It is of no surprise that Warren observed the same criteria for phase separation, which is driven by the microions to have macroion-rich and macroion-sparse regions.

The importance of the Warren paper is the acknowledgment of the Langmuir model in which all three electrostatic components act to destabilize the system: the microion−microion, macroion−microion, and macroion−microion interactions (after the background subtraction counter term).

5. Langmuir Model

Langmuir[12] proposed a model for unipolar coacervates based on the three criticisms of the DLVO theory as given in the previous section.

The osmotic pressure based on part (A) was taken to be

$$P = (n_1 + n_2)k_BT = \left(1 + \frac{z_1}{z_2}\right)n_1k_BT \tag{5.1}$$

where z_1 (z_2) is the magnitude of charge on the micelles (counterions) of concentrations n_1 (n_2). Added to this is the osmotic pressure from the Debye−Hückel theory, which after some manipulation, gives for the total osmotic pressure,

$$P = \left(1 + \frac{z_1}{z_2}\right)n_1k_BT - \frac{(\pi e^6\varepsilon^3k_BT)^{1/2}{z_1}^{3/2}(z_1 + z_2)^{3/2}}{3}n_1 \tag{5.2}$$

With a judicious choice of parameters, Langmuir rewrote eq 5.2 in the simplified form

$$P = 3n - 2n^{3/2} \tag{5.3}$$

It is now transparent from eq 5.3 that the pressure exhibits a van der Waals type loop, thus giving rise to coexisting phase equilibrium.

We now examine part B in the Langmuir criticisms. The electrostatic interactions are summed over all of the micelles and counterions as if they were in a crystalline structure of alternating positive and negative charges. The total electrical interaction is therefore negative, that is, attractive, as one obtains for a simple salt crystal. Because of this result, Langmuir stated that one must introduce a new repulsive force to overcome this attraction or show that the electrostatic attraction is a function of the distance between the micelles. An important feature in the Langmuir development is the adjustment of charge on the micelles in the dense phase compared to the dilute phase. The argument is that the charge carried by the solvate between the micelles in the dense phase must be the same as the charge carried by the solvate in the sparse phase. In order for this condition to be obtained, the charge on the micelles in the dense phase must correspondingly decrease in value, thus leading to part C of the Langmuir criticisms.

6. Disposition of the Microions

Screened Coulomb theories can say nothing about the role of the microions in the description of macroion systems. The contributions of the microions are generally relegated to the screening parameter and Debye−Hückel contributions to the electrical energy of the system. The counterions associated with the macroions are assumed to follow, faithfully, the motions of their parent macroions.

Few studies are made of the disposition of the microions in a system of highly charged colloid particles. An early attempt to look at the effects of microion−microion correlations was by Woodward and co-workers.[13,14] Each macroion in the calculation was placed in its own spherical computation cell. The spherical computation cells were then placed in contact as if they were in a crystal lattice. The counterions were confined to the parent computation cell, and Monte Carlo methods were used to move the microions, which were under the influence of not only the parent macroion but also the particles in the neighboring computation cell(s). The microions were restrained from leaving their computation cells.

The "configuration" Helmholtz free energy, A_{config}, for this system was defined as the deviation from the ideal case. They reported values of the practical osmotic coefficient for systems that differed in macroion concentration and charge. The osmotic pressure was calculated from the thermodynamic relationship

$$\pi = -\left(\frac{\partial A}{\partial V}\right)_{T,n} = \pi_{\text{ideal}} - \left(\frac{\partial A_{\text{config}}}{\partial V}\right)_{T,n} \tag{6.1}$$

where π_{ideal} represents the ideal part of the microion contribution to the osmotic pressure. The major findings were that the microion−microion correlations were negligible for highly charge macroions (the counterions remained near the parent macroion) or very dilute suspensions.

The main problem with these Monte Carlo simulations was the geometry of the computation system. By using spherical cells surrounding each macroion, the counterions were unrealistically confined to a predetermined region in the system. That is, there was no "exchange" of the microions between the macroion cells, which could be very important for closely spaced macroions. Furthermore, by limiting the calculations to two or three macroions, these systems are not sufficiently large to represent a realistic multicomponent system. The lack of exchange and multicomponent effects are clearly brought out in the structure of potential fields, as discussed in the next paragraph.

