

Volume-term theories, Sogami-Ise potential, and the Langmuir model for phase separation in macroion systems: A resolution

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(Received 24 August 2001; revised manuscript received 3 December 2001; published 10 June 2002)

There is a controversy regarding the mechanism of phase separation in highly charged macroion systems. Volume-term (VT) theories propose that the transition is due to a spinodal instability sensitive only by the microions, the Sogami-Ise theory gives an attractive tail in the pair interaction potential, which promotes the formation of clusters and voids, and the Langmuir (L) model views the transition as an instability of the pressure. It is shown herein that these three seemingly different models can be brought under the same formalism and that they reflect different contributions to the same overall process. Within the context of the VT formalism, the attractive tail in the macroion-macroion pair interaction is a direct result of the screened Coulomb form of the interaction and is identified as a microion-modified electrostatic pressure. Within the context of the VT formalism the L theory is associated with the microion-microion interaction for the added electrolyte. Finally this holistic view of the VT approach is extended to include the contribution of the solvent via the Gibbs-Duhem expression.

DOI: 10.1103/PhysRevE.65.061402

PACS number(s): 82.70.-y

I. INTRODUCTION

There have recently been a series of “volume-term” (VT) theories [1–5] to explain the two-state structure of colloidal systems observed, among other techniques, by video microscopy methods [6–17]. The apparent motivation behind these studies is twofold: (1) to provide a plausible explanation for the observed phase separation within the context of an effective one-component model, and (2) to show that a phase separation can exist with a “purely repulsive pair potential” operating between the macroions. The precept of the VT approach, according to Grimson and Silbert [18], if one wanted to utilize the one-component system, is “...it has been found convenient to average out those variables which are not of primary interest, or those about which very little is known. As a result, the effective potential becomes a function of the thermodynamic state of the system.” To provide an indication of what the volume term entails we write down the complete Hamiltonian for the system of N_p colloidal particles of surface charge Z_p and $|Z_p|N_p = N_c$ neutralizing univalent counterions in the presence of $N_s = N_+ + N_-$ symmetric salt particles also of unit valency. The Hamiltonian for the system thus may be written symbolically as

$$H_{\text{system}} = K_p + K_c + K_+ + K_- + V_{pp} + V_{pc} + V_{p+} + V_{p-} + V_{cc} + V_{c+} + V_{c-} + V_{+-}, \quad (1)$$

where K_j is the kinetic energy of the j th particle and V_{jm} is the potential of interaction between the j th and m th particles, where the appropriate summation over all particles is implicit in the notation. One can summarize these contributions to the reduced Helmholtz free energy per unit volume as

$$\beta \frac{A}{V} = \bar{A} = \bar{A}_{\text{id}} + \bar{A}_{\text{bc}} + \bar{A}_{\text{ss}} + \bar{A}_{\text{ps}} + \bar{A}_{\text{pp}}^{\text{elec}}, \quad (2)$$

where $\beta = 1/k_B T$ (k_B is the Boltzmann constant and T the absolute temperature), \bar{A}_{id} is the ideal contribution, \bar{A}_{bc} is the hard core contribution, \bar{A}_{ss} is the added electrolyte contribution, \bar{A}_{ps} is the contribution of the ion cloud about the parent macroion, and $\bar{A}_{\text{pp}}^{\text{elec}}$ is the macroion-macroion contribution. The precise form of all the terms is not important for the present discussion. The terms that are relevant are the pairwise electrostatic interaction $\bar{A}_{\text{pp}}^{\text{elec}}$, the electrolyte interaction term \bar{A}_{ss} , and the term responsible for driving the spinodal instability \bar{A}_{pc} [1]. The pairwise interaction between the macroions is assumed to be the screened Coulomb form,

$$\begin{aligned} \bar{A}_{\text{pp}}^{\text{elec}} &= \frac{\lambda_B}{2} \sum_{i=1}^{N_p} \sum_{\substack{j=1 \\ j \neq i}}^{N_p} n_i n_j Z_i Z_j F(\kappa a_i) F(\kappa a_j) \frac{\exp(-\kappa r_{ij})}{r_{ij}} \\ &= \frac{\lambda_B}{2} \sum_{i=1}^{N_p} \sum_{\substack{j=1 \\ j \neq i}}^{N_p} n_i n_j Z_i Z_j B_{ij}^{\text{elec}}, \end{aligned} \quad (3)$$

where κ is the screening parameter. The function $F(\kappa a_m)$ is a model-dependent function for the m th macroion of radius a_m and number concentration n_m . For example, $F(\kappa a_m) = 1$ results in the Yukawa form of the pair interaction. The macroion-microion contribution to the Helmholtz free energy is

$$\bar{A}_{\text{ps}} = - \frac{2 \kappa Z_p^2 \lambda_B n_p f(\kappa a_p)}{3} \cong - \frac{2 \kappa Z_p^2 \lambda_B n_p}{3}, \quad (4)$$

where $f(x) = (3/x^3)[\ln \eta(1+x) - x + (x^2/2)]$. Finally, the microion-microion contribution is

$$\bar{A}_{\text{ss}} = - \frac{\kappa^3}{12\pi}. \quad (5)$$

The approach to the calculation of the phase diagram is to equate the chemical potentials of all relevant species and the pressure of the coexisting phases. In the present notation, the prescription set forth by van Roij, Dijkstra, and Hansen [3] for the equilibrium between the two regions (1) and (2) is given by their Eq. (67) for the chemical potentials μ_j and pressure P ,

