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Volume-term theories of phase separation in colloidal systems and long-range attractive tail in the pair potential between colloidal particles

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To explain the experimental observation that colloidal dispersion exhibits a ''two-state'' structure under certain conditions, Sogami and Ise (SI) proposed a model for an ''effective'' pair potential between colloidal particles which had an ''attractive tail'' more than a decade ago. The SI paper spawned several papers that dwelled on the shortcoming of the SI paper or strived to provide other explanations for the observed inhomogeneity of the suspension. We show herein that a long range attraction in the pair potential between colloidal particles is also obtained in ''volume-term'' theories in which the repulsive DLVO potential is retained.

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Experimental evidence indicates that under certain experimental conditions a colloidal system exhibit a heterogeneous distribution of the constituent particles [1–13]. Such observations are not consistent with the well-established DLVO potential [14],

$$\beta U_{jk}^{\mathrm{DLVO}}=Z_jZ_k\lambda_B\frac{\exp(-\kappa R_{jk})}{R_{jk}}. \tag{1}$$

Here, Z_m is the macroion charge (with sign); $\beta=1/k_BT$ where k_B is Boltzmann's constant and T is the absolute temperature, $\lambda_B=\beta(q_e)^2/\varepsilon$ is the Bjerrum parameter where ε is the bulk dielectric constant, q_e is the magnitude of the electron charge, and the screening parameter κ is defined as

$$\kappa^2=4\pi\lambda_B(2n_s+|Z_m|n_m)=4\pi\lambda_B\frac{(2N_s+|Z_m|N_m)}{V}, \tag{2}$$

where V is the volume of the system, $n_S=N_S/V$ is the number density of added 1:1 electrolyte to give $2N_s$ ions, $|Z_m|n_m=|Z_m|N_m/V$ is the number density of counterions that arise from the N_m macroions of charge magnitude $|Z_m|$ and number density n_m, and V is the total volume of the system. It is noted that the number density of the counterions should be based on the macroion-free volume in the system, $V(1-\phi_m)$, where ϕ_m is the volume fraction of the colloidal particles. To simplify the mathematics without loss of generality we will ignore the volume fraction correction factor, and further justify its omission as it was not employed in the primary papers used as a basis of this note. To explain the inhomogeneity in colloidal particle distribution, Sogami and Ise [15] (SI) proposed a model based on the Gibbs free energy, $G=A+PV$, where G is the Gibbs free energy, A is the Helmholtz free energy, and P is the pressure. The resulting SI potential form, as expressed in terms of the DLVO potential, is

$$\beta U_{jk}^{\mathrm{SI}}=\left(2+\frac{\kappa}{2}\frac{\partial}{\partial\kappa}\right)\beta U_{jk}^{\mathrm{DLVO}}=\left(2-\frac{\kappa R_{jk}}{2}\right)\beta U_{jk}^{\mathrm{DLVO}}. \tag{3}$$

The statement that the Gibbs and Helmholtz free energies were different for colloidal systems precipitated several attempts to discredit the validity of the SI theory, the most often quoted are those of Overbeek [16] and Woodward [17], which we will return to later in this paper. More recently ''volume-term'' (VT) theories have been proposed to explain the two-phase structure of colloidal systems [18–22]. One of the motivating features of these studies is to provide a mechanism for these two-state colloidal systems in which the colloid–colloid interaction remains repulsive rather than attractive, as evidenced from the following excerpt from van Roij and Hansen [19],

> ''In fact, the current belief in this statement is so strong that recent experimental observations of gas–liquid [2,3] and gas–solid [4] coexistence in low-salt suspension of charged colloidal particles have been interpreted as proof of the existence of long-range *attractions* between colloids of the *same* charge-sign! This nature of the interaction between colloidal particles is not only counterintuitive, but also in contradiction with the standard and well-established DLVO theory (which predicts purely repulsive screened Coulomb interaction [5]).''

Briefly, to exhibit a phase separation there must be both attraction and repulsion terms in the energy expression for the system. Upon equating to zero the first derivative of the Helmholtz free energy with respect to appropriate system variables one determines the location of the equilibrium while equating the second derivative to zero gives the location of the spinodal instability line. 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. For example, in the system of macroions and added electrolyte the relevant expressions for the two regions (1) and (2) are given in Ref. [20] as

