



Historical perspective

## Electrostatic interaction of soft particles

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### ARTICLE INFO

Available online 9 May 2015

#### Keywords:

Electrostatic interaction  
Soft particle  
Interdigitation  
Interpenetration  
Counterion only system  
Discrete-charge effect

### ABSTRACT

Theories of the electrostatic interaction between two soft particles (i.e., particles covered with an ion-penetrable surface layer of polyelectrolytes) in an electrolyte solution are reviewed. Interactions of soft particles after contact of their surface layers are particularly discussed. Interaction in a salt-free medium and the discrete-charge effect are also treated.

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### 1. Introduction

As is shown in the DLVO (Derjaguin–Landau–Verwey–Overbeek) theory of colloid stability of colloid stability [1,2], electrostatic interactions of charged colloidal particles in an electrolyte solution or in a medium containing only counterions play an essential role in determining various electric phenomena in colloidal suspensions [3–13]. In this paper we discuss the electrostatic interaction between soft particles, i.e., hard particle covered with an ion-penetrable surface layer of polyelectrolytes. Interfacial electric phenomena covering electrokinetics

[8,10,14–27] and electrostatic interactions of soft particles [8,10,28–37] are quite different from those of hard particles without surface structures. Here we start with the interaction between two parallel soft plates and then on the basis of Derjaguin's approximation [35,38,39] we derive the corresponding interaction energies for two spheres and two cylinders. For the case of weakly charged soft particles with no particle core, one can derive exact expressions for the interaction energy without recourse to Derjaguin's approximation [31]. We treat not only interactions of soft particles before contact of their surface layers but also interactions after contact. By extending de Gennes' theory [40] for the steric interaction between two parallel uncharged brush layers to the electrostatic interaction between two charged brush layers, we propose a compression model (a two-stage model) [41] and an interdigitation-compression model (a three-stage model) [42] for

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the electrostatic interaction between two parallel soft plates. As another model for the electrostatic interaction between soft particles after contact, we extend the theory of Dähler–Rödenbeck’s theory [43] on the interaction between two interpenetrating vesicle-like surface-charged particles to the interaction between two interpenetrating soft spheres with no particle core [44,45]. We also discuss the electrostatic interaction of soft particles in a salt-free medium containing only counterions [46–48]. Finally, we deal with the discrete-charge effect [49–54] and its effect on the electrostatic interaction of soft particles [55].

## 2. Interaction between soft particles before contact

We start with the electrostatic interaction between two soft particles before contact of their surface layers. In order to calculate the electrostatic interaction between soft particles, one must solve the Poisson–Boltzmann equations for both regions inside and outside the surface layer [17–26].

### 2.1. Interaction between two parallel soft plates

Consider two parallel dissimilar soft plates 1 and 2 of thicknesses  $d_1$  and  $d_2$ , respectively, separated by a distance  $h$  immersed in an electrolyte solution containing  $N$  ionic species with valence  $z_i$  and bulk concentration (number density)  $n_i^\infty$  ( $i = 1, 2 \dots N$ ). We treat the case where fixed-charges are distributed in the surface layers of plates 1 and 2 at uniform densities of  $\rho_{\text{fix}1}$  and  $\rho_{\text{fix}2}$ , respectively. We take an  $x$ -axis perpendicular to the plates with its origin at the right surface of plate 1, as in Fig. 1.

We assume that the electric potential  $\psi(x)$  outside the plates ( $0 < x < h$ ) and inside the plates ( $-d_1 < x < 0$  and  $h < x < h + d_2$ )

obeys the following one-dimensional planar Poisson–Boltzmann equations:

$$\frac{d^2\psi(x)}{dx^2} = -\frac{1}{\epsilon_r\epsilon_0} \sum_{i=1}^N z_i e n_i^\infty \exp\left(-\frac{z_i e \psi(x)}{kT}\right) - \frac{\rho_{\text{fix}1}}{\epsilon_r\epsilon_0} \quad \text{for } -d_1 < x < 0 \quad (2.1)$$

$$\frac{d^2\psi(x)}{dx^2} = -\frac{1}{\epsilon_r\epsilon_0} \sum_{i=1}^N z_i e n_i^\infty \exp\left(-\frac{z_i e \psi(x)}{kT}\right) \quad \text{for } 0 < x < h \quad (2.2)$$

$$\frac{d^2\psi(x)}{dx^2} = -\frac{1}{\epsilon_r\epsilon_0} \sum_{i=1}^N z_i e n_i^\infty \exp\left(-\frac{z_i e \psi(x)}{kT}\right) - \frac{\rho_{\text{fix}2}}{\epsilon_r\epsilon_0} \quad \text{for } h < x < h + d_2 \quad (2.3)$$

where  $\epsilon_r$  is the relative permittivity of the electrolyte solution,  $\epsilon_0$  is the permittivity of a vacuum,  $e$  is the elementary electric charge,  $k$  is Boltzmann’s constant, and  $T$  is the absolute temperature. In the above Poisson–Boltzmann equations, we have assumed that the relative permittivity  $\epsilon_r$  of the electrolyte solution takes the same value in the both regions outside and inside the surface layers. Note that if the ionized group of valence  $Z_i$  and number density  $N_i$  are distributed within the surface layer of particle  $i$  ( $i = 1, 2$ ), then we have  $\rho_{\text{fix}i} = Z_i e N_i$ .