The juxtaposition of potential fields (JPF) method[15,16] was proposed as a means of obtaining landscape information relevant to the distribution of the microions in a truly multibody interaction system. The JPF method is based on the work of Bader[17,18] regarding the electron energies and bonding orbitals in molecules. In the JPF method, the potential fields of all of the macroions in the system are represented by constant potential surfaces. The idea is that the potential field that results from all of the macroions in solution or suspension provides a potential landscape for the distribution of microions just as the atoms provide a potential profile in the quantum mechanical placement of electrons.

In a typical situation the macroions are placed in position, and constant potential surfaces are generated. The highest potential surfaces are found around the single macroions and appear as "distorted spherical surfaces" with distortions pointing toward other spheres in the vicinity of the target sphere. Counterions found within this distorted spherical surface are identified as "neutralizing counterions" since they are tightly associated with the target macroion. Counterions confined to this region contribute to what is usually referred to as "charge renormalization" or "effective charge" when parameters are adjusted to interpret the data. Because of the high charge on the parent macroion, co-ions are excluded from the interior of this localized sphere, which we refer to as the "neutralizing sphere". Because of the superposition of potential fields, it is possible that the neutralizing sphere surrounding any one macroion within a cluster can accommodate more counterions than required for charge neutrality. A situation may arise, therefore, that leads to "charge reversal" for the target macroion. As one lowers that value of the potential, surfaces appear that surround two or more macroions. Counterions with energies associated with these surfaces are "shared" between the participating macroions. Further out the surfaces encompass the collection of macroions within the cluster.

Clearly, the JPF method is a simple qualitative tool to gain insight on the distribution of counterions on the potential landscape. As the microions are introduced onto the potential landscape, their potential fields alter the landscape for the remaining microions to be added. This approach is similar to that used in quantum mechanics in the determination of electronic energies. Since these potential surfaces mimic atomic and molecular orbitals in stable molecules, Gröhn and Antionietti[19] referred to this approach as a "molecular orbital model." In this view, the sharing of the counterions as if in molecular orbitals adds further stability to the "dense" state in the heterogeneous structure of colloid suspensions.

Computer simulations using Brownian dynamics (BD)[20−22] methods on systems of eight and more macroions and Monte Carlo energy minimization (MCEM)[23,24] of counterions on the surface of a single macroion shed further light on the disposition of the microions and confirm the qualitative nature of the system as inferred from the JPF method.

In the BD simulations, the distributions of both the positive and the negative microions (counterions plus added electrolyte, where "counterion" now refers to ions of opposite sign to the macroion, and "co-ion" refers to ions having a charge the same sign as the macroion) were determined in the presence of a fixed configuration of macroions. The computational box was subdivided into smaller cubic boxes of equal size. The "equilibrium" configuration, or "starting" configuration, was first established after one million moves of each coordinate of each microion. The distributions of positive and negative ions, separately determined, were tallied after a fixed number of cycles, and then these numbers were averaged over all of the cycles. In all cases the counterions accumulated at the surface of the macroions, more on the interior (to the cluster) side of the macroion than to the exterior side. Of importance is the distribution of microions interior to the cluster as a function of macroion separation distance. For sufficiently large distances, both counterions and co-ions were found in the interior of the cluster. Of course, the concentration of the co-ions was considerably reduced because of the repulsion due to the presence of the macroions. However, at smaller macroion separation distances the co-ions were completely excluded from the interior of the cluster, and the counterion concentrations were greatly enhanced. The presence of excess counterions within the cluster may engage in a "charge reversal" of the local macroion, which acts to further stabilize the macroion cluster in the "dense state". The stability of the "charge reversal" structures was examined by MCEM methods.

In the MCEM studies, counterions were placed on the surfaces of several geometries (spherical, prolate and oblate ellipsoids, and cylinders). Counterions were added to the surfaces, and the energy was minimized to obtain the redistribution of the counterions. In all cases studied, the energy initially became more negative upon the initial introduction of excess counterions, eventually went through a minimum, and then increased toward zero. What these simulation say is that the attractive interaction of the counterions to the macroion exceeds the repulsive interactions between the counterions as additional "excess" counterions are added to the surface. Thus, an excess of counterions can condense on those macroions interior to the cluster for small intermacroion separation distances.