$$\begin{aligned}\mu_p(n_p^{(1)}, n_s^{(1)}) &= \mu_p(n_p^{(2)}, n_s^{(2)}), \\ \mu_s(n_p^{(1)}, n_s^{(1)}) &= \mu_s(n_p^{(2)}, n_s^{(2)}), \\ P(n_p^{(1)}, n_s^{(1)}) &= P(n_p^{(2)}, n_s^{(2)}),\end{aligned}\quad (6)$$

where the chemical potentials are obtained from the standard thermodynamic relationships by their Eq. (68),

$$\begin{aligned}\mu_p &= \left(\frac{\partial \bar{A}(n_p, n_s)}{\partial n_p} \right)_{n_s}, \\ \mu_s &= \left(\frac{\partial \bar{A}(n_p, n_s)}{\partial n_s} \right)_{n_p},\end{aligned}\quad (7)$$

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

The screening parameter is given by

$$\kappa^2 = 4\pi\lambda_B(2Z_s^2 n_s + Z_c^2 |Z_p| n_p). \quad (8)$$

It is crucial for the VT theories that the screening parameter contain contributions from both the added electrolyte and the counterions released by the macroions, for it is only if the form given by Eq. (8) does the role of the screening parameter become clear in the determination of ‘‘phase’’ boundaries. The screening parameter is the thread that connects the Helmholtz free energies to the microion concentrations from the added electrolyte and the counterions from the macroions.

II. RELATIONSHIP OF THE VT MODEL TO THE DERJAGUIN-LANDAU-VERWEY-OVERBEEK (DLVO) THEORY

Verwey and Overbeek present in their monumental work ([19], p. 58) arguments for the omission of the contributions of the charging of the macroion (chemical work cancels this work) and the added electrolyte (ions appear in neutralizing numbers), which leads to their conclusion: ‘‘The very simple result is that we find the total free energy of the double layer if only we calculate the *electric* work necessary to discharge stepwise all ions of the *solution*,’’ where they have used italics to emphasize that the electrostatic energy is localized to *the solution phase of the system*. The resulting pair potential in the DLVO theory is

$$\bar{A}_{pp}^{\text{elec}} = \frac{\lambda_B}{2} \sum_{l=1}^{N_p} \sum_{\substack{j=1 \\ j \neq l}}^{N_p} n_l n_j Z_l Z_j \frac{\exp(\kappa a_l)}{(1 + \kappa a_l)} \frac{\exp(\kappa a_j)}{(1 + \kappa a_j)} \frac{\exp(-\kappa r_{lj})}{r_{lj}}. \quad (9)$$

Another feature of the DLVO theory is the definition of κ . As pointed out by Verwey and Overbeek ([19], pp. 197 and 198), ‘‘The double layer theory, however, shows that this thickness is determined by the electrolyte concentration in the sol medium, far from any particle, and is, therefore, independent of the sol concentration (in dilute sols).’’ In other words the screening parameter in the DLVO theory is given, in the present notation, by

$$\kappa_{\text{DLVO}}^2 = 4\pi\lambda_B(2Z_s^2 n_s). \quad (10)$$

To emphasize this difference between the DLVO and VT models we rewrite Eq. (8) as

$$\kappa_{\text{VT}}^2 = 4\pi\lambda_B(2Z_s^2 n_s + Z_c^2 |Z_p| n_p) = \kappa_{\text{DLVO}}^2 + \kappa_c^2. \quad (11)$$

III. RELATIONSHIP OF THE VT MODEL TO THE SOGAMI-ISE THEORY

The Sogami-Ise [20] (SI) theory is a linearized theory based on the Poisson equation in which the macroions as well as the microions contribute to the electrical potential. It is of value to the later discussion to summarize the main steps in the SI theory to emphasize that the microions play a major role in their theory.

In their formal expressions only the counterion ions are present, and only the counterion distribution is assumed to be of the Boltzmann type. In the present notation the Poisson equation in the SI theory is

$$\begin{aligned}\nabla^2 \langle \psi(\mathbf{r}) \rangle &\cong -\frac{4\pi}{\varepsilon} \left(\sum_{m=1}^{N_p} Z_m q_e n_m(\mathbf{r}) + \sum_{i=1}^{|Z_p|N_p} Z_i q_e n_{i,o} \right. \\ &\quad \left. - \sum_{i=1}^{|Z_p|N_p} Z_i^2 q_e^2 n_{i,o} \langle \psi(\mathbf{r}) \rangle \right).\end{aligned}\quad (12)$$

Rearrangement with obvious substitutions of parameters gives their Eq. (8) [20],

$$\begin{aligned}\varepsilon(\nabla^2 - \kappa_c^2) \langle \psi(\mathbf{r}) \rangle &\cong -4\pi \sum_{m=1}^{N_p} Z_m q_e n_m(\mathbf{r}) \\ &\quad - 4\pi \sum_{i=1}^{|Z_p|N_p} Z_i q_e n_{i,o}.\end{aligned}\quad (13)$$

