

Gibbs Pair Potential of Highly-charged Particles in Colloid Dispersions

K. KOIZUMI¹, T. SHINOHARA¹, M.V. SMALLEY², B.V.R. TATA³ and I. S. SOGAMI^{1,4}

Abstract

By integrating all degrees of freedom of the electric field and small ions with an ensemble averaging, we construct thermodynamic quantities for colloid dispersions. The unoccupied volume is accepted as the proper thermodynamic variable to describe the chemical and thermal equilibrium of the small ions in the region outside of all the particles. Using the electric potential of the dispersion which satisfies a set of equations derived by linearizing the inhomogeneous Poisson-Boltzmann equation, we calculate the electric part of the internal energy and obtain that of the Helmholtz free energy by applying the Legendre transformation with respect to temperature. The electric part of the Gibbs free energy can be deduced from that of the Helmholtz free energy by the two means of the total sum of chemical potentials and the Legendre transformation with respect to the unoccupied volume. Thus the thermodynamic theory has been successfully formulated for the colloid dispersion. The pair potential derived from the Gibbs free energy possesses a medium-range strong repulsive part and a long-range weak attractive tail being additionally affected by the fraction of the unoccupied volume.

Keyword(s): Colloid dispersion, Ensemble average, Gibbs free energy, Long-range weak attraction

Received 20 February 2019, Accepted 10 May 2019, Published 31 July 2019

1. Introduction

Adiabatic pair potentials are the key concepts required to explain a rich variety of phenomena taking place in colloid dispersions. By calculating the Helmholtz free energy F of the dispersion, Derjaguin and Landau¹⁾ and independently Verwey and Overbeek²⁾ (DLVO) derived a purely-repulsive pair potential U^F of screened Coulombic type. Combining this repulsive potential U^F with the van der Waals-London attractive potential U_A , they succeeded in proving the Schulze-Hardy rule for coagulation and explaining short-range phenomena related to the stability and instability of concentrated colloid dispersions.

The DLVO scheme, however, failed to describe long-range phenomena such as the instability of colloid crystals. Namely, while the theory predicted³⁾ that an increase of the salt concentration works to stabilize the colloid crystals, Hachisu *et al.* demonstrated⁴⁾ that the increase of the salt concentration causes the colloid crystals to melt into disordered states by careful observations of the iridescence in dispersions of polystyrene latexes with different particle fractions and salt concentrations. The DLVO theory has faults in the description of long-range electric phenomena in colloid dispersions.

To elucidate the origin of the salt-induced melting of colloid crystals⁴⁾ and the coexisting ordered and disordered states in the dispersions⁵⁾, Sogami *et al.*⁶⁻⁹⁾ calculated the Gibbs free energy G of the dispersion by taking the sum of all chemical potentials. The Gibbs pair potential U^G derived from G has been shown to describe the long-range as well as short-range behaviors of col-

loid dispersions¹⁰⁻¹²⁾. Applying the Monte Carlo simulation with U^G , Tata *et al.*¹³⁻¹⁷⁾ made extensive studies of the long-range phase behavior of colloid dispersions and succeeded in describing the main features of phase transitions observed in the dilute dispersions of highly charged particles of polystyrene latex and silica colloids¹⁸⁻²⁵⁾.

In this article, we re-investigate closely the relation between the Helmholtz and Gibbs free energies of the dispersions in the framework of the inhomogeneous Poisson-Boltzmann equation^{6,7)}. As a key ingredient of the theory, we employ an ensemble averaging²⁶⁾ to the domains for the integrals which define thermodynamic quantities of the dispersion. By applying this statistical procedure and accepting the *unoccupied volume* of the colloid dispersion as the proper thermodynamic quantity^{8,26)}, we find that the two free energies can be related through the two ways of the total sum of chemical potentials and the Legendre transformation, just as for a homogeneous thermodynamic system. The pair potential U^G derived from the Gibbs free energy G possesses a long-range weak attraction tail being additionally affected by the fraction of the unoccupied volume.

2. The Poisson-Boltzmann equation and ensemble averagings to integral domains

In a colloid dispersion with temperature T and volume V , the particles are tentatively presumed to take the configuration $\{\mathbf{R}\} = \{\mathbf{R}_1, \mathbf{R}_2, \dots, \mathbf{R}_N\}$ where \mathbf{R}_n is the center of mass coordinate of the n -th particle. The electric potential of the dispersion

1 Department of Physics, Kyoto Sangyo University, Kyoto 603-8555, Japan

2 Department of Physics, University of York, Heslington, York YO10 5DD, UK

3 School of Physics, University of Hyderabad, Hyderabad- 500 046, Telangana, India

4 Yukawa Institute for Theoretical Physics, Kyoto University, Kyoto 606-8502, Japan
(E-mail: sogami@cc.kyoto-su.ac.jp)

$\Psi(\mathbf{r})$ satisfies the Poisson equation

$$\epsilon \nabla^2 \Psi(\mathbf{r}) = -4\pi \sum_j z_j e n_j(\mathbf{r}) - 4\pi \bar{f}^{-1} \sum_n Z_n e \rho_n(\mathbf{r}), \quad (1)$$

where $n_j(\mathbf{r})$ is the distribution function of the small ions of the j -th species and $\rho_n(\mathbf{r})$ is the surface-charge distribution function of the n -th particle with the valence Z_n . The meaning and necessity of the factor \bar{f}^{-1} are clarified below. See Eqs.(3), (5) and (8).