We next use these results for the disposition of microions under varying conditions to construct a scenario for a collection of macroions under electrostatic stress.

7. Clustering of Colloidal Particle: A Scenario in Electrostatic Stress

For pedagogical reasons, we adapt Okubo's suggestion[25] that the repulsive interaction between charged colloidal particles can be treated as if it was a "hard sphere" interaction. The "effective radius" of the colloidal particle involves the screening length, that is, $R_{\mathrm{eff}} = a_{\mathrm{p}} + (1/\kappa_{\mathrm{eff}})$, where κ_{eff} is the screening parameter associated with the charged particle.

Consider a system of colloidal particles with sufficient excess added salt that $R_{\mathrm{eff}} \approx a_{\mathrm{p}}$. The concentration of added salt is now systematically removed from the system, in which case the value of R_{eff} correspondingly increases in value. Eventually the situation obtains in which the system becomes an exercise in packing solid balls in a container as the "effective hard spheres" begin to overlap. Further reduction in the added salt does not change the configuration of the "effective hard sphere" colloidal particles for there is no more available space in the system. But the thing that continues to increase is the internal electrical pressure. This will put an electrical stress on the colloidal system. How does the system respond to this electrical stress? According to Le Chatelier's principle, the system will move in the direction to reduce the stress. The most obvious way is simply to remove the counterions from the solution and place them on the macroion to reduce the charge of the colloidal particles. But it may be too much to ask of the system to simultaneously reduce the charge of all the colloid particles in the system.

What evolves upon continued reduction in the added salt concentration is a system of variable sized spheres. Driven by entropic considerations, the system now "separates" into regions of large spheres and small spheres. Rather than confine the microions in the colloid-rich regions to particular colloidal particles, free energy considerations allow many of the microions to be shared among a collection of colloidal particles of reduced charge.

8. Parallels of Colloidal Suspensions and the van der Waals Gas

Phase separation in the Langmuir theory of unipolar coacervates exhibits a "van der Waals loop" in accordance with eq 5.3. If we treat the colloidal particle as an "effective hard sphere", then one might gain insight about the equations regarding highly charged colloidal systems from the knowledge of the van der Waals theory of imperfect gases.

The van der Waals gas equation can be viewed as a theory involving an "effective pressure" and an "effective volume", to retain the form of the ideal gas law,

$$P_{\mathrm{eff}}V_{\mathrm{eff}} = \left(P + \frac{an^2}{V^2}\right)(V - bn) = nRT \tag{8.1}$$

where P is the external pressure, a is the van der Waals pairwise attraction term, and b is the excluded volume parameter. But what is the role of the term an^2/V^2 in eq 8.1? To answer this question we apply the thermodynamic equation of state to the pressure P,

$$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V - P = a\rho^2 \tag{8.2}$$

where U is the energy of the system and $\rho = n/V$ is the particle density. The term $a\rho^2$ represents the *internal pressure* of the system. How does this result relate to highly charged colloidal systems? Since the product PV involves external pressure and the total volume of the system, one has $\Delta(PV) = 0$ regardless of the value of the internal pressure $a\rho^2$. The internal pressure of the colloidal system is the osmotic pressure as calculated from the difference between the Gibbs and Helmholtz free energies, in accordance with eq 4.11. Since the volume of a colloidal system is virtually that of the solvent, the product $\Delta(PV) = 0$ can be obtained, while changes can be made with the internal pressure or osmotic pressure.

We next address the effect of changes in the excluded volume b on the entropy change, where in the case of a highly charged colloid the effective radius of Okubo is adopted. The process is to take a fixed number of colloidal particles and follow the changes as the volume associated with these particles changes as the associated volume decreases with the "effective" particle size. The mechanism for change in b is the response of the system to "electrical stress" as described in the previous paragraph. To simplify the integrations, the parameter a is held constant. After the integrations the two volumes of the suspension are set equal to assess the effect of changing the excluded volume b on the entropy. The entropy change is given by the general thermodynamic relationship,

$$\mathrm{d}S = \frac{\delta q}{T} = \left(\frac{1}{T}\right)\left(\frac{\partial U}{\partial V}\right)_T \mathrm{d}V - \frac{\delta w}{T} \tag{8.3}$$