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$$\begin{aligned}\mu_m(n_m^{(1)},n_s^{(1)})&=\mu_m(n_m^{(2)},n_s^{(2)}),\\ \mu_s(n_m^{(1)},n_s^{(1)})&=\mu_s(n_m^{(2)},n_s^{(2)}),\\ p(n_m^{(1)},n_s^{(1)})&=p(n_m^{(2)},n_s^{(2)}),\end{aligned}\tag{4}$$

where the chemical potentials are obtained from the standard thermodynamic relationships

$$\begin{aligned}\mu_m&=\left(\frac{\partial\phi(n_m,n_s)}{\partial n_m}\right)_{n_s},\\ \mu_s&=\left(\frac{\partial\phi(n_m,n_s)}{\partial n_s}\right)_{n_m},\end{aligned}\tag{5}$$

where $\phi(n_m,n_s)=A/V$ is the Helmholtz free energy per unit volume. An example of the role of the volume term in the generation of the phase diagram is that of van Roij, Dijkstra, and Hansen [20]

$$\Phi_0=F_{\rm id}+k_BTV\frac{\eta\overline{\sigma}}{1-\eta}-\frac{Z_m^2q_e^2}{2\varepsilon a_m}\frac{N_m\kappa a_m}{1+\kappa a_m}-\frac{1}{2}\frac{4\pi q_e^2}{\varepsilon\kappa^2}(Z_mn_m)^2V,\tag{6}$$

where $F_{\rm id}$ is the ideal contribution from the electrolyte ions n_+ and n_-, $\overline{\sigma}=2n_+n_-/(n_++n_-)$, η is the packing fraction of macroions of radius a_m, and the other parameters were previously defined in Eqs. (1)–(3). These authors note that the last two terms in Eq. (6) are responsible for the spinodal instability [20].

It is of interest to note that Grimson and Silbert [23] point out, with reference to the SI theory,

> ''...that volume terms are present in the potential energy of interaction of charge-stabilized colloidal dispersion..''

Hence if the potential in the SI model is said to include a ''volume term,'' then it is a fair conjecture that there should be some explicit relationship between the current VT approaches and the SI potential. Indeed this is what we report herein and comment further that the volume-term models validate the SI theory in regard to the criticisms of Overbeek and Woodward.

Our focus is solely on the colloid–colloid pair potential and its participation in the VT models. To this end we turn to Eq. (11) of Warren [22] for the expression of the macroion–macroion (mm) interaction energy,

$$\frac{E_{\rm mm}}{Vk_BT}\approx\frac{n_m^2}{2}\int d^3\mathbf{r}\frac{Z_m^2\lambda_B\exp(-\kappa r)}{r}g_{\rm mm}(r)-\frac{2\pi Z_p^2\lambda_Bn_m^2}{\kappa^2},\tag{7}$$

where $g_{\rm mm}(r)$ is the pair distribution function for the macroions and the second term is a correction for the neutralizing background by subtracting off the mean field term $[g_{\rm mm}(r)=1]$. For our purposes we will ignore the second term, and recognize that the first term represents an average of the screened Coulomb interaction contribution to the Helmholtz free energy. Hence we define the total mean field macroion–macroion pairwise interaction,

$$\begin{aligned}A_{\rm mm}^{\rm elec}&=\frac{N_m(N_m-1)}{2}\frac{Z_m^2\lambda_B}{\beta V}\times\int\left[\frac{\exp(-\kappa R_{\rm mm})}{R_{\rm mm}}\right]g_{\rm mm}(R_{\rm mm})d^3\mathbf{R}_{\rm mm}\\ &\cong\frac{Vn_m^2}{2}\frac{Z_m^2\lambda_B}{\beta}\left\langle\frac{\exp(-\kappa R_{\rm mm})}{R_{\rm mm}}\right\rangle=\frac{Vn_m^2}{2}\langle U_{\rm mm}^{\rm elec}\rangle,\end{aligned}\tag{8}$$

where the factor of 1/2 is to correct for the double counting. Attention is now given to the application of Eqs. (4), (5), and (8) to the electrostatic part of the pair potential between macroions. From Eq. (5) we obtain for the macroion contributions using Eq. (8),

$$\begin{aligned}n_m\mu_m^{\rm elec}&=n_m\left(\frac{\partial(\phi_{\rm mm}^{\rm elec})}{\partial n_m}\right)_{n_s}=\frac{n_m}{2}\left[2n_m\langle U_{\rm mm}^{\rm elec}\rangle+n_m^2\left(\frac{\partial\langle U_{\rm mm}^{\rm elec}\rangle}{\partial n_m}\right)_{n_s}\right]\\ &=\phi_{\rm mm}^{\rm elec}\left[2-\frac{\kappa R_{\rm mm}}{2}\frac{|Z_m|n_m}{(2n_s+|Z_m|n_m)}\right]\end{aligned}\tag{9}$$

and

$$\begin{aligned}n_s\mu_s^{\rm elec}&=n_s\left(\frac{\partial(\phi_{\rm mm}^{\rm elec})}{\partial n_s}\right)_{n_m}=\frac{n_s}{2}\left[n_m^2\left(\frac{\partial\langle U_{\rm mm}^{\rm elec}\rangle}{\partial n_s}\right)_{n_m}\right]\\ &=-\phi_{\rm mm}^{\rm elec}\left[\left(\frac{\kappa R_{\rm mm}}{2}\right)\frac{2n_s}{(2n_s+|Z_m|n_m)}\right],\end{aligned}\tag{10}$$