In the dispersion with a definite particle-configuration $\{\mathbf{R}\}$, the small ions are distributed in the *unoccupied region* $\bar{V}(\{\mathbf{R}\})$ which is outside of all particles, i.e.,

$$\bar{V}(\{\mathbf{R}\}) = \{\mathbf{r} \in V : \mathbf{r} \notin v_n(\mathbf{R}_n), \forall n\}, \quad (2)$$

where $v_n(\mathbf{R}_n)$ is the region occupied by the n -th particle. It is crucial to recognize the point that there exist an overwhelming number of the unoccupied regions which are thermodynamically equivalent in the dispersion. Accordingly, to construct a thermodynamic quantity of the dispersion, we have to apply an appropriate Ensemble Averaging to the domains for the integral of its density.

Taking an analogy with the *micro-canonical ensemble in statistical mechanics* in its simplest form, we postulate here that the thermodynamic quantities are obtained by averaging contributions from all patterns of unoccupied regions $\bar{V}(\{\mathbf{R}\})$ with equal weight. With this averaging, called Flat Ensemble Averaging (FEA), the thermodynamic quantity $Q[\Psi]$ is determined by the integral of its density $Q[\Psi(\mathbf{r})]$ over the whole dispersion with the volume V as follows:

$$Q[\Psi] = \left[\int_{\bar{V}(\{\mathbf{R}\})} Q[\Psi(\mathbf{r})] dV \right]_{\text{FEA}} = \bar{f} \int_V Q[\Psi(\mathbf{r})] dV \quad (3)$$

with a proportionality factor \bar{f} . Remark that the FEA procedure concerning exclusively the integral domain does not affect the information on the particle configuration $\{\mathbf{R}\}$ stored in the electric potential $\Psi(\mathbf{r})$.

To determine the factor \bar{f} , it is sufficient to calculate the volume \bar{V} of the unoccupied region in the FEA scheme. By setting $Q[\Psi(\mathbf{r})] = 1$ in Eq.(3), we obtain

$$\begin{aligned} \bar{V} &\equiv \left[\int_{\bar{V}(\{\mathbf{R}\})} dV \right]_{\text{FEA}} = V - \left[\sum_n \langle v_n(\{\mathbf{R}_n\}) \rangle \right]_{\text{FEA}} \\ &= V - \sum_n \langle v_n \rangle = \bar{f} V, \end{aligned} \quad (4)$$

where $\langle v_n \rangle$ is the volume occupied by the n -th particle. Therefore, the proportionality factor \bar{f} is determined to be

$$\bar{f} = \frac{\bar{V}}{V} = 1 - \frac{1}{V} \sum_n \langle v_n \rangle = 1 - \phi. \quad (5)$$

The quantities $\phi = \sum \langle v_n \rangle / V$ and \bar{f} are interpreted, respectively, as the *volume fraction of the particles* and the *fraction of the un-*

occupied volume of the system. The fraction \bar{f} plays an indispensable role in the present formalism. Notice that the FEA procedure which concerns exclusively the integral domain does not affect the information stored in the electric potential $\Psi(\mathbf{r})$.

Following the convention of colloid science, we postulate that the small ions in the dispersion are in a thermal equilibrium described by the Boltzmann distribution function

$$n_j(\mathbf{r}) = n_{j0} \exp\left(-\frac{z_j e}{k_B T} \Psi(\mathbf{r})\right) \quad (6)$$

with the normalization constant n_{j0} . By applying the FEA formula (3) to the density function $n_j(\mathbf{r})$, the number N_j of the small ions of j -th species is expressed as follows:

$$N_j = \left[\int_{\bar{V}(\{\mathbf{R}\})} n_j(\mathbf{r}) dV \right]_{\text{FEA}} \quad (7)$$

which relates the normalization constant n_{j0} to the number N_j . Note that the surface-charge distribution function $\rho_n(\mathbf{r})$ of the n -th particle in the last term of Eq.(1) is normalized as

$$\left[\int_{\bar{V}(\{\mathbf{R}\})} \bar{f}^{-1} \rho_n(\mathbf{r}) dV \right]_{\text{FEA}} = \int_V \rho_n(\mathbf{r}) dV = 1. \quad (8)$$

Let us cast the Poisson equation (1) as a whole into the FEA formula (3). Then, Eqs.(7) and (8) bring forth the condition of charge neutrality, viz.,

$$\sum_j z_j N_j + \sum_n Z_n = 0. \quad (9)$$

Equations (1), (6), (7) and (8) constitute the framework for the well-known Poisson-Boltzmann (PB) equation. Evidently, the PB equation is invariant under the *weak gauge* transformation

$$\Psi(\mathbf{r}) \rightarrow \Psi(\mathbf{r}) + c, \quad (10)$$

where c is an arbitrary constant.

The proportionality factor \bar{f} plays the vital role of taking compactly the effect of the unoccupied volume into account in the theory. While it works to reduce effectively the value of the integral over the volume of the dispersion in the defining equation (3), its inverse \bar{f}^{-1} acts to enhance the effect of the electric charge of the particles in the Poisson equation (1). Consistent cancellation of these effects assures the condition of charge neutrality (9) to hold. If the factor \bar{f}^{-1} were not included in the term of the surface-charge distribution function in the Poisson equation (1), the FEA prescription would fail to produce the neutrality relation (9). It is this factor that enables us to interrelate the two free energies F and G through the Legendre transformation, as proved in section 5.