They then proceed to shift the potential to eliminate the second term on the right-hand side of Eq. (13), viz., in our notation their Eq. (9) is

$$\langle \psi(\mathbf{r}) \rangle = \langle \phi(\mathbf{r}) \rangle + \frac{4\pi}{\varepsilon} \sum_{i=1}^{|Z_p|N_p} Z_i q_e n_{i,o}, \quad (14)$$

which results is a Poisson equation for the charge density involving only the macroions,

$$\varepsilon(\nabla^2 - \kappa_c^2) \langle \phi(\mathbf{r}) \rangle \cong -4\pi \sum_{m=1}^{N_p} Z_m q_e n_m(\mathbf{r}), \quad (15)$$

which they refer to as a “true charge density” in their Eq. (12),

$$-\frac{\varepsilon}{4\pi}\nabla^2\langle\psi(\mathbf{r})\rangle\equiv-\frac{\varepsilon\kappa_c^2}{4\pi}\langle\phi(\mathbf{r})\rangle+\sum_{i=1}^{N_p}Z_iq_en_i(\mathbf{r}), \quad (16)$$

where $-(\varepsilon\kappa_c^2/4\pi)\langle\phi(\mathbf{r})\rangle$ represents the charge density of the counterions. The claim of the SI theory is that the distributions of the macroions and the counterions are mutually interactive, and that the “effective interaction” between the macroions is *moderated* by the small ions.

As in the case with the VT theories, the Helmholtz free energy of interaction between the macroions appears as a form of a screened Coulomb interaction, whose precise mathematical form in the SI paper for $\bar{A}_{pp}^{\text{elec}}$ is

$$\begin{aligned} \bar{A}_{pp}^{\text{elec}} &= \frac{\lambda_B}{2} \sum_{i=1}^{N_p} \sum_{\substack{j=1 \\ j \neq i}}^{N_p} n_i n_j Z_i Z_j \frac{\sinh(\kappa a_i)}{\kappa a_i} \frac{\sinh(\kappa a_j)}{\kappa a_j} \\ &\quad \times \frac{\exp(-\kappa r_{ij})}{r_{ij}}. \end{aligned} \quad (17)$$

Hence the only difference between the VT and the SI theories at this point is the definition of $F(\kappa a_m)$. The next step is the controversial step that has generated many papers over the past two decades. Sogami and Ise laid claim that the proper pairwise interaction between the macroions *should be the Gibbs free energy and not the Helmholtz free energy*. They then proceeded to use as their fundamental expression, Eq. (26), which in the present notation is

$$\bar{G}_{pp}^{\text{elec}} = \left[\sum_i n_{i,o} \left(\frac{\partial \bar{A}_{pp}^{\text{elec}}}{\partial n_{i,o}} \right) + \sum_m Z_m \left(\frac{\partial \bar{A}_{pp}^{\text{elec}}}{\partial Z_m} \right) \right]. \quad (18)$$

According to Sogami and Ise [20] the first term in the square brackets represents the chemical potential of the small ions, as also given in the VT theories via Eq. (7). The second term is defined by Sogami and Ise as being the contribution of the “immobile ions” to the macroions. From the mathematical form of the pair interaction given by Eq. (17) and the definition of κ_c , it is noted that n_m and Z_m always appears as a product. What necessarily follows is the operator identity $Z_m(\partial/\partial Z_m) = n_m(\partial/\partial n_m)$. Hence we may rewrite Eq. (18) as

$$\bar{G}_{pp}^{\text{elec}} = \left[\sum_i n_{i,o} \left(\frac{\partial \bar{A}_{pp}^{\text{elec}}}{\partial n_{i,o}} \right) + \sum_m n_m \left(\frac{\partial \bar{A}_{pp}^{\text{elec}}}{\partial n_m} \right) \right]. \quad (19)$$

If one isolates the application of Eq. (7) to the Helmholtz free energy of the macroion pair interaction, then one obtains the mathematical form of Eq. (19). Hence the formalism of the VT theories contain as a subset of expressions the SI equations.

Let us focus on the general expression for the Helmholtz free energy of the macroion pair interaction given by Eq. (3). A key feature of Eqs. (7) and (19) is that the set of concentration variables in the VT and SI theories dictate that derivatives must be taken of the screening parameter as well as the preexponential factors. The contributions of the macroions

appear in two locations, in the prefactor and the screening parameter, whereas that of the added electrolyte appear only once: in the screening parameter. Consider first the derivatives of the generalized form of the screening parameter

$$\kappa = \left(4\pi\lambda_B \sum_{\alpha} Z_{\alpha}^2 n_{\alpha} \right)^{1/2}, \quad (20)$$

where the Greek subscript denotes all of the ions regardless of origin. It follows directly that

$$\sum_{\alpha} n_{\alpha} \left(\frac{\partial \kappa}{\partial n_{\alpha}} \right) = \frac{\kappa}{2}. \quad (21)$$

We write for the Gibbs free energy associated with the generalized form of the Helmholtz free energy of the pairwise interaction given by Eq. (3),

$$\begin{aligned} \bar{G}_{pp}^{\text{elec}} &= \sum_m n_m \left(\frac{\partial A_{pp}^{\text{elec}}}{\partial n_m} \right) + \sum_{\alpha} n_{\alpha} \left(\frac{\partial A_{pp}^{\text{elec}}}{\partial n_{\alpha}} \right) \\ &= \frac{\lambda_B}{2} \sum_{i=1}^{N_p} \sum_{\substack{j=1 \\ j \neq i}}^{N_p} \left[\sum_m n_m \left(\frac{\partial n_i n_j Z_i Z_j B_{ij}^{\text{elec}}}{\partial n_m} \right) \right. \\ &\quad \left. + \sum_{\alpha} n_{\alpha} \left(\frac{\partial n_i n_j Z_i Z_j B_{ij}^{\text{elec}}}{\partial n_{\alpha}} \right) \right]. \end{aligned} \quad (22)$$