Work is defined as a change in volume against an external pressure. The work for a van der Waals gas, in general, is thus given by

$$\begin{aligned} w_{\mathrm{vdW}} &= -\int_{V_1}^{V_2} P\,\mathrm{d}V \\ &= -\int_{V_1}^{V_2}\left(\frac{nRT}{V - nb} - \frac{n^2 a}{V^2}\right)\mathrm{d}V \\ &= -nRT\ln\left(\frac{V_2 - nb}{V_1 - nb}\right) - n^2 a\left(\frac{1}{V_2} - \frac{1}{V_1}\right) \end{aligned} \tag{8.4}$$

To associate this result with the charged colloid system, we express the desired result in terms of the densities and excluded volumes of the particles before and after the counterion condensation process, denoted by the subscripts "1" and "2", respectively,

$$-\frac{w_{\mathrm{vdW}}}{T} = nR\ln\left(\frac{V_2}{V_1}\right) + nR\ln\left(\frac{1 - \rho_2 b_2}{1 - \rho_1 b_1}\right) + \frac{na(\rho_2 - \rho_1)}{T} \tag{8.5}$$

Likewise we have,

$$\left(\frac{1}{T}\right)\int_{V_1}^{V_2}\left(\frac{\partial U}{\partial V}\right)_T \mathrm{d}V = \frac{an^2}{T}\int_{V_1}^{V_2}\left(\frac{1}{V^2}\right)_T \mathrm{d}V = -\frac{an(\rho_2 - \rho_1)}{T} \tag{8.6}$$

Combining eqs 8.5 and 8.6 gives the desired result,

$$\Delta S = nR\ln\left(\frac{V_2}{V_1}\right) + nR\ln\left(\frac{1 - \rho_2 b_2}{1 - \rho_1 b_1}\right) \tag{8.7}$$

As in the case of the external pressure, the volume is held constant when the charge of the particles is changed. Therefore we set $V_2 = V_1$ and $\rho_1 = \rho_2 = \rho$ since the number of macroion particles does not change. An expression for the entropy change of the system when the excluded volume changes is thus obtained,

$$\Delta S = nR\ln\left(\frac{1 - \rho b_2}{1 - \rho b_1}\right) \tag{8.8}$$

In the scenario regarding to the electrical stress on the system, the condensation of counterions onto the macroion surface reduces the excluded volume of that particular particle, namely, $b_2 < b_1$. Clearly, the contraction of b results in an increase in the local entropy and therefore an increase in entropy of the system. The scenario of the system response to electrical stress is, at least partially, entropy-driven.

It is noted that the concepts of an "excluded volume" surrounding a macroion and charge reduction by binding counterions were originally proposed by Oosawa, Imai, and Kagawa in 1954.[26] Oosawa also used the concept of "free volume" of the system in his theory of the thermodynamic properties of polyelectrolyte solutions.[27]

9. Generalized Osmotic Coefficient

Let us combine the above results for the van der Waals gas and apply them to a system of colloid particles. The standard relationship between the Helmholtz and Gibbs free energies is given by

$$P_{\mathrm{eff}}V_{\mathrm{eff}} = G - A = \sum_{\mathrm{j}} \mu_{\mathrm{j}} n_{\mathrm{j}} - (U - TS) \tag{9.1}$$

where the summation is over all of the particles in the system (including the solvent), the "effective pressure" P_{eff} is the standard result in any physical chemistry book,

$$P_{\mathrm{eff}} = P + \pi \tag{9.2}$$

where P is the external pressure and π is the osmotic pressure. The question about the effective volume is not straightforward. As discussed in Section 8, electrostatic repulsion between the macroions alters the excluded volume of the macroions. However, the solvent and microions are not excluded from this region surrounding the macroions that appear in the summation. We therefore set $V_{\mathrm{eff}} = V$, the total volume of the system.