3. Linearization of the PB equation

To obtain analytical solutions of the PB equation in the three dimensional problem, the Boltzmann distribution function $n_j(\mathbf{r})$ must be linearized. Expanding the distribution function and retaining terms up to the first order with respect to $\Psi(\mathbf{r})$ in Eq.(1), we find the linearized inhomogeneous equation

$$\begin{aligned} \varepsilon (\nabla^2 - \bar{\kappa}^2) \Psi(\mathbf{r}) + 4\pi \bar{f}^{-1} \sum_n Z_n e \rho_n(\mathbf{r}) \\ = -4\pi e \frac{1}{V} \sum_j z_j N_j - \varepsilon \bar{\kappa}^2 \frac{1}{V} \int_V \Psi(\mathbf{r}) dV, \end{aligned} \quad (11)$$

where $\bar{\kappa}$ is a new quantity related to the Debye shielding factor κ as follows:

$$\begin{aligned} \bar{\kappa}^2 &= \frac{4\pi e^2}{\varepsilon k_B T V} \sum_j z_j^2 N_j \\ &= \bar{f}^{-1} \left(\frac{4\pi e^2}{\varepsilon k_B T V} \sum_j z_j^2 N_j \right) = \bar{f}^{-1} \kappa^2. \end{aligned} \quad (12)$$

Here it is requisite to recognize that the linearized equation (11) still preserves the weak gauge symmetry in Eq.(10). Further, by applying the FEA procedure in Eq.(3) to Eq.(11), the condition of charge neutrality in Eq.(9) can be confirmed to hold.

The redundancy of the weak gauge symmetry of the linearized equation can be fixed in a natural way. Expressing the right-hand side of the equation (11) by a constant \mathcal{R} , we can rewrite it into two relations. Then the replacement $\Psi(\mathbf{r}) \rightarrow \Psi(\mathbf{r}) - \mathcal{R}/(\varepsilon \bar{\kappa}^2)$ in both relations provides us with the Linearized Poisson-Boltzmann (LPB) equation, with the square of the new shielding parameter $\bar{\kappa}^2$, as

$$(\nabla^2 - \bar{\kappa}^2) \Psi(\mathbf{r}) = -4\pi \bar{f}^{-1} \sum_n Z_n e \rho_n(\mathbf{r}) \quad (13)$$

and additionally the integral equation as follows:

$$4\pi e \sum_j z_j N_j + \varepsilon \bar{\kappa}^2 \bar{f} \int_V \Psi(\mathbf{r}) dV = 0. \quad (14)$$

The fraction of the unoccupied volume \bar{f} in Eqs.(13) and (14) works consistently to determine the magnitude of the electric potential $\Psi(\mathbf{r})$ in the whole dispersion.

Colloid science had started its history with the legacy of the Debye-Hückel theory^{27,28)} for strong electrolytes which consist solely of small ions. We should realize that, since then, the original linearized PB equation with the Debye shielding parameter κ has been used for more than 80 years to investigate the colloid dispersions. Surprisingly it was not till the linear approximation had been formulated in the FEA scheme²⁶⁾ that the LPB equation (13) with the new shielding parameter $\bar{\kappa}$ and the constraint relation (14) were found.

4. The electric potential of the dispersion

Hereafter, a mathematical expedient of the thermodynamic limit ($V \rightarrow \infty$) is taken in order to solve the equations (13) and (14) analytically and carry out coordinate integrations for construction of the thermodynamic functions in compact ways.

Substituting the integral representations

$$\Psi(\mathbf{r}) = \frac{1}{(2\pi)^3} \int \tilde{\Psi}(\mathbf{k}) e^{i\mathbf{k}\cdot\mathbf{r}} dV_k \quad (15)$$

and

$$\rho_n(\mathbf{r}) = \frac{1}{(2\pi)^3} \int \tilde{\rho}_n(\mathbf{k}) e^{i\mathbf{k}\cdot\mathbf{r}} dV_k \quad (16)$$

into the LPB equation (13), we find the relation

$$\tilde{\Psi}(\mathbf{k}) = \bar{f}^{-1} \sum_n 4\pi \frac{Z_n e}{\varepsilon} \frac{1}{k^2 + \bar{\kappa}^2} \tilde{\rho}_n(\mathbf{k}) \quad (17)$$

between the Fourier transforms $\tilde{\Psi}(\mathbf{k})$ and $\tilde{\rho}_n(\mathbf{k})$.

To represent the surface charge of the particle, let us adopt Dirac's distribution^{6,7)} as follows:

$$\rho_n(\mathbf{r}) = \frac{1}{4\pi a_n^2} \delta(|\mathbf{r} - \mathbf{R}_n| - a_n). \quad (18)$$

Its Fourier transform is given by

$$\tilde{\rho}_n(\mathbf{k}) = \int \rho_n(\mathbf{r}) e^{-i\mathbf{k}\cdot\mathbf{r}} dV = e^{-i\mathbf{k}\cdot\mathbf{R}_n} f_n(\mathbf{k}) \quad (19)$$

with the form factor

$$f_n(\mathbf{k}) = \frac{\sin k a_n}{k a_n}. \quad (20)$$

Then we can readily confirm that the electric potential $\Psi(\mathbf{r})$ represented by the integral in Eq.(15) with the Fourier transform (17) satisfies the restrictive condition (14) in the thermodynamic limit since $\tilde{\rho}_n(0) = 1$.