At this point we have to keep the bookkeeping straight, for the counterions can be expressed either in terms of the macroion concentrations, as in the VT theories and given by Eq. (11), or in terms of the ion concentration such as $n_{i,o}$ in Eq. (12). To simplify matters, we chose to group the released counterions from the macroions as part of the α notation, so that under “salt-free” conditions Eqs. (18) and (19) survive. It is further noted that in Eq. (22) the value of m is restricted to the values $m=i$ or $m=j$. Hence we may partition Eq. (22) to obtain

$$\begin{aligned} \bar{G}_{pp}^{\text{elec}} &= \frac{\lambda_B}{2} \sum_{i=1}^{N_p} \sum_{\substack{j=1 \\ j \neq i}}^{N_p} \left[Z_i Z_j B_{ij}^{\text{elec}} \sum_m n_m \left(\frac{\partial n_i n_j}{\partial n_m} \right) \right. \\ &\quad \left. + n_i n_j Z_i Z_j \sum_{\alpha} n_{\alpha} \left(\frac{\partial B_{ij}^{\text{elec}}}{\partial n_{\alpha}} \right) \right] \\ &= \frac{\lambda_B}{2} \sum_{i=1}^{N_p} \sum_{\substack{j=1 \\ j \neq i}}^{N_p} \left\{ 2 + \frac{1}{2} \left[\frac{\kappa a_i}{F_i(\kappa a_i)} \left(\frac{\partial F_i(\kappa a_i)}{\partial \kappa a_i} \right) \right. \right. \\ &\quad \left. \left. + \frac{\kappa a_j}{F_j(\kappa a_j)} \left(\frac{\partial F_j(\kappa a_j)}{\partial \kappa a_j} \right) \right] - \frac{\kappa r_{ij}}{2} \right\} n_i n_j Z_i Z_j B_{ij}^{\text{elec}}, \end{aligned} \quad (23)$$

where we have changed the variable from κ to κa in the application of Eq. (21). It is now evident that the attraction term $-\kappa r_{ij}$ arises solely from the Yukawa screened Coulomb form $\exp(-\kappa r_{ij})$. We now draw the important conclusion that any model employing a repulsive screened Coulomb pair potential *must* result in an attractive term in the

calculation of the chemical potential when standard thermodynamic relationships are employed.

IV. RELATIONSHIP OF THE VT MODEL TO THE LANGMUIR MODEL

In 1938 Langmuir posted his objections to using potential energy curves for the calculation of the free energy of the system [21]. These criticisms are given as the following factors [21].

(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 dispersed throughout the liquid giving an osmotic pressure $p = \Sigma nkT$.

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

Factor (a) is a direct consequence of using the Poisson-Boltzmann equation. On the basis of factor (a) it was concluded that thermal agitation was not a repulsive force. Factor (b) was represented in terms of an ionic crystal of alternating charge, thus giving rise to an *attractive* force between particles. Hence factors (a) and (b) give a net attraction between all of the particles in the micellar system. The dilemma at this stage is to find a way to diminish the electrostatic term. This can be achieved in two ways: find a source of a repulsion or decrease the charge on the micelles. The latter possibility is factor (c). It was envisioned that as the concentration of the micelles (of positive charge) increased, the effective charge decreased until a stable situation occurred between the two phases. A parallel was drawn between the colloidal system and tungsten filaments in equilibrium with cesium.

The micellar system was partitioned into two regions by a semipermeable membrane. In one region, the “dense” region, the membrane was compressed to such an extent that the particles were envisioned as being so close that there is extensive overlap of the ion clouds. Since the ξ potential for all of the particles on both sides of the membrane is to remain constant, the charge on the micelles engaged with overlapping ion clouds must change. The other region, the “dilute” region, was treated as if it were a Debye-Hückel fluid. Langmuir then addressed the situation of highly charged micelles, in which there was a sheath of counterions with the exclusion of coions. Thus in the “dilute” region the micelle was treated as a “point ion” of a fictitious charge dictated by the counterions in the surrounding “sheath.” In the parlance of the VT theories, this represents the “dressed macroion” composed of the macroion and its charge neutralizing counterions.

The stage is now set to “squeeze” the micelles in the dense phase to the point that counterions in the fluid between the macroions are forced to decrease. Since the ξ potential for these micelles now in closer proximity must be the same

as in the dilute phase, the charge on the micelles must decrease. Further squeezing of the micelles results in the whole phase having the ξ potential to match that of the individual micelles in the dilute phase.

Langmuir then employed two different approximations of the Debye-Hückel theory: point charges and finite size ions. It is not necessary to review both, for the point charge approximation will suffice. The pressure P for the dilute phase is then given by Eq. (15) in the textbook by McQuarrie [22],

$$P = k_B T \left[\sum_j n_j - \frac{(\pi)^{1/2}}{3} \left(\lambda_B \sum_j Z_j^2 n_j \right)^{3/2} \right] \\ = k_B T \left(\sum_j n_j - \frac{\kappa^3}{24\pi} \right). \quad (24)$$

The first term on the right-hand side of Eq. (24) is the ideal pressure from the micelles and the microions. The second term is the electrostatic pressure as given by Eqs. (15) and (16) on page 337 of McQuarrie [22],

$$\beta P^{\text{elec}} = - \frac{\kappa^3}{24\pi} \sigma(\kappa a) \cong - \frac{\kappa^3}{24\pi}, \quad (25)$$

where the last expression is for $\kappa a \rightarrow 0$.