We now differentiate eq 9.1 and make the substitution $\mathrm{d}U = T\mathrm{d}S - P\mathrm{d}V$, with the result,

$$\pi\, \mathrm{d}V + V\, \mathrm{d}P + V\, \mathrm{d}\pi = \sum_{\mathrm{j}} \mu_{\mathrm{j}}(\mathrm{d}n_{\mathrm{j}}) + \sum_{\mathrm{j}} n_{\mathrm{j}}(\mathrm{d}\mu_{\mathrm{j}}) + S\, \mathrm{d}T \tag{9.3}$$

If the process is carried out under constant total volume V and external pressure P conditions, then we arrive at the desired result,

$$V\, \mathrm{d}\pi = \sum_{\mathrm{j}} \mu_{\mathrm{j}}(\mathrm{d}n_{\mathrm{j}}) + \sum_{\mathrm{j}} n_{\mathrm{j}}(\mathrm{d}\mu_{\mathrm{j}}) = \sum_{\mathrm{j}} \mu_{\mathrm{j}}(\mathrm{d}n_{\mathrm{j}}) + k_{\mathrm{B}}T \sum_{\mathrm{j}} n_{\mathrm{j}}(\mathrm{d}\ln(\gamma_{\mathrm{j}})) \tag{9.4}$$

where γ_{j} is the activity coefficient of the j-th particle, which is a measure of the nonideal effects. It is noted that eq 9.4 allows two alternate interpretations of the ratio $\phi = \pi_{\mathrm{measued}}/\pi_{\mathrm{ideal}}$ for $\phi \neq 1$: a change in the number of particles by association ($\phi < 1$) or dissociation ($\phi > 1$), or a corresponding change in the activity coefficients of the components. Hence, a reduction in the number of "free" particles is synonymous to a reduction in the activity coefficients of these particles.

The activity coefficient contains all of the electrical interactions of the system as well as other nonideal effects. These electrical effects are symbolically represented by γ_{elec}, which includes the charged colloid particles as well as the microions and, to a lesser extent, the polar properties of the solvent. The microions are quite dynamic in a system of highly charged colloidal particles. Those counterions found in the JPF shell surrounding one macroion act to reduce the effective charge of the macroion and under certain circumstances may even reverse the macroion charge within a cluster. It is this reduction in the charge of micelles that Langmuir proposed as a mechanism to equate the chemical potential of the micelles in the two phases, that is, part C. Counterions found in JPF shells that surround several colloidal particles act as "bonding counterions" in a similar manner that electrons may bond atoms together to form molecules. These counterions, as a group, are localized about the colloidal clusters, which necessarily reduces their entropy contribution to the system. One may view all of the counterions associated with these clusters as a reduction in the number of particles that contribute to the osmotic pressure of that region.

Let us now re-examine the generalized form of the pair interaction free energies as given by eq 2.13. The difference between the two free energies is thus obtained

$$\bar{G}^{\mathrm{elec}}_{\mathrm{I,J}}(r_{\mathrm{I,J}}, \kappa) - \bar{A}^{\mathrm{elec}}_{\mathrm{I,J}}(r_{\mathrm{I,J}}, \kappa) = \left(1 - \frac{\kappa r_{\mathrm{I,J}}}{2}\right)\bar{A}^{\mathrm{elec}}_{\mathrm{I,J}}(r_{\mathrm{I,J}}, \kappa) \tag{9.5}$$

Within the context of the RDH theory,[11] eq 9.5 is interpreted as colloid−colloid pair contribution to the osmotic pressure.

10. The Problem of Voids

Confocal laser scanning microscopy (CLSM) studies on highly charged colloid particles revealed "voids" in the suspension in which there were no discernible colloid particles.[9,28−31] Since CLSM measurements extend well into the suspension, the formation of voids cannot be due to glass-dispersion (wall) effects. According to Ise, Konishi, and Tata,[9] voids grow in structure over a period of months, where voids of size 50 × 200 × 50 μm^3 can be obtained. The voids in the suspension give rise to a "Swiss cheese" structure (holes) to the colloid system rather than a "Colby-Jack" structure (regions of varying concentrations) for the distribution of the colloid particles. Real-time videos also revealed oscillatory motions of colloid particles at the cluster−void interface, as if these particles were in a harmonic oscillator potential well. Furthermore, these observations were made on systems with no added electrolyte.

The presence of void structures is not compatible with molecular dynamic simulations of the type reported by Robbins, Kremer, and Grest.[10] While the purely repulsive Yukawa interaction might be used to interpret a "two-state" structure of dense and sparse regions of the colloid particles, a purely repulsive interaction does not support stable bounded regions coexisting with void regions within the system.