5. Thermodynamic functions

For the sake of brevity, we investigate the thermodynamic functions of a dispersion consisting of mono-disperse particles with effective valence Z and radius a . The Fourier transform of the electric potential $\Psi(\mathbf{r})$ of the dispersion is expressed as follows:

$$\tilde{\Psi}(\mathbf{k}) = \bar{f}^{-1} 4\pi \frac{Z e}{\varepsilon} \sum_n f(\mathbf{k}) \frac{1}{k^2 + \bar{\kappa}^2} e^{-i\mathbf{k}\cdot\mathbf{R}_n}, \quad (21)$$

where $f(k)$ is the form factor in Eq.(20) with the radius a .

5.1 Internal electric energy

The Z -dependent part of the internal electric energy can be obtained by integrating the electric field energy density $\varepsilon [\nabla \Psi(\mathbf{r})]^2 / 8\pi$ in the FEA scheme as follows:

$$E_Z = \frac{\varepsilon}{8\pi} \left[\int_V [\nabla \Psi(\mathbf{r})]^2 dV \right]_{\text{FEA}} = \frac{\varepsilon}{8\pi} \bar{f} \int [\nabla \Psi(\mathbf{r})]^2 dV, \quad (22)$$

where the integral is taken at the thermodynamic limit of infinite volume.

Substituting the Fourier integral representation of $\Psi(\mathbf{r})$ into Eq.(22) and carrying out the coordinate integration, we obtain the Z -dependent part of the internal energy in the form

$$\begin{aligned} E_Z &= \frac{\varepsilon}{8\pi} \bar{f}^{-1} \frac{1}{(2\pi)^3} \int \mathbf{k}^2 \bar{\Psi}(-\mathbf{k}) \bar{\Psi}(\mathbf{k}) dV_k \\ &= \frac{1}{2} \sum_{m \neq n} U^E(R_{mn}) + \sum_n V^E, \end{aligned} \quad (23)$$

where

$$U^E(R_{mn}) = \frac{1}{\pi i} \bar{f}^{-1} \frac{Z^2 e^2}{\varepsilon R_{mn}} \int_{-\infty}^{\infty} [f(k)]^2 \frac{k^3}{(k^2 + \bar{\kappa}^2)^2} e^{iR_{mn}k} dk \quad (24)$$

is the electric pair potential between the m -th and n -th particles with center to center distance $R_{mn} = |\mathbf{R}_m - \mathbf{R}_n|$ and the R -independent term

$$V^E = \frac{1}{2\pi} \bar{f}^{-1} \frac{Z^2 e^2}{\varepsilon} \int_{-\infty}^{\infty} [f(k)]^2 \frac{k^4}{(k^2 + \bar{\kappa}^2)^2} dk \quad (25)$$

indicates the single potential of the particle in the dispersion.

The integral in Eq.(24) is computed from the contribution of the double pole at $k = i\bar{\kappa}$. The particles with the effective valence Z and radius a have the adiabatic electric pair potential

$$U^E(R) = \bar{f}^{-1} \frac{Z^{*2} e^2}{\varepsilon} \left[\frac{\bar{\kappa} a \coth(\bar{\kappa} a)}{R} - \frac{1}{2\bar{\kappa}} \right] e^{-\bar{\kappa} R}, \quad (26)$$

where R is the center-to-center distance and Z^* is the effective valence defined by

$$Z^* = Z f_n(i\bar{\kappa}) = Z \frac{\sinh \bar{\kappa} a}{\bar{\kappa} a}. \quad (27)$$

The electric pair potential $U^E(R)$ thus obtained possesses medium-range repulsion and long-range attraction of intermediate strength.

Similarly, the electric single potential can be calculated as follows:

$$V^E = \bar{f}^{-1} \frac{Z^2 e^2}{4\varepsilon a} \left[\frac{1}{2\bar{\kappa} a} \left(1 - e^{-2\bar{\kappa} a} \right) + e^{-2\bar{\kappa} a} \right]. \quad (28)$$

For the sake of simplicity, we concentrate our attention to the pair potentials and do not consider the single potentials of the free energies.

The internal energy is the thermodynamic function possessing the entropy as one independent thermodynamic variable. Therefore, it is not suitable to use the pair potential $U^E(R)$ in Eq.(26) for the description of the isothermal processes taking place in colloid dispersions. Historically, Levine and Dube^{29,30} had investigated the internal energy of the colloid dispersion and derived first the adiabatic pair potential. Their pair potential which is essentially equivalent with $U^E(R)$ in Eq.(26) was the forerunner of the DLVO potential. In the present formalism also, we carried

out here foremost the Z -dependent part of the internal energy E_Z and its associate pair potential $U^E(R)$ as a preliminary step necessary to deduce the quantities related with the free energies which possess the temperature as one thermodynamic variable.