The interaction force  $P$  per unit area between two parallel soft plates can be calculated by integrating the excess osmotic pressure and the Maxwell stress over an arbitrary closed surface  $\Sigma$  enclosing either one of the two interacting plates. As  $\Sigma$ , we choose two planes located at  $x = -\infty$  (in the bulk solution far from the plates) and  $x = x'$  ( $0 < x' < h$ ) enclosing plate 1. Here  $x'$  is an arbitrary point in the region  $0 < x < h$  between plates 1 and 2. Thus the force  $P(h)$  of the double layer interaction per unit area is given by

$$P_{\text{pl}}(h) = \sum_{i=1}^N n_i^\infty kT \left[ \exp\left(-\frac{z_i e \psi(x')}{kT}\right) - 1 \right] - \frac{1}{2} \epsilon_r \epsilon_0 \left( \frac{d\psi}{dx} \Big|_{x=x'} \right)^2 \quad (2.4)$$

which, for the low potential case, can be linearized to

$$P_{\text{pl}}(h) = \frac{1}{2} \epsilon_r \epsilon_0 \left\{ \kappa^2 \psi^2(x') - \left( \frac{d\psi}{dx} \Big|_{x=x'} \right)^2 \right\} \quad (2.5)$$

with

$$\kappa = \left( \frac{1}{\epsilon_r \epsilon_0 kT} \sum_{i=1}^N z_i^2 e^2 n_i^\infty \right)^{1/2} \quad (2.6)$$

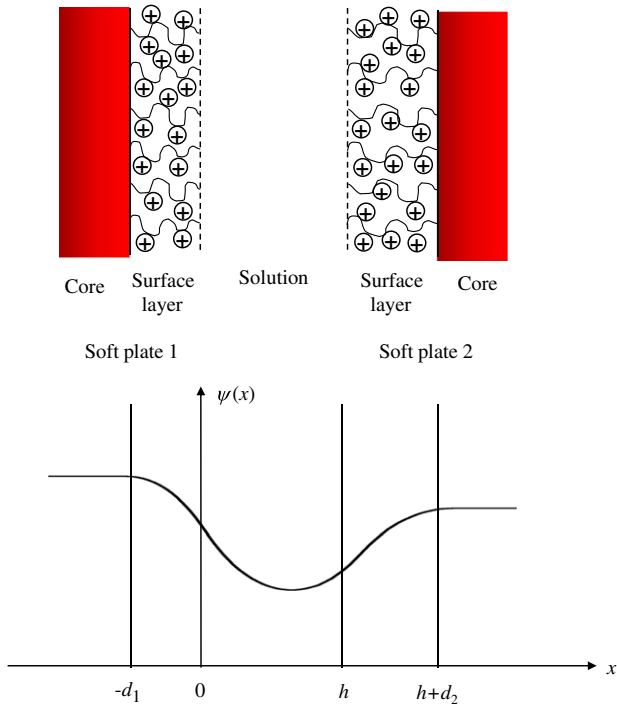
where  $\kappa$  is the Debye–Hückel parameter and the electroneutrality condition  $\sum_{i=1}^N z_i n_i^\infty = 0$  has been used. In Eq. (2.5),  $P_{\text{pl}}(h) > 0$  corresponds to repulsion and  $P(h) < 0$  to attraction. The corresponding interaction energy  $V_{\text{pl}}(h)$  between two parallel plates per unit area can be obtained by integrating  $P_{\text{pl}}(h)$  with the result that

$$V_{\text{pl}}(h) = \int_h^\infty P_{\text{pl}}(h) dh. \quad (2.7)$$

For the low potential case, an expression for the interaction energy between two parallel soft plates is easily derived. The results for the low potential case are given by [29]

$$V_{\text{pl}}(h) = \frac{1}{4\epsilon_r\epsilon_0\kappa^3} \left[ \left\{ \rho_{\text{fix}1} \sinh(\kappa d_1) + \rho_{\text{fix}2} \sinh(\kappa d_2) \right\}^2 \left\{ \coth\left(\frac{\kappa(h+d_1+d_2)}{2}\right) - 1 \right\} - \left\{ \rho_{\text{fix}1} \sinh(\kappa d_1) - \rho_{\text{fix}2} \sinh(\kappa d_2) \right\}^2 \left\{ 1 - \tanh\left(\frac{\kappa(h+d_1+d_2)}{2}\right) \right\} \right]. \quad (2.8)$$

For the arbitrary potential case, a simple approximation method (the linear superposition approximation (LSA)) is available to derive the interaction energy between particles at large particle separations.



**Fig. 1.** Interaction between two parallel dissimilar soft plates 1 and 2 covered with surface layers of thicknesses  $d_1$  and  $d_2$ , respectively, at separation  $h$  and potential distribution  $\psi(x)$  across them.

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