

Electrical Interaction of a System Containing Arbitrary Shaped, Ion-Penetrable Charged Particles

Jyh-Ping Hsu* and Bo-Tau Liu

Department of Chemical Engineering, National Taiwan University, Taipei, Taiwan 10617, R.O.C

Received: September 26, 1997; In Final Form: December 31, 1997

A mean field approach is proposed to derive the electrical interaction energy for a system containing arbitrarily shaped, ion-penetrable particles bearing fixed charges in an electrolyte solution. We show that this energy can be decomposed into the product of two terms. One of these terms is a function of particle properties, and the other term is independent of particle properties. The electrical interaction energies of spheroids and tori are evaluated. Numerical results are presented to show that arbitrary assumptions concerning the shape of a particle can lead to a significant deviation in the estimation of the electrical interaction energy. Care must be taken in estimating the properties of a particle on the basis of the electrical interaction energy.

Introduction

Information about the interactions between two dispersed entities is essential to various problems in colloid science. For example, the classic DLVO theory,¹ which provides the theoretical background for the coagulation behavior of a colloidal suspension, is based on the electrostatic and van der Waals interactions between two charged particles. According to the Gouy–Chapman model of the electrical double layer, the distribution of electrical potential at equilibrium is governed by the Poisson–Boltzmann equation. Solving this equation is a prerequisite to the estimation of the electrostatic interaction energy between two charged entities. Unfortunately, due to its nonlinearity, the only solvable case is two infinite planar surfaces in a symmetric electrolyte solution. The nonlinearity problem can be alleviated if the potential of a charged system is low. In this case, the Poisson–Boltzmann equation can be approximated by a linear expression, which is more readily solvable. Various approximate methods were proposed to obtain an analytical expression for electrical potential distribution, which is then used to evaluate the electrostatic interaction force and the electrostatic interaction energy between two particles.^{2–9} Ohshima and Kondo,¹⁰ for example, considered the problem of two charged, ion-penetrable spheres. The analysis was extended by Hsu and Liu¹¹ to the case of two charged, ion-penetrable spheroidal particles. Onsager¹² considered the interaction between two rigid spherocylinders. The electrostatic interaction between two cylinders was modeled by several workers.^{13–16}

Rigorously, the interaction between two particles represents only the local behavior of a dispersed system; it ignores the presence of other nearby particles. In general, the global behavior of a system needs to be considered. Extending the result for two particles to the case of multiple particles, however, is nontrivial even for the case where the former has an analytical form. One possible method to solve this problem is to apply a statistical mechanics approach.^{17–19} This approach is adopted for a system containing arbitrary shaped, ion-penetrable particles in the present study. It is an extension of the reported results in the literature, which are limited mainly to the interactions between two regularly shaped particles. We focus on the case

where two nearby particles are sufficiently separated such that they can assume an arbitrary relative orientation. For example, if the concentration of electrolyte is low, the double layer around a charged particle is thick, the electrical repulsive force will prohibit direct contact between two nearby particles, and a colloidal suspension is stable. A typical example in practice is the slurry used in the chemical–mechanical polishing process.^{20,21} Here, the colloidal suspension needs to remain stable for at least several months. One of the possible ways to achieve this is to keep the concentration of electrolyte lower than a critical level.

Analysis

By referring to Figure 1, we consider a system containing arbitrarily shaped, porous (ion-penetrable) particles in an electrolyte solution. These particles bear fixed charges due to, for example, the dissociation of the functional groups they carry. Let R_{ij} be the center-to-center distance between particles i and j , and r_i the distance measured from the center of particle i . Suppose that the electrical potential is low, and the dielectric constant inside a particle is the same as that outside the particle. Then the Poisson–Boltzmann equation governing the electrical potential distribution at equilibrium can be approximated by the linearized form

$$\nabla^2 y = \kappa^2 y, \quad \text{in solution} \quad (1)$$

$$\nabla^2 y = \kappa^2 y - \kappa^2 \rho_i^*, \quad \text{inside particle } i \quad (2)$$

where

$$y = e\psi/k_B T \quad (2a)$$

$$\kappa^2 = 8\pi e^2 I / \epsilon k_B T \quad (2b)$$

$$\rho_i^* = \rho_i / 2eI \quad (2c)$$

In these expressions, ψ and y are, respectively, the electrical potential and the corresponding scaled quantity, ρ_i is the volume density of the fixed charge inside particle i , ∇^2 is the Laplace operator, ϵ is the dielectric constant, κ and k_B are the reciprocal

* To whom correspondence should be addressed.