5.2 Helmholtz free energy

It is relevant to regard the colloid dispersion as a homogeneous system with respect to the temperature T since the solvent molecules possessing the largest thermodynamic degrees of freedom work to preserve the system in an isothermal state. Therefore, the internal energy and the Helmholtz free energy, E and F , can be related through the Legendre transformation $E = F - T(\partial F / \partial T)$, which provides the relation

$$\frac{\partial}{\partial T} \left(\frac{F_Z}{T} \right) = -\frac{E_Z}{T^2} \quad (29)$$

for their Z -dependent parts E_Z and F_Z .

Following the decomposition in Eq.(23), we express the Z -dependent part of the Helmholtz free energy F_Z in terms of its pair potentials $U^F(R_{mn})$. Then the relation (29) holds also for the pair potentials $U^F(R_{mn})$ and $U^E(R_{mn})$. By using the expression for $U^E(R_{mn})$ in Eq.(24) and applying the integral formula

$$\int_{\infty}^T \frac{k^2}{(k^2 + \bar{\kappa}^2)^2 T^2} dT = -\frac{1}{(k^2 + \bar{\kappa}^2) T}, \quad (30)$$

it is straightforward to obtain the integral representation

$$U^F(R_{mn}) = \frac{1}{\pi i} \bar{f}^{-1} \frac{Z^2 e^2}{\varepsilon R_{mn}} \int_{-\infty}^{\infty} [f(k)]^2 \frac{k}{k^2 + \bar{\kappa}^2} e^{iR_{mn}k} dk \quad (31)$$

for the Helmholtz pair potential. The residue calculation in the integral leads to the Helmholtz pair potential in the following compact form as

$$U^F(R) = \bar{f}^{-1} \frac{Z^{*2} e^2}{\varepsilon} \frac{1}{R} e^{-\bar{\kappa} R}. \quad (32)$$

This repulsive potential has the same functional form as the widely-accepted DLVO potential. Using the fact that the Helmholtz free energy is the thermodynamic function related directly to the mechanical work in an isothermal process, the DLVO potential had been determined³¹⁾ without resort to calculating thermodynamic functions. Namely, we can interpret the DLVO potential as the work done by a particle in the shielded Coulombic field of another particle from infinity to the position with relative distance R . Such a heuristic method, however, fails to estimate correctly effects of the small ions possessing a large thermodynamic degrees of freedom. To properly evaluate their effects, we have to investigate explicitly the relations of the Helmholtz and Gibbs free energies of the dispersion.

5.3 Gibbs free energy

For the mono-disperse system consisting of the N particles with valence Z , the charge neutrality condition (9) takes the form

$\sum_j z_j N_j + NZ = 0$. The Helmholtz free energy of the system where the small ions are in chemical and thermal equilibrium coexisting with the particles can be schematically expressed as $F(T, \bar{V}; N_j, Z : \{\mathbf{R}\})$ where the information on the configuration $\{\mathbf{R}\}$ is assumed to be preserved through the electric potential $\Psi(\mathbf{r})$. Let us postulate that the quantities N_j, Z, \bar{V} and F can preserve *extensive* properties provided that their variations are limited to be sufficiently small. Accordingly, there holds the relation

$$(1 + \varepsilon)F(T, \bar{V}; N_j, Z : \{\mathbf{R}\}) = F(T, (1 + \varepsilon)\bar{V}; (1 + \varepsilon)N_j, (1 + \varepsilon)Z : \{\mathbf{R}\}) \quad (33)$$

for an infinitesimal ε . Expanding this with respect to ε and retaining its first order, we find the equation

$$F - \bar{V} \frac{\partial F}{\partial \bar{V}} = \sum_j N_j \frac{\partial F}{\partial N_j} + Z \frac{\partial F}{\partial Z}. \quad (34)$$

The right-hand side of the relation (34) represents the Gibbs free energy G in terms of the total sum of the chemical potentials^{6,7)}. Consequently, its Z -dependent part G_Z can be calculated from F_Z through the equation $G_Z = \sum_j N_j (\partial F_Z / \partial N_j) + Z (\partial F_Z / \partial Z)$. Just like the decomposition of E_Z in Eq.(23), the Z -dependent part G_Z can be expressed in terms of its pair potential $U^G(R_{mm})$. Then, the pair potentials $U^G(R)$ and $U^F(R)$ satisfy the equation

$$U^G(R) = \sum_j N_j \frac{\partial U^F(R)}{\partial N_j} + Z \frac{\partial U^F(R)}{\partial Z}. \quad (35)$$

The left-hand side of Eq.(34) shows that the Gibbs free energy G is given from the Helmholtz free energy F via the Legendre transformation with respect to the unoccupied volume \bar{V} . Consequently, the Z -dependent parts of the two free energies, G_Z and F_Z , have to obey the relation $G_Z = F_Z - \bar{V} (\partial F_Z / \partial \bar{V})$ which provides the equation for the Gibbs and Helmholtz pair potentials, $U^G(R)$ and $U^F(R)$, as follows:

$$U^G(R) = U^F(R) - \bar{V} \frac{\partial U^F(R)}{\partial \bar{V}}. \quad (36)$$