where we have also utilized Eq. (2). Combining Eqs. (9) and (10) gives the desired result

$$n_m\mu_m^{\rm elec}+n_s\mu_s^{\rm elec}=\left[2-\frac{\kappa R_{\rm mm}}{2}\right]\phi_{\rm mm}^{\rm elec}\tag{11}$$

which is the form of the SI potential given in Eq. (3). The contribution to the osmotic pressure is calculated from [20]

$$\Pi=n_m\mu_m+n_s\mu_s-\phi(n_m,n_s).\tag{12}$$

Thus from Eq. (11) the contribution of the pair potential to the osmotic pressure is

$$\Pi_{\rm mm}^{\rm elec}=\left[1-\frac{\kappa R_{\rm mm}}{2}\right]\phi_{\rm mm}^{\rm elec}.\tag{13}$$

We have shown that strictly within the formalism of the VT model the Sogami–Ise potential naturally arises from the screened Coulomb potential. The origin of this ''attraction'' was previously attributed to the ''electrostatic osmotic pressure'' which was attributed to the difference between the ''Gibbsian'' and Helmholtz free energies [24,25]. A similar situation between the Gibbs and Helmholtz free energy exists for simple ion systems. For example, McQuarrie [26] gives the relationship

$$\frac{\beta G^{\mathrm{el}}}{V}=\frac{\beta A^{\mathrm{el}}}{V}+\beta p^{\mathrm{el}}=-\frac{\kappa^3}{24\pi}\tau(\kappa a)-\frac{\kappa^3}{24\pi}\left[\frac{3}{1+\kappa a}-2\tau(\kappa a)\right], \tag{14}$$

where the form of $\tau(\kappa a)$ is not important in the present discussion. What is relevant is the limiting forms, $\beta G^{\mathrm{el}}/V \rightarrow -\kappa^3/8\pi$ and $\beta A^{\mathrm{el}}/V \rightarrow -\kappa^3/12\pi$ in the limit $\kappa a \rightarrow 0$. The presence of the electrostatic osmotic pressure clearly shows that the Gibbs and Helmholtz free energies remain different for simple ion systems in the limit of infinite dilution and point ion size.

Since the SI potential naturally results from the repulsive pair potential in the volume-term theories, the criticisms of Overbeek [16] and Woodward [17] of the SI theory must likewise apply to the VT models. Overbeek noted that the inclusion of a ''solvent correction term'' in the SI model exactly cancelled the attractive part of the SI potential. Overbeek further specified that inclusion of the solvent, identified with the subscript ''*o*,'' is easily achieved through the charging process using the Gibbs–Duhem expression, as shown through his Eq. (15), viz.,

$$N_o\mu_o^{\mathrm{elec}}+\sum_j N_j\mu_j^{\mathrm{elec}}=\int_{q=0}^{q=q}\left(N_o d\mu_o^{\mathrm{elec}}+\sum_j N_j\, d\mu_j^{\mathrm{elec}}\right)_{P,T}=0. \tag{15}$$

Inclusion of the solvent correction term to the VT theories leads to the absurd result of a negative electrical osmotic pressure contribution for a repulsive pair potential, viz.,

$$\Pi_{\mathrm{mm}}^{\mathrm{elec}}=\underbrace{n_m\mu_m^{\mathrm{elec}}+n_s\mu_s^{\mathrm{elec}}+n_o\mu_o^{\mathrm{elec}}}_{0}-\phi_{\mathrm{mm}}^{\mathrm{elec}}(n_m,n_s) \tag{16}$$

Woodward [17] criticized the SI model for ''confinement'' of the counterions into a volume less than that of the container by some ''fictitious'' membrane,

> ''In reality, nature provides no membrane and counterions sample all the available solution volume (solute plus solvent).''

Quite clearly the VT models likewise ''confine'' the microions in two different regions, or phases. Furthermore the counterions in the VT models are confined to the regions about their parent macroions in order to maintain charge neutrality. What the VT theories do provide, however, is a mechanism for the inhomogeneous distribution objected to by Woodward. This mechanism is manifested as a spinodal instability rather than a ''fictitious membrane.''

What we have shown is that an ''attractive tail'' of the SI form does indeed arise from the volume term as alluded to by Grimson and Silbert [23] in the above quote. The ''PV'' term in the SI theory does not arise from an external pressure as usually assumed, but rather from an internal ''electrostatic osmotic pressure'' as likewise occurs in systems of simple salts. The ''attraction'' is thus, within the current interpretation of the equations, a many-bodied effect.

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