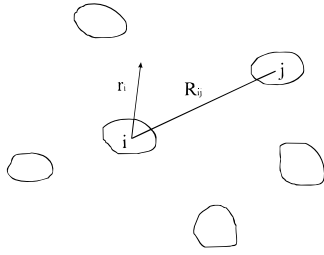


Figure 1. Schematic representation of the problem under consideration. R_{ij} is the center-to-center distance between particles i and j , and r_i the distance measured from the center of particle i .

Debye length and the Boltzmann constant, respectively, T is the absolute temperature, and e and I are the elementary charge and the ionic strength, respectively. It can be shown that the solution to eqs 1 and 2 takes the form²²

$$y(\vec{r}) = \sum_{i=1}^n \int_{\bar{V}_i} G(\vec{\xi}, \vec{r}) \rho_i^*(\vec{\xi}) d\bar{V}_i(\vec{\xi}) \quad (3)$$

where n denotes the number of particles, \vec{r} the position vector, $\vec{\xi}$ the position vector locating the fixed charges, and \bar{V}_i the dimensionless volume of particle i scaled by κ^3 , and the free Green function G is defined by

$$G(\vec{\xi}, \vec{r}) = \frac{\exp(-\kappa|\vec{r} - \vec{\xi}|)}{4\pi\kappa|\vec{r} - \vec{\xi}|} \quad (4)$$

$|\vec{r} - \vec{\xi}|$ is the distance between the end points of vectors \vec{r} and $\vec{\xi}$. The scaled free energy of the system under consideration, with the scaling factor $(4\pi/\epsilon)(e/k_B T)^2 \kappa$, can be calculated by²³

$$F = \frac{1}{2} \sum_{i=1}^n \int_{\bar{V}_i} \rho_i^* y d\bar{V}_i \quad (5)$$

The scaled electrostatic interaction energy, V_R , can be evaluated by

$$V_R = F - F(\infty) = \sum_{i=1}^{n-1} \sum_{j=i+1}^n \int_{\bar{V}_i} \int_{\bar{V}_j} \rho_i^* \rho_j^* G d\bar{V}_i d\bar{V}_j \quad (6)$$

where $F(\infty)$ represents the free energy for the case in which each pair of particles is infinitely separated. If all the possible orientations of particles are described by a distribution function, the averaged interaction energy, \bar{V}_R , can be expressed as

$$\bar{V}_R = \sum_{i=1}^{n-1} \sum_{j=i+1}^n \int_{\Omega_i} \int_{\Omega_j} f_i(\Omega_i) f_j(\Omega_j) \times \int_{\bar{V}_i(\Omega_i)} \int_{\bar{V}_j(\Omega_j)} \rho_i^* \rho_j^* G d\bar{V}_i d\bar{V}_j d\Omega_i d\Omega_j \quad (7)$$

where f_i and f_j are the oriented distribution probability functions of particles i and j , respectively, and Ω_i and Ω_j are, respectively, the oriented distribution range for particles i and j . Suppose that the system under consideration is isotropic, that is, the probability of finding a particle in each direction is the same, $f_i = f_j = 1/4\pi$. We define a charge distribution function for particle i , $P_i(r)$, as

$$P_i(r) = \frac{\int_{S_i} \rho_i^* dS_i}{4\pi r^2} \quad (8)$$

where S_i is the intersection of a sphere of radius r with particle i . The center of the former coincides with the center of gravity of the latter, O_i , as illustrated in Figure 2.