Substituting the integral representation of $U^F(R)$ in Eq.(31) into the two equations (35) and (36) and using the integral expression (24) for $U^E(R)$, we can prove that both of the equations bring forth the identical relation

$$\begin{aligned} U^G(R) &= U^E(R) + U^F(R) \\ &= \bar{f}^{-1} \frac{Z^2 e^2}{\varepsilon} \left[\frac{\sinh(\bar{\kappa}a)}{\bar{\kappa}a} \right]^2 \\ &\quad \times \left[\frac{1 + \bar{\kappa}a \coth(\bar{\kappa}a)}{R} - \frac{1}{2} \bar{\kappa} \right] e^{-\bar{\kappa}R} \end{aligned} \quad (37)$$

for the Gibbs pair potential. The resultant potential $U^G(R) = U^E(R) + U^F(R)$ inherits the advantageous aspects of the two component potentials $U^E(R)$ and $U^F(R)$. In the long-range region, the attraction of medium strength of $U^E(R)$ is suppressed

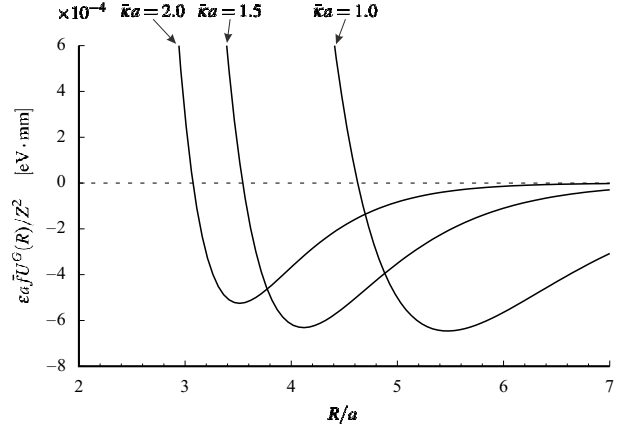


Fig. 1 The Gibbs pair potential in the reduced form $\varepsilon a \bar{f} U^G / Z^2$ versus R/a for values of the parameter $\bar{\kappa}a$ from 1.0 to 2.0.

by $U^F(R)$ leaving the weak attractive tail which can explain a variety of phase transformations with small energy differences. In the short-range region, both of the component potentials enhance cooperatively the repulsive effect so as to stabilize the dispersion. **Figure 1** shows schematically the behavior of the Gibbs pair potential in the reduced form $\varepsilon a \bar{f} U^G / Z^2$ against R/a for the values of the parameter $\bar{\kappa}a$ from 1.0 to 2.0.

6. Comparison of the new and original Gibbs pair potentials

In the previous theory^{6,7)} formulated before the notion of ensemble averaging was introduced, the Gibbs free energy was calculated one-sidedly by taking the summation of chemical potentials and the associated pair potential $U_o^G(R)$ was obtained in the following form as

$$U_o^G(R) = \frac{Z^2 e^2}{\varepsilon} \left[\frac{\sinh(\kappa a)}{\kappa a} \right]^2 \left[\frac{1 + \kappa a \coth(\kappa a)}{R} - \frac{1}{2} \kappa \right] e^{-\kappa R} \quad (38)$$

which we call here the original Gibbs pair potential. The new pair potential $U^G(R)$ legitimized in the FEA scheme is reduced to this preceding potential $U_o^G(R)$ by removing the multiplier \bar{f}^{-1} and replacing the shielding parameter $\bar{\kappa}$ with κ . The two potentials $U^G(R)$ and $U_o^G(R)$ have the same structure as the function of inter-particle distance R . The difference between them exists exclusively in the dependence of their coefficients on the fraction factor \bar{f} .

To concretely compare the two potentials $U^G(R)$ and $U_o^G(R)$, we consider a dispersion of mono-disperse particles in which counterions and salt ions are assumed to be univalent. Using the condition of charge neutrality, the shielding parameters κ and $\bar{\kappa}$ can be expressed as follows:

$$\kappa^2 = \frac{4\pi e^2}{\varepsilon k_B T} (|Z|n_p + 2C_s) = (1 - \phi) \bar{\kappa}^2, \quad (39)$$

where n_p is the particle concentration related to the particle vol-

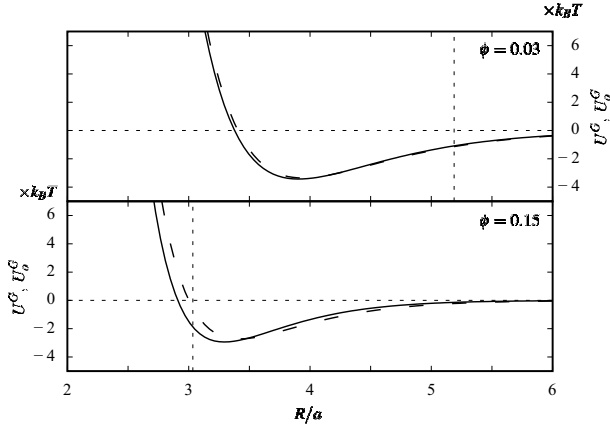


Fig. 2 Comparison of the new and original Gibbs pair potentials, U^G and U_0^G , in the unit of thermal energy $k_B T$ for the salt concentration $C_s = 4 \times 10^{21} \text{ l/m}^3$. The solid and dashed lines represent, respectively, the curves of the potentials U^G and U_0^G for the volume fraction $\phi = 0.03$ (upper panel) and $\phi = 0.15$ (lower panel). The vertical dotted lines indicate the average interparticle separations.

ume fraction as $\phi = (4\pi a^3/3)n_p$ and C_s is the salt concentration.