Van Roij, Dijkstra, and Hansen [3] dismissed the theory of Langmuir [21] on the basis that his arguments were only “qualitative,” and based on the Debye-Hückel approximation for osmotic pressure. This statement was probably based on the treatment of the “dressed” micelle as a point charge in the Langmuir model and therefore included in the screening parameter. The electrostatic pressure defined by Eq. (25) is also obtained from the VT formulation and the expression for \bar{A}_{ss} defined by Eq. (5) and used in Eq. (7),

$$\bar{G}_{ss} - \bar{A}_{ss} = n_s \left(\frac{\partial \bar{A}_{ss}}{\partial n_s} \right) - \bar{A}_{ss} = - \frac{\kappa^3}{24\pi} = \beta P_{ss}^{\text{elec}}. \quad (26)$$

Therefore the VT theories are in concert with the model of Langmuir with the identity $P_{ss}^{\text{elec}} = P^{\text{elec}}$ in Eq. (25). Hence the mathematical expressions of the L theory are a crucial part of the VT theory and play the role of the volume terms in effecting a phase separation. The primary difference in regard to the physical model is that in the Langmuir theory the macroions are treated as point charges that contribute directly to the screening parameter, which we may symbolically write in terms of the simple ion (s) and the “point macroion” (p) contributions,

$$\kappa_L^2 = 4\pi\lambda_B Z_s^2 n_s + 4\pi\lambda_B Z_p^2 n_p = \kappa_s^2 + \kappa_p^2. \quad (27)$$

Since $Z_p \gg Z_s$ one can ignore the small ion contribution so that κ_L is proportional to $n_p^{1/2}$, hence the pressure in Eq. (24) could be written as [21]

$$P \approx 3n_p - 2n_p^{3/2}. \quad (28)$$

For small values of n_p the pressure increased as n_p and at a higher value of n_p the pressure varied as $-n_p^{3/2}$. A similar

argument was put forth by van Roij and Hansen [1] as the “essence” of the term responsible, for the spinodal instability is based on $\kappa \approx n_p^{1/2}$ just as in the Langmuir model. An important difference is the origin of the factor n_p , which in the case of van Roij and Hansen’s theory is from κ_c for which the counterion concentration is $n_c = |Z_p|n_p$.

Many cite Verwey and Overbeek as proving the Langmuir model to be incorrect (pp. 195–199 of [19]). Verwey and Overbeek pointed out that κ is, by definition in the DLVO model, independent of the macroion concentration since it is determined far from the macroions, i.e., $\kappa = \kappa_{\text{DLVO}} \approx n_s^{1/2}$ for all values of n_s and n_p . However, the argument put forth by Verwey and Overbeek is applicable for either the Langmuir model or the VT theories, since both models exhibit a P^{elec} that is proportional to $-n_p^{3/2}$ in the appropriate range. Therefore if one accepts the argument of Verwey and Overbeek that the Langmuir model is incorrect then one must also accept the argument to also show that the VT theories are incorrect. On the other hand if one accepts the precepts of the VT theories then one cannot eliminate the Langmuir model as contributing to a viable mechanism for phase separation in highly charged macroions.

V. PARTITIONING OF THE MICROIONS—PARALLELS WITH THE HAMILTONIAN FOR THE VALENCE BOND AND MOLECULAR ORBITAL THEORIES

The valence bond and molecular orbital theories of electronic structures differ only in the manner in which the Hamiltonian of the system is partitioned. In a similar way theories on the phase separation in colloidal systems also are a result of how the microions are partitioned. To examine in more detail the significance of the counterions in the problem we look at the usual approach for the Poisson-Boltzmann equation with the potential $\langle \psi(\mathbf{r}) \rangle$ at some point \mathbf{r} in the solution. The general expression, including the macroion density, is

$$\nabla^2 \langle \psi(\mathbf{r}) \rangle = -\frac{4\pi}{\epsilon} \sum_{m=1}^{N_p} Z_m q_e n_m(\mathbf{r}) - \frac{4\pi}{\epsilon} \sum_{j=1}^{2N_s+N_c} Z_j q_e n_j(\mathbf{r}), \quad (29)$$

where the microion summation encompasses the added electrolyte and the free counterions. According to renormalization theories a certain number of the counterions released by the macroions are associated with the macroions to reduce the macroion charge to an effective charge Z_{eff} [23,24]

$$\nabla^2 \langle \psi(\mathbf{r}) \rangle = -\frac{4\pi}{\epsilon} \sum_{m=1}^{N_p} Z_{\text{eff}} q_e n_m(\mathbf{r}) - \frac{4\pi}{\epsilon} \sum_{j=1}^{2N_s+N_c^*} Z_j q_e n_j(\mathbf{r}), \quad (30)$$

where $N_c^* = N_c - \langle N_c \rangle_b$, N_p is the number of free counterions, $\langle N_c \rangle_b$ is the average number of bound (charge neutralizing) counterions, and $Z_{\text{eff}} = Z_p + Z_c \langle N_c \rangle_b$. We now express the microion contribution as a Boltzmann distribution

$$\frac{4\pi}{\epsilon} \sum_{j=1}^{2N_s+N_c^*} Z_j q_e n_j(\mathbf{r}) = \frac{4\pi}{\epsilon} \sum_{j=1}^{2N_s+N_c^*} Z_j q_e n_{j,0} \times \exp[-\beta Z_j q_e \langle \psi(\mathbf{r}) \rangle]. \quad (31)$$