Let Ξ be the scaled volume of an arbitrary spherical shell centered at k with thickness dr_k , r_{kj} the distance between k and a point j , and r_j the distance between j and a point on the spherical shell. Then, we have

$$\int_{\Xi} \frac{\exp(-\kappa r_j)}{\kappa r_j} d\Xi = 4\pi \kappa r_k \sinh(\kappa r_k) \frac{\exp(-\kappa r_{kj})}{r_{kj}} dr_k \quad (9)$$

The scaled differential electrical interaction energy between two spherical shells, $d\bar{V}_R$, is

$$d\bar{V}_R = 4\pi \kappa \frac{\exp(-\kappa R_{ij})}{R_{ij}} \prod_{i=1}^2 \kappa P_i \sinh(\kappa r_i) r_i dr_i \quad (10)$$

The interaction energy between two arbitrary shaped particles can be expressed as

$$\bar{V}_R = \frac{4\pi B_1 B_2}{\kappa} \frac{\exp(-\kappa R_{ij})}{R_{ij}} \quad (11)$$

where

$$B_i = \kappa^2 \int P_i \sinh(\kappa r) r dr \quad (11a)$$

For a system containing n particles, eq 7 leads to

$$\bar{V}_R = \frac{4\pi}{\kappa} \sum_{i=1}^{n-1} \sum_{j=i+1}^n \frac{B_i B_j \exp(-\kappa R_{ij})}{R_{ij}} \quad (12)$$

Examples

According to eq 12, the effect of the shape of a particle on the electrical interaction energy is incorporated in the coefficient B_i , which is a function of the charge distribution function P_i defined in eq 8. Two examples are presented to illustrate the present method.

Spheroids

The spheroid is one the significant models for the description of the shape of a colloidal particle. By adjusting its parameters, various shapes can be simulated. Let us consider first a prolate spheroid with a uniform fixed charge distribution. In this case eq 8 gives

$$\begin{aligned} P_i(r_i)/\rho_i &= 1, \quad r_i \leq b \\ &= 1 - \frac{a}{r_i} \sqrt{\frac{r_i^2 - b^2}{a^2 - b^2}}, \\ &= 0, \quad a \leq r_i \end{aligned} \quad (13)$$

where a and b are the semimajor and semiminor axes, respectively. Similarly, for an oblate spheroid with a uniform fixed charge distribution, we have

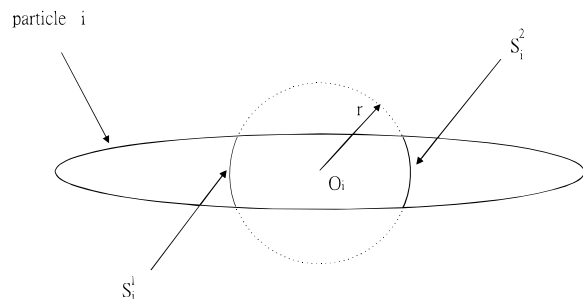


Figure 2. Intersection of a sphere with its center coincides with the center of gravity of particle i , O_i , with particle i , S_i . $S_i = S_i^1 \cup S_i^2$, r is the radius of the sphere.

$$\begin{aligned}
 P_i(r_i)/\rho_i &= 1, \quad r_i \leq b \\
 &= \frac{b}{r_i} \sqrt{\frac{a^2 - r_i^2}{a^2 - b^2}}, \quad b \leq r_i \leq a \\
 &= 0, \quad a \leq r_i
 \end{aligned} \quad (14)$$

Substituting eqs 13 and 14 into eq 11a gives the value of B_i which can be used to evaluate \bar{V}_R through eq 12.

Torus

Consider next a torus with uniform fixed charge distribution. Let R_0 be the radius of the revolving circle, and R_i the distance of its center from the axis of rotation. It can be shown that eq 8 leads to

$$\begin{aligned}
 P_i(r_i)/\rho_i &= 0, \quad r_i \leq R_i \\
 &= \sqrt{1 - \frac{(R_i R_0 + r_i^2)^2}{r^2 (R_0 + R_i)^2}}, \quad R_i \leq r_i \leq R_0 \\
 &= 0, \quad R_0 \leq r_i
 \end{aligned} \quad (15)$$

Substituting this expression into eq 11a gives the value of B_i , and eq 12 is then used to evaluate \bar{V}_R .

Discussion

In a study of the electrical interaction between two ion-penetrable spheres, Ohshima and Kondo¹⁰ showed that, for the case of uniform fixed charge distribution,

$$B_i = a_i \rho_i^* \kappa \left[\cosh(\kappa a_i) - \frac{\sinh(\kappa a_i)}{\kappa a_i} \right] \quad (16)$$

In this case, since $P_i = \rho_i^*$, eq 11a leads to eq 16. In other words, the result of Ohshima and Kondo¹⁰ can be recovered as a special case of the present study.