The model of van Roij, Dijkstra, and Hansen[11] likewise cannot explain the coexistence of void structures with crystalline-like structures. They noted in their introduction, "More evidence of phase coexistence has been provided by the observation of extremely dilute voids (a gas phase) in the bulk of an apparently homogeneous deionized suspension (a liquid or solid)."

These authors define a void as a dilute gas phase, meaning that there are very few colloid particles in this region. This interpretation is inconsistent with the visual observation of long-lived void regions with no colloid particles.

There was hope that Warren explained the presence of voids by the title of his paper: "A theory of void formation in charge-stabilized colloid suspensions at low ionic strength".[6] After noting the relative colloid concentrations are determined by the tie line in the phase diagram, Warren stated: "Typically, though, the colloid volume fraction in the depleted phase is vanishingly small and this phase is essentially pure brine." Unfortunately, the presence of voids is for deionized water, in which case there is no "excess brine" to fill in the void region.

Mention should be made of the Monte Carlo simulations using the SI potential.[32−34] In contrast with other studies, these simulations do show the formation of stable void regions, which one would expect because of the minimum in the pair interaction.

There is, however, a possible explanation of the stability of void regions when one considers the picture painted by the JPF method and the entire volume of the system rather than localized regions. According to the JPF constant potential surfaces, there are "orbitals" that encompass the entire cluster. Counterions in this outer region act as an "effective double layer" for the cluster, that is, a second double layer.[16] As the size of a cluster grows, it becomes unstable and separates into two or more clusters. Because each cluster has its own "double layer" composed of the counterions in the outermost "orbitals", the repulsion set up between clusters acts to form and stabilize the void regions. While there may be several reasons for the instability of a large cluster, one cannot dismiss the possibility that the solvent might also be involved. The local activity of the solvent within the cluster is subject to local effects of the charged particles implied by local application of the Gibbs−Duhem relationship. But this does not account for the absence of macroions in the void region if one insists, as did Langmuir, that the chemical potential of the macroions must be the same in the void as in the cluster. However, this argument is synonymous to requiring the region between two macroions in the crystalline phase to have the same macroion chemical potential as the region surrounding each macroion. This apparent paradox of having large void regions in equilibrium with large crystalline regions can be avoided by looking at the system as a whole, that is, a "holistic approach" when considering multibody interactions. A parallel situation in statistical mechanics is the difference between "fine graining" and "coarse graining".

11. Discussion

The current practitioners of the DLVO theory have strayed far from the original model as described by Verwey and Overbeek.[1] In the original model, there was no direct interaction between the macroions because of the assumption that the electrical and chemical work canceled exactly. Rather, the interaction between the macroions was by means of their associated double layers set up by the counterions surrounding each macroion. Partly motivated as a criticism of the theory of Langmuir,[12] the screening parameter was calculated by the ions far removed from the macroions. This criterion means that only added electrolyte contributes to the screening parameter since the counterions are restricted to regions in the vicinity of the macroion. A consequence of this definition is that macroions in "salt-free" solutions should interact through unscreened Coulomb potentials since the screening parameter is zero. In contrast, current practitioners include the counterions in the calculation of the screening parameter, which means that the macroions interact directly and the tightly associated counterions act to reduce the interaction charge between the macroions. Also, the current practice is to introduce "effective charges", "effective radii", "effective screening parameters", and "effective concentrations" as parameters to describe the system. The question therefore arises as to whether or not these "effective parameters" have any aspect of reality of the system or if they simply preserve the mathematical form of the Yukawa-type screened pairwise interaction between macroions.

In regards to the question regarding the physical properties of a real system, use of the Yukawa-type potential can lead to inconsistent conclusions. Consider, for example, the concentrations of salt in a two-phase system. Robbins, Kremer, and Grest[10] represented their phase diagram in the $k_BT/U_a - \lambda$ plane, where $\lambda = \kappa a$ with a as the average distance between colloid particles. In their model the microions are assumed to be uniformly distributed throughout the medium except for those that give rise to the effective charge. This means that the local κ has the same value regardless of the density of the macroions. This result drastically differs with the studies of van Roij, Dijkstra, and Hansen[11] and of Warren,[6] in which the "sparse" macroion region has a higher salt concentration than the "dense" macroion region.