This Boltzmann factor is then expanded and the terms collected,

$$\begin{aligned} \frac{4\pi}{\epsilon} \sum_{j=1}^{2N_s+N_c^*} Z_j q_e n_{j,0} \exp[-\beta Z_j q_e \langle \psi(\mathbf{r}) \rangle] \\ = \frac{4\pi}{\epsilon} \sum_{j=1}^{N_c} Z_j q_e n_{j,0} - 4\pi \lambda_B \sum_{j=1}^{2N_s+N_c^*} Z_j^2 n_{j,0} \langle \psi(\mathbf{r}) \rangle \\ = \vartheta_D - (\kappa_{\text{DH}}^2 + \kappa_c^2) \langle \psi(\mathbf{r}) \rangle, \end{aligned} \quad (32)$$

where ϑ_D is a previously introduced Donnan term [25] and does not contain added electrolyte contributions due to electrical neutrality of these components. The Poisson-Boltzmann equation for the mean potential is now expressed as

$$\begin{aligned} \nabla^2 \langle \psi(\mathbf{r}) \rangle = -\frac{4\pi}{\epsilon} \sum_{m=1}^{N_p} Z_{\text{eff}} q_e n_m(\mathbf{r}) - \vartheta_D + (\kappa_{\text{DH}}^2 + \kappa_c^2) \\ \times \langle \psi(\mathbf{r}) \rangle. \end{aligned} \quad (33)$$

We have thus partitioned the counterions to function as a partial neutralization of the macroion charge to the value of Z_{eff} a Donnan contribution as manifested in the uniform distribution of excess counterions, and those that are free to be distributed throughout the system and contribute to the screening parameter.

The reason that the macroions do not appear in the calculation of the screening parameter, as employed by Langmuir, is that the macroions do not exhibit a Boltzmann distribution. It is for this reason that the Langmuir proposal to treat the macroions as point charges is incorrect. However, the counterions do appear in the total screening parameter in accordance with the VT and SI theories, and therefore the objection by Verwey and Overbeek to the Langmuir model is incorrect. That is, the counterions that make up the term κ_c are in the vicinity of the macroion and are identified with the electric double layer. The SI theory is limited to the counterions only, thus $\kappa_{\text{DH}} = 0$ in their model. Neither the DLVO nor VT theories explicitly consider the Donnan term ϑ_D , whereas this term is explicit in the SI theory as shown in Eq. (12) and is the shift in the potential in Eq. (14).

VI. DISCUSSION

The primary thrust of this study is on the *mathematics* of the volume-term theories, the Langmuir model, and the Sogami-Ise pair potential as applied to the experimental observations of heterogeneous distributions of colloidal particles suspended in a continuum medium. The one parameter that serves as a thread connecting these three views on colloidal systems is the screening parameter κ and its subse-

quent contribution in the calculation of the chemical potential contribution of the microions for the two phases in the system.

In regard to the VT and SI theories, both have a modified form of the Yukawa screened Coulomb expression of the Helmholtz free energy of interaction between the macroions. Regardless of the fully charged species that comprise this screening parameter, the calculation of the chemical potential using standard, and well-established thermodynamic relationships as given by Eq. (7), we have the general result for the exponential part of the pair potential,

$$\sum_i n_i \left(\frac{\partial \exp(-\kappa r_{mn})}{\partial n_i} \right) = -\frac{\kappa r_{mn}}{2} \exp(-\kappa r_{mn}), \quad (34)$$

where the sum is over all of the i fully charged species that contribute to the screening parameter. It is this term that is responsible for the attraction when converting from the purely repulsive Helmholtz free energy to the chemical potential, which was identified with the Gibbs free energy in both the VT and SI models. In regard to the VT and Langmuir theories, both the “ideal particle” contribution (repulsive part) and the microion-microion contribution \bar{A}_{ss} (the attraction part) are included in the calculation of the Helmholtz free energy. Such a combination gives rise to a competition between a repulsive part and an attraction part that drives the spinodal instability of the system. As previously mentioned, the contribution of the macroions to the screening parameter in the Langmuir model is due to the treatment of the microions as point particles, whereas in the VT approach the counterion contribution is expressed in terms of the macroion concentration.

The apparent importance of the screening parameter in dictating the presence or absence of a heterogeneous structure of the colloidal suspension presents a conundrum in view of the underlying philosophy behind volume-term theories. This philosophy, as given in the Introduction by means of the quote by Grimson and Silbert [18], is to average out those variables which are *deemed unimportant* and thus reduce the system to the one component that is thought to be important. This is what is done for the microions in the system, with the macroions being the effective one component. Nonetheless it is the unimportant microion component *that is the driving force behind the spinodal instability* that leads to a phase separation [1–5]. Apparently van Roij, Dijkstra, and Hansen [3] might have been aware of this paradox when one considers their statement, in reference to the fluid-gas phase transition, as providing no indication as to whether the macroion-macroion interaction is attractive or repulsive, “This seemingly surprising result is a direct consequence of the reduction of the initial multicomponent problem, involving mesoscopic coions and counterions, to a one-component system of dressed polyions interacting via effective screened forces....” An unstated implication whose spirit is within the bounds of this comment is that the *mathematical form* resulting from the compression of the equations to a one-component system gives rise to a phase separation.