In **Fig. 2**, the behaviors of the new and original pair potentials for a dispersion with temperature $T = 297 \text{ K}$ and dielectric constant $\epsilon = 80$ consisting of particles with valence $Z = 1500$ and radius $a = 200 \text{ nm}$ are shown for different values of the volume fraction ϕ and the salt concentration $C_s = 4 \times 10^{21} \text{ l/m}^3$. The curves of the two potentials are almost degenerate for the semi-dilute dispersion with $\phi = 0.03$ in the upper panel. Since the average interparticle separation indicated by the vertical dotted line around $R/a \approx 5.2$ is larger than the minima of the two potentials, the particles are affected by the weak attractive tails of both potentials. In the semi-concentrated dispersion with $\phi = 0.15$, the two potential curves become somewhat different as exhibited in the lower panel. As the vertical line around $R/a \approx 3$ implies, the interparticle separation becomes smaller than the potential minima and the particles experience the repulsive parts of both of the adiabatic potentials.

In the literature, there exist many reports of experimental studies on the phase structures of colloid dispersions with various values of volume fraction^{4,5,18–25,32}. It is crucial to notice that the rich variety of phase behaviors are observed mainly in the dilute dispersions ($\phi \leq 0.03$) of highly-charged particles and that the original potential $U_0^G(R)$ played a crucial role in clarifying the existence of the long-range weak attraction in the particle interaction. In such dilute dispersions, the difference between the pair potentials $U^G(R)$ and $U_0^G(R)$ is so small, as confirmed in the upper panel of **Fig. 2** that it will be very difficult to experimentally verify or falsify the subtle difference between them. Accordingly, we can accept safely all results of the past analyses on

experimental data of dilute dispersions carried out by the Monte Carlo^{13–16} and Molecular Dynamics^{33–35} simulations with the original Gibbs pair potential U_0^G without any modification.

Comparison of the two panels in **Fig. 2** shows that the difference between the new and original Gibbs pair potentials is enhanced in proportion to the volume fraction ϕ . Nevertheless, we must be aware that the phenomena induced by purely-repulsive forces in concentrated dispersions are not conspicuous enough to quantitatively distinguish the two potentials. Therefore, we have to design a programme of future experiments using the mono-disperse colloid dispersions with the volume fraction covering the concentrated and intermediate regime in order to observe the difference of the new and original Gibbs pair potentials.

7. Summary and discussion

By postulating the FEA scheme and choosing the unoccupied volume as the proper thermodynamic variable of the dispersion, we have succeeded in deriving the Gibbs pair potential $U^G(R)$ in Eq.(37) through the two routes of the Legendre transformation and the summation of the chemical potentials. This is a remarkable result since a colloid dispersion is a complex system consisting of multi-components with different time scales and exhibiting a variety of phase behaviors depending sensitively on the volume fraction of particles and the salt concentrations. With a suitable statistical prescription and appropriate choice of variables, thermodynamics turns out to provide a potent framework which can describe essential characteristics of macroionic complex systems.

Here it is worthwhile and instructive to question what results from the Legendre transformation in Eq.(36) when \bar{V} is replaced by the volume of the dispersion V . We can readily confirm that this attempt leads to the relation $U^G(R) = (\bar{f}^{-1} - 1)U^F(R) + U^E(R)$ which disagrees with the result $U^G(R) = U^E(R) + U^F(R)$ obtained from Eq.(35). Therefore, the choice of the unoccupied volume \bar{V} as the proper thermodynamic variable is attested to be indispensable in the present theory of colloid dispersions in the FEA scheme.

The original potential $U_0^G(R)$ which played a decisive role in establishing the existence of the long-range attraction between highly-charged particles has now been superseded in principle by the new potential $U^G(R)$ derived from the Gibbs free energy in the present thermodynamic theory for colloid dispersions formulated with the FEA prescription. To experimentally demonstrate the superiority of the new potential $U^G(R)$ over the original potential $U_0^G(R)$, it is necessary to prepare highly mono-disperse colloid dispersions, both with respect to particle charge and radius, and undertake systematic and precise observations of characteristics of the dispersions over wide ranges of the values of the volume fraction of particles and the salt concentration. One promising method for such precise observations is the Kikuchi-Kossel diffraction experiments^{21,22} of colloid dispersions under the microgravity environment in the ‘‘Kibo module’’ on the In-

ternational Space Station (ISS). In parallel, we have to carry out Monte Carlo and Molecular Dynamics simulations by using both of the Gibbs pair potentials and compare the results with the data obtained by the experiments. In this connection, we should remark the report³⁶⁾ that the sharp boundary of a void observed in the complex plasma requires the existence of an attractive force between dust particles. The ISS provides an idealistic microgravity environment being suitable to study homogeneous 3D systems of complex plasma³⁷⁾.

Acknowledgements

We express our sincere thanks to Professor N. Ise for his discussions and encouragement. Sogami and Tata acknowledge Doctors K. Kogure, S. Adachi and Y. Ito for in depth scientific discussions on the Kikuchi-Kossel diffraction experiments of colloid dispersion on the ISS supported by JAXA and JSF.