If $\kappa \rightarrow 0$, or the concentration of electrolyte is low, the first term on the right-hand side of eq 2 is negligible, and the second term becomes, by eqs 2b and 2c, $4\pi e \rho_i / \epsilon k_B T$. In this case, an ion-penetrable particle behaves like a rigid charged particle, and eq 11a becomes

$$B_i = Q_i \quad (17)$$

where Q_i is the scaled total amount of fixed charge contained in particle i with scaling factor $e\kappa/\epsilon k_B T$. Q_i is independent of the shape of the particle.

In a study of the interaction between two identical spheres, Sader et al.⁸ derived the following expression for the electrical interaction energy for thin to moderate thick double layers:

$$V_R = \epsilon \left(\frac{k_B T}{e} \right)^2 Y^2(R) \frac{a^2}{R} \ln(1 + \exp(-\kappa(R - 2a))) \quad (18)$$

with

$$Y(R) = 4 \exp\left(\frac{\kappa(R - 2a)}{2}\right) \tanh^{-1} \left[\exp\left(\frac{-\kappa(R - 2a)}{2}\right) \tanh\left(\frac{y_s}{4}\right) \right] \quad (18a)$$

where a is the radius of a particle, R the center-to-center distance between two particles, and Y a weak function of R . For the case of a thick double layer, Verwey and Overbeek²³ derived

$$V_R = \epsilon a^2 \left(\frac{k_B T}{e} \right)^2 y_s^2 \frac{\exp(-\kappa(R - 2a))}{R + 2a} \quad (19)$$

If, in addition, the surface potential of a particle is high, and/or the electrolyte concentration is low, then the separation between two particles is far, and both eqs 18 and 19 reduce to

$$V_R = \gamma \frac{\exp(-\kappa R)}{R} \quad (20)$$

where

$$\gamma = \epsilon a^2 \left(\frac{k_B T}{e} \right)^2 y_s^2 \exp(2\kappa a) \quad (20a)$$

The potential energy expressed in eq 20 is sometimes referred to as the Yukawa potential energy.²⁴ Note that both eqs 11 and 20 take the form

$$V_R \propto \frac{\exp(-\kappa R)}{R} \quad (21)$$

In other words, the behavior of a system containing arbitrary shaped, ion-penetrable particles is similar to that containing rigid spheres. It should be pointed out, however, that according to eq 11, the proportional constant in eq 21 depends on B_i and B_j , which are functions of the characteristics of two interacting particles. This suggests that the nature of the dispersed entities is significant. As will be discussed later, assuming an arbitrary shape of a particle, for example, may lead to an appreciable deviation in the estimation of the electrical interaction energy. From the other point of view, if the properties of a particle, such as its linear size and charged conditions, needed to be estimated through some measurements on the interaction energy, then choosing an adequate B_i is essential.

More often than not, it is assumed that a particle is spherical in order to simplify the mathematical treatment. Figure 3 shows the variation of the ratio $B_i^2/B_i^2(b/a = 1)$ as a function of the ratio b/a for two prolates. That for two oblates is illustrated in Figure 4. For two identical particles, eq 11 suggests that \bar{V}_R is proportional to B_i^2 . Therefore the ratio $B_i^2/B_i^2(b/a = 1)$ is a measure of the difference between the \bar{V}_R for two spheroids and that for two spheres. The greater this ratio, the greater the difference. Also, the closer the ratio b/a to unity, the closer a spheroid to a sphere. As can be seen from Figures 3 and 4, approximating a spheroid by a sphere is not satisfactory, in general. For example, if two prolates are treated as two spheres, the deviation in the electrical interaction is on the order of 90%