The experimental observation is that, under certain experimental conditions, the colloidal particles in a suspension

appear to conjugate together to form a heterogeneous structure. Such behavior is indicative of a negative change in the free energy. We have thus far refrained from identifying physical processes with specific mathematical expressions. In line with the above theories the key to any physical model for macroion congregation is the disposition of the microions as manifested in the screening parameter κ .

Both the VT and SI theories calculate κ on the basis of a fixed volume, and treat the solvent as a passive bystander. However, the sizes of the simple ions are comparable to that of water, so there must be some exchange of solvent between the two regions as the dense and void regions are being formed. Michaeli, Overbeek, and Voorn [26] showed that the entropy of the mixing of solvent and small counterions can contribute significantly to the stability of the separated phase. To illustrate the importance of the solvent, consider a region in the system of volume V^* which contains macroions, counterions, added electrolyte, and solvent particles. This volume is a mathematical construct, so it remains fixed before and after the phase separation, but is chosen such that it lies within the boundaries of the “dense” phase that is soon to be created. The volume is expressed in terms of the molecular volumes \bar{v}_j of the j th species,

$$V^* = N_p \bar{v}_p + N_c \bar{v}_c + N_+ \bar{v}_+ + N_- \bar{v}_- + N_o \bar{v}_o. \quad (35)$$

Since this volume, by definition, is fixed, the following must hold:

$$\bar{v}_p dN_p + \bar{v}_c dN_c + \bar{v}_+ dN_+ + \bar{v}_- dN_- + \bar{v}_o dN_o = 0. \quad (36)$$

Upon phase separation the number of macroions increases in V^* since this is in the zone of the dense phase. Hence dN_p and also dN_c are positive numbers, the latter reflecting the assumption of a “dressed” macroion. In accordance with the results of the VT theories dN_+ and dN_- are negative numbers in order to maintain a constant pressure in the dense and sparse regions. We now cast Eq. (36) into the form

$$\bar{v}_o dN_o \cong -(\bar{v}_+ + \bar{v}_-) dN_+ - (\bar{v}_p + |Z_p| \bar{v}_c) dN_p. \quad (37)$$

One can further simplify this expression by making the approximation $\bar{v}_+ \cong \bar{v}_- \cong \bar{v}_o$ with the result

$$dN_o = -2 dN_+ - \left(\frac{\bar{v}_p}{\bar{v}_o} + |Z_p| \right) dN_p. \quad (38)$$

Assuming that the radius of the macroion is 50 nm and of the solvent is 0.2 nm, the ratio of molecular volumes is on the order of $\bar{v}_p/\bar{v}_o \cong 1.6 \times 10^7$, which means that $|Z_p|$ may be neglected as it is usually on the order of 10^3 . The result is that $\approx 8 \times 10^6$ ions of each charge must exchange with each macroion that enters the volume V^* if $dN_o = 0$. Since the number of solvent molecules is several orders of magnitude larger than the added salt of molar concentration in the micromolar range, it is more probable that the solvent will be displaced than the salt, upon formation of the dense region.

There are other reasons that the solvent may play a role in phase separation. Raman scattering measurements [26,27] indicate three water structures in gels: free, inside the gel,

and attached to the polyelectrolyte gel. Also, Raman scattering indicates that water is structured around flexible polyelectrolytes [28,29]. Quesada-Pérez, Callejas-Fernández, and Hidalgo-Álvarez [30] reported that the presence of different alcohols results in ordered structures with different behaviors. The solvent may therefore affect the microion distributions in ways not contained within the context of simpler theories. Even as an inactive component, the accumulation of macroions and associated counterions in the “dense” phase must necessarily affect the activity of the water. Consider the integrated expression of the Helmholtz free energy,

$$A = Q - PV - TS + \sum_j \mu_j n_j, \quad (39)$$

where Q is the heat. We now differentiate this expression, substitute the second law identity $dQ = T dS$, and group the results to obtain the usual thermodynamic expression for dA ,

$$dA = -S dT - P dV + \sum_j \mu_j dn_j \quad (40)$$

and the Gibbs-Duhem relationship

$$0 = -V dP + \sum_j n_j d\mu_j. \quad (41)$$

If we now restrict Eq. (41) to the electrostatic component only and include the solvent as one of the components as it is a dielectric medium, we have for the reduced pressure,

$$\begin{aligned} \beta dP^{\text{elec}} &= \beta \sum_i n_j d\bar{\mu}_j^{\text{elec}} + \beta n_o d\bar{\mu}_o^{\text{elec}} \\ &= \sum_j n_j d \ln(a_j^{\text{elec}}) + n_o d \ln(a_o^{\text{elec}}). \end{aligned} \quad (42)$$