As shown in Section 2, the Gibbs and Helmholtz forms of the Yukawa-type potential are different if one uses the standard thermodynamic relationship between these two quantities as given by eqs 2.1 and 2.2. Although the SI derivation may be in question [cf. eq 1.6], this difference in the form of the Gibbs and Helmholtz free energies was first shown by Sogami and Ise.[5] Opponents of the SI theory argue that the Gibbs and Helmholtz free energies must be equal since the charging process was carried out under constant pressure and volume conditions, that is, $\Delta(PV) = 0$. However, these arguments are based on the external volume and pressure. A well-known example that distinguishes between external and internal pressures is the van der Waals gas, as discussed in Section 8. The van der Waals attraction term $a\rho^2$ causes the collection of particles to contract relative to the ideal gas case. Hence the van der Waals gas, if treated as an ideal gas, acts as if it were responding to a larger (effective) pressure than the external pressure, that is, $P + a\rho^2$. By analogy, the particles in a solvent milieu act as a gas subject to an internal pressure in the form of the osmotic pressure. This distinction is an integral component in the theory of van Roij, Dijkstra, and Hansen. As also indicated in Section 8, changes in the van der Waals excluded volume term alter the "free volume" accessible to the macroions. In fact, Sogami and Ise[5] applied the concept of a change in "free volume" in their discussion.

Strong supporters of the Yukawa-type potential also cite the efforts of Overbeek[7] to discredit the SI theory by the introduction of the solvent into the derivation. The fallacies of the Overbeek correction factor were brought out in Section 3. If the solvent was objectively applied as well to the pre-exponential factors of the macroion concentrations as well as the microion concentrations in the screening parameter, then one obtains the unacceptable conclusion that the electrical interactions in the Gibbs form of the free energy vanishes while retaining all the electrical interactions in the Helmholtz form of the free energy. Rather than go through the mathematical exercise of including solvent in the SI derivation, some opponents of the "attractive tail" cite Overbeek's conclusion based on the "simpler result" from the Gibbs−Duhem expression in which the solvent cancels all electrical interactions. As first noted by Smalley,[8] this "simpler result" would eliminate all electrical contributions to the DLVO theory as well.

While the Yukawa form of the pairwise interaction between macroions may be easy to apply to complex charged colloid systems, it is based on the premise that the microions play a minor role in modulating these interactions. This shortcoming of the Yukawa-type potential is partially corrected by the introduction of two or more "screening parameters" to the different regions of the system. However, this ad hoc correction has no foundations in the DLVO theory. Even with the introduction of multiple screening parameters, the Yukawa-type "repulsive only" interaction cannot explain the presence of voids under "salt free" conditions.

BD simulations[20−22] regarding the distribution of microions for fixed macroion positions clearly expose the assumption that microions can be relegated to a "background" role, such as the chorus in a Greek play. These simulations indicate that two things occur upon decreasing the interparticle spacing in the macroion lattice at fixed volume of the rectangular computation cell. First, the co-ions are excluded from the interior of the cluster and the infusion of counterions, as previously mentioned. The second change is that the Helmholtz free energy from the expanded to the contracted lattice structure is negative, meaning that the smaller cluster is more stable. This result is consistent with part C of Langmuir's postulates that the effective charge on the macroion is reduced when in the cluster (see Section 4). Also, the JPF profiles indicate a very strong distortion of the macroion landscape in the vicinity of the interior macroions toward the interior of the cluster. Although not yet examined, it is possible that this section of the interior macroions may have a partial charge reversal in accordance with the MCEM calculations.[23,24] These simulations indicate that the osmotic pressure given by eq 9.4 is very complex and involves changes in the number of particles and the activity of all the particles in the system. A corollary of these simulations is that the so-called "volume term", with the specific purpose of mapping a multibody problem to a one-component system by averaging quantities such as ideal kinetics terms and a correction for the neutralizing background, is inadequate for describing a system in which the number of particles and their activities change.

The Yukawa-type screened pair potential may be adequate for application to charged colloidal systems under the low surface charge and high added salt conditions for which it was derived. However, it is inadequate for highly charged systems in which multibody interactions are prominent, including those of the microions.

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