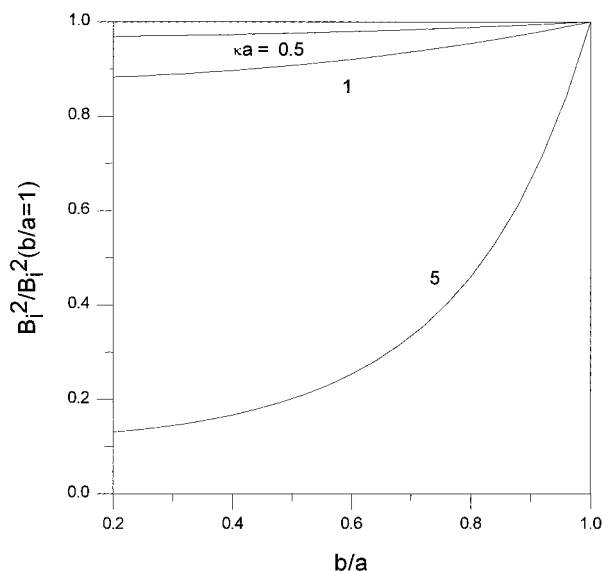


Figure 3. Variation of $B_i^2/B_i^2(b/a=1)$ as a function of b/a for prolates. The total amount of fixed charges contained in a particle is fixed.

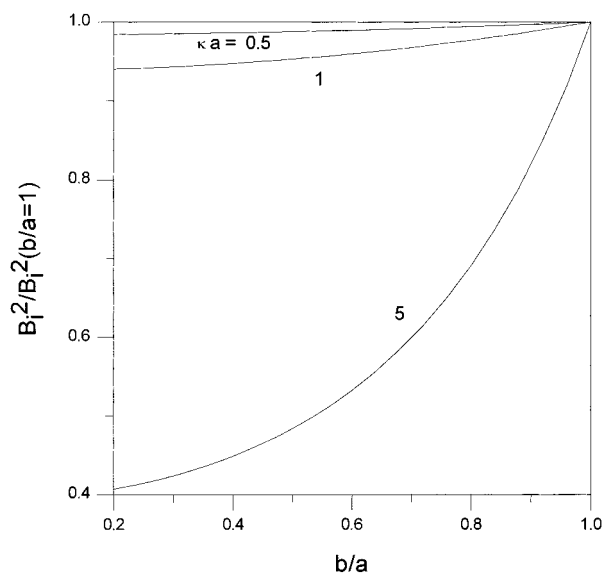


Figure 4. Variation of $B_i^2/B_i^2(b/a=1)$ as a function of b/a for oblates. The total amount of fixed charges contained in a particle is fixed.

if $\kappa a = 5$ and is on the order of 60% for two oblates. Figures 3 and 4 also show that the greater the κa , and/or the greater the ratio b/a , the greater the difference between the interaction energy of two spheroids and that of two spheres. A comparison between Figures 3 and 4 reveals that, for fixed κa and b/a , the difference between the interaction energy of two oblates and that of two spheres is smaller than the interaction energy between two prolates and that of two spheres.

A Particle and a Planar Surface

Let consider the interaction between an arbitrarily shaped ion-penetrable particle and a rigid planar surface. Suppose that the latter is maintained at a constant surface potential. In this case, the method of images used by Ohshima and Kondo is applicable.²⁵ Let particle k be the image of particle i with respect to the planar surface which has the inverse electrical properties as particle i . It can be shown that the scaled electrical potential is

$$y = \frac{B_i \exp(-\kappa r_i)}{\kappa r_i} + \frac{B_k \exp(-\kappa r_k)}{\kappa r_k} + y_p \exp(-\kappa z) \quad (22)$$

where $B_k = -B_i$, z is the distance from the planar surface, and y_p the scaled surface potential. The electrical interaction energy is

$$V_R = \left[y_p B_i \exp(-\kappa R_Z) - \frac{B_i^2 \exp(-2\kappa R_Z)}{16\pi\kappa R_Z} \right] \quad (23)$$

where R_Z denotes the distance of the center of the particle from the surface.

If the planar surface is assumed to have a constant charge, then we assume that the image particle k has the same electrical properties as that of particle i , but with different sign. In this case, $B_k = B_i$ in eq 22, and it can be shown that

$$V_R = \left[\frac{4\pi\epsilon\sigma_p}{\epsilon\kappa k_B T} B_i \exp(-\kappa R_Z) + \frac{B_i^2 \exp(-2\kappa R_Z)}{16\kappa R_Z} \right] \quad (24)$$

where σ_p is the surface charge density of the surface. The results obtained can be extended without too much difficulty to a system containing multiple particles and a planar surface.