The electrostatic pressure of the system has its origin in the change in the chemical potential, or activity, of the electrical components upon the formation of the heterogeneous suspension. According to the grand canonical Monte Carlo simulations of Delville [31], the electrical component to the pressure is negative. The reduced electrical pressure based on the VT approach is given by the equation $\beta P^{\text{elec}} = \bar{G}^{\text{elec}} - \bar{A}^{\text{elec}}$. As given in Eq. (26) the electrostatic pressure for the salt gives the inequality $\beta P_{ss}^{\text{elec}} < 0$. This means that the salt solution is intrinsically unstable and it is the random motion of the ions that offset this tendency for the ions to form pairs and higher order aggregates. It is also true that the electrical pressure calculated for the $\bar{A}_{ps}^{\text{elec}}$ term is also negative, viz.,

$$\beta P_{ps}^{\text{elec}} = -\frac{\kappa Z_p^2 \lambda_B n_p}{3} = -\frac{\kappa \kappa_p^2}{12\pi}, \quad (43)$$

where κ_p is defined in Eq. (27). It is a curious feature of Eq. (43) that in the ionic strength region for which the counterions dominate in the calculation of the screening parameter, we have the proportionality $\beta P_{ps}^{\text{elec}} \approx n_p^{3/2}$, as proposed in the Langmuir and VT models but for different reasons. The similarity of Eq. (43) with Eq. (25) is interpreted in terms of the

instability of the total macroion-microion system. The electrostatic pressure for the screened Coulomb pair interaction between the macroions is likewise found to be

$$\begin{aligned} \beta P_{DLVO-VT}^{\text{elec}} &= \sum_{i=1}^{N_p-1} \sum_{j>i}^{N_p} \left[1 + \frac{y^2}{1+y} - \frac{yx_{ij}}{2} \right] \frac{n_i n_j Z_i Z_j \lambda_B}{a_p} \\ &\times \left[\frac{\exp(y)}{1+y} \right]^2 \frac{\exp(-yx_{ij})}{x_{ij}}. \end{aligned} \quad (44)$$

In contrast to the results for $\beta P_{ss}^{\text{elec}}$ and $\beta P_{ps}^{\text{elec}}$, the value for $\beta P_{DLVO-VT}^{\text{elec}}$ can be either negative (large values of yx_{ij}) or positive (small values of yx_{ij}). Since the negative contribution arises *solely from the screening parameter*, the attractive nature of this term may be interpreted in a manner parallel to that for $\beta P_{ss}^{\text{elec}}$ and $\beta P_{ps}^{\text{elec}}$. Because of the tendency of a collection of particles of opposite sign to congregate, the screening ions must therefore modulate the repulsive tendency between the macroions of like charge. Based on the work of Delville the inequality $\beta P_{ss}^{\text{elec}} + \beta P_{ps}^{\text{elec}} + \beta P_{DLVO-VT}^{\text{elec}} < 0$ must hold for the macroion-rich region of the heterogeneous suspension. Within the context of the VT formalism, this means that the positive electrostatic pressure that might arise from the macroion-macroion term does not outweigh the negative pressures generated by the microions.

There is some ambiguity as to exactly what constitutes the spinodal instability and the resulting phase separation. The problem is that the phase separation in the VT approach is virtually oblivious to the presence of interactions between pairs of macroions. As previously noted [3] the simulations of the phase diagram were insensitive to even the *sign* of the macroion-macroion interaction and were only slightly affected if there were not interactions at all between the macroions [36]. Hence the system effectively is an “independent particle” system. We draw a parallel with adsorption isotherm expressions for independent binding sites. Exactly the same mathematical expression is obtained for an N -particle system each with one binding site and a one-particle system with N binding sites. It is suggested that the VT expressions are equally applicable for the formation of N microphases centered about each of the N macroions, or two macrophases in which the dense phase houses all of the N macroions [32]. Recent BD simulations on a cluster of seven macroions indicate that the added salt is totally expelled from the cluster and that the counterions are drawn into the cluster [32,33]. This distribution of microions indicates that the Donnan potential may also be assigned to the boundaries of the cluster itself, with the formation of a “superdouble layer” as previously suggested [34]. In this regard the physical mechanism for phase separation and stability is that the very large electric field for the collection of macroions results in a redistribution of microions such that the counterions are shared by macroions to form a cluster with a concomitant exclusion of the coions to the exterior solvent (void region), thereby setting up a double layer about the cluster. The exclusion of the coions as a result of their interaction with the highly charged macroion cluster is a critical part of the mechanism, and

clustering or phase separation may not occur in the idealized salt-free system. A similar conclusion was drawn by Diehl, Barbosa, and Levin [35].

VII. CONCLUSION

The Sogami-Ise and Langmuir views of the stability of colloidal suspensions have been shown to be a subset of the holistic volume-term formalism for colloid stability. The common thread between these theories is the screening parameter, which must include the added electrolyte and counterions contributions to bridge microion and macroion concentrations that define the thermodynamic state of the system. The picture that emerges from the VT formalism is that the heterogeneous structure is composed of a macroion dense region with the expulsion of salt to the external void region. It has also been demonstrated that the “attractive tail” in the macroion-macroion chemical potential is a nec-

essary result of using the screened Coulomb form of the Helmholtz pair interaction. Hence this attractive tail is either a real effect or an artifact of the screened Coulomb form of the pair interaction. If the effect is real then its origin lies in the change in the activities of the electrical components comprising the heterogeneous region of the suspension. If the latter is true, then conclusions drawn from the use of the preaveraged screened Coulomb form of electrical interactions must be suspect.

ACKNOWLEDGMENTS

I wish to acknowledge the many stimulating correspondences with P. Warren, R. van Roij, and A. Denton regarding their views on volume-term theories. I also wish to acknowledge the discussions with L. B. Bhuiyan in the preparation of this manuscript.

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