References

- 1) B.V. Derjaguin and L. Landau: *Acta. Physicochim. URSS*, **14** (1941) 633 .
- 2) E.J.W. Verwey and Th. G. Overbeek: *Theory of the Stability of Lyophobic Colloids* Elsevier, (1948).
- 3) *Ibid.*, pp.182-185.
- 4) S. Hachisu, Y. Kobayashi and A. Kose: *J. Colloid Interface Sci.*, **42** (1973) 342.
- 5) N. Ise and T. Okubo: *Acc. Chem. Res.*,**13** (1980) 303.
- 6) I. Sogami: *Phys. Lett. A*, **96** (1983) 199.
- 7) I. Sogami and N. Ise: *J. Chem. Phys.*, **81** (1984) 6320.
- 8) I. S. Sogami, M. V. Smalley and T. Shinohara: *Prog. Theor. Phys.*, **113** (2005) 235.
- 9) I.S. Sogami: *Chemistry Letters*, **41**(10) (2012) 1331.
- 10) A.K. Sood, *Solid State Physics* (Academic Press), **45** (1991) 1.
- 11) A.K. Arora and B.V.R. Tata: *Ordering and phase transitions in charged colloids*, VCH, New York, (1996).
- 12) N. Ise, and I.S. Sogami: *Structure Formation in Solution*, Springer, (2005).
- 13) B.V.R. Tata, E. Yamahara, P.V. Rajamani and N. Ise: *Phys. Rev. Lett.*, **78** (1997) 2660 .
- 14) B.V.R. Tata and N. Ise: *Phys. Rev.*, **B56** (1998) 6050, *Phys. Rev.*, **E58** (1998) 2237.
- 15) B.V.R. Tata, A.K. Arora and M.C. Valsakumar: *Phys. Rev.*, **E47** (1993) 3404.
- 16) B.V.R. Tata and A.K. Arora: *J. Phys. Condens. Matter*, **3** (1991) 7389, **4** (1992) 7699, **7** (1995) 3817.
- 17) B.V.R. Tata, R.G. Joshi and I.S. Sogami: *Int. J. Microgravity Sci. Appl.*, **32** (2015) 320209 .
- 18) S. Doshio, N. Ise, K. Ito, S. Iwai, H. Kitano, H. Matsuoka, H. Naka-mura, H. Okumura, T. Ono, I.S. Sogami, Y. Ueno, H. Yoshida and Yoshiyama: *Langmuir*, **9** (1993) 394.
- 19) A.K. Arora, B.V.R. Tata, A.K. Sood and R. Kesavamoorthy: *Phys. Rev. Lett.*, **60** (1988) 2438.
- 20) B.V.R. Tata, M. Rajalakshmi and A.K. Arora: *Phys. Rev. Lett.*, **69** (1992) 3778.
- 21) T. Yoshiyama, I. Sogami and N. Ise: *Phys. Rev. Lett.*, **53** (1984) 2153.
- 22) I. S. Sogami and T. Yoshiyama: *Phase Transitions*, **21** (1990) 171.
- 23) J. Yamanaka, H. Yoshida, T. Koga, N. Ise and T. Hashimoto: *Phys. Rev. Lett.*, **5806** (1998) 80, *Langmuir*, **15** (1999) 4198.
- 24) A. Toyotama, T. Sawada, J. Yamanaka and K. Kitamura, *Langmuir*, **19** (2003) 3236.
- 25) K. Ito, H. Yoshida and N. Ise, *Science*, **269** (1994) 66 .
- 26) I.S. Sogami: *Prog. Theor. Exp. Phys.*, **2018** (2018) 033J01.
- 27) P. Debye and E. Hückel: *Physik.*, **Z24**, 185 (1923) 305, **25** (1924) 97.
- 28) P.J.W. Debye: *The Collected Papers of Peter, J.W. Debye*, Interscience Publishers, New York (1954).
- 29) S. Levine and G.P. Dube: *Trans. Faraday Soc.*, **35**,1125 (1939) 1141.
- 30) S. Levine and G.P. Dube: *Phil. Mag.*, **29** (1940) 105, *J. Chem. Phys.*, **46** (1942) 239.
- 31) E.J.W. Verwey and Th.G. Overbeek: *opt. cit.*, p.143.
- 32) E.B. Sirota, H.D. Ou-Yang, S.K. Sinha, P.M. Chaikin, J.D. Axe and Y. Fujii: *Phys. Rev. Lett.*, **62** (1989) 1524 .
- 33) W. Ouyang, H. Zhou, S. Xu and Z. Sun: *Colloid. Surf.*, **A441** (2014) 598 .
- 34) H. Zhou, S. Xu, W. Ouyang, Z. Sun and L. Liu: *J. Chem. Phys.*, **139** (2015) 064904.
- 35) Y. Kataoka: *Int. J. Microgravity Sci. Appl.*, **33** (2016) 330308 .
- 36) O. Ishihara and N. Sato: *Phys. Plasmas*, **12** (2005) 070705.
- 37) V.I. Molotkov, H.M. Thomas, A.M. Lipaev, V.N. Naumkin, AV. Ivlev and S.A. Khrapak: *Int. J. Microgravity Sci. Appl.*, **32** (2015) 320302.