It should be pointed out that the present analysis is adequate for the case where two nearby particles are sufficiently separated such that they can assume an arbitrary relative orientation. If this is not satisfied, the mean field concept proposed here becomes inappropriate. One of the possible approaches to solve this problem is that adopted by Onsager.¹⁰

Conclusion

In summary, an analytical expression for the electrical interaction energy for a system containing arbitrary shaped, ion-penetrable particles bearing fixed charges in an electrolyte solution under the Debye–Huckel condition is derived using a mean field approach. This is an extension of previously reported results, which are limited to the interactions between two regularly shaped particles. We show that the interaction energy between two particles can be decomposed into the product of two terms. One of these terms is a function of the properties of the particles, such as shape and charged conditions, and the other term is independent of these properties. This implies that assuming arbitrarily the shape of a particle can lead to a significant deviation in the estimation of the interaction energy between two particles. Also, care must be taken if the properties of a particle are to be estimated on the basis of the interaction energy.

Acknowledgment. This work was supported by the National Science Council of the Republic of China.

References and Notes

- (1) Hunter, R. J. *Foundation of Colloid Science*, Vol. I; Oxford University Press: London, 1989.
- (2) Derjaguin, B. V.; Landau, L. D. *Acta Phys.-Chim. USSR* **1941**, *14*, 633.
- (3) Hogg, R.; Healy, T. W.; Fuerstenau, D. W. *Trans. Faraday Soc.* **1966**, *62*, 1638.
- (4) Bell, G. M.; Levine, S.; McCartney, L. N. *J. Colloid Interface Sci.* **1970**, *33*, 335.
- (5) Ohshima, H.; Healy, T. W.; White, L. R. *J. Colloid Interface Sci.* **1982**, *90*, 17.
- (6) Ohshima, H.; Chan, D. Y. C.; Healy, T. W.; White, L. R. *J. Colloid Interface Sci.* **1983**, *92*, 232.
- (7) Glendinning, A. B.; Russel, W. B. *J. Colloid Interface Sci.* **1983**, *93*, 95.

- (8) Sader, J. E.; Carnie, S. L.; Chan, D. Y. C. *J. Colloid Interface Sci.* **1995**, *171*, 46.
- (9) McCartney, L. N.; Levine, S. J. *J. Colloid Interface Sci.* **1969**, *30*, 345.
- (10) Ohshima, H.; Kondo, T. *J. Colloid Interface Sci.* **1993**, *155*, 499.
- (11) Hsu, J. P.; Liu, B. T. *J. Colloid Interface Sci.* **1997**, *190*, 371.
- (12) Onsager, L. *Ann. N.Y. Acad. Sci.* **1949**, *51*, 627.
- (13) Stroobants, A.; Lekkerkerker, H. N. W.; Odijk, T. *Macromolecules* **1986**, *19*, 2232.
- (14) Brenner, S. L.; Parsegian, V. A. *Biophys. J.* **1974**, *14*, 327.
- (15) Stigter, D. *Biopolymers* **1977**, *16*, 1435.
- (16) Fixman, M.; Skolnick, J. *Macromolecules* **1978**, *11*, 863.
- (17) Chu, X.; Wasan, D. T. *J. Colloid Interface Sci.* **1996**, *184*, 268.
- (18) Rallison, J. M.; Harding, S. E. *J. Colloid Interface Sci.* **1985**, *103*, 284.
- (19) Sato, T.; Teramoto, A. *Mol. Cryst. Liq. Cryst.* **1990**, *178*, 143.
- (20) Martinez, M. A. *Solid State Technol.* **1994**, *37*, 26.
- (21) Patrick, W.; Guthrie, W. L.; Standley, C. L.; Schiavone, P. M. *J. Electrochem. Soc.* **1991**, *138*, 1778.
- (22) Greenberg, M. D. *Application of Green's Functions in Science and Engineering*; Prentice Hall: Englewood Cliffs, NJ, 1971.
- (23) Verwey, E. J. W.; Overbeek, J. Th. G. *Theory of the Stability of Lyophobic Colloids*; Elsevier: Amsterdam, 1948.
- (24) Krieger, I. M.; Hiltner, P. A. Order and Disorder in Monodisperse Latexes. In *Polymer Colloids*; Fitch, R. M., Ed.; Plenum Press: New York, 1971; pp 63–72.
- (25) Ohshima, H.; Kondo, T. *J. Colloid Interface Sci.* **1993**, *157*, 504.