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Study on Interaction Between Two Parallel Plates with Iteration Method in Functional Theory

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By introducing the functional theory into the calculation of electric double layer (EDL) interaction, the interaction energies of two parallel plates were calculated respectively at low, moderate, and high potentials. Compared with the results of two existing methods, Debye-Hückel and Langmuir methods, which are applicable just to the critical potentials and perform poorly in the intermediate potential, the functional approach not only has much simpler expression of the EDL interaction energy, but also performs well in the entire range of potentials.

Key words: Interaction energy, Functional theory, Electric double layer, Parallel plate

I. INTRODUCTION

It is well known that an electric double layer (EDL) exists around a charged particle (or ion) in aqueous solution and the EDL interaction between any neighboring particles plays a major role in the stability of an emulsion, such as aggregation, coagulation, coalescence, flocculation, as well as interactions with boundary surface leading to adsorption, adhesion, and deposition [1-8]. Many efforts have been focused on the study of the EDL interaction for long time due to the development of material science, biophysics, medicine, and so on. Though Verwey *et al.* had developed an expression of EDL interaction at constant surface potential as early as in 1948 [9], since EDL properties of electrolyzed particle are characterized by the so-called Poisson-Boltzmann equation (PB equation), which is a second-order nonlinear differential equation of potential with constant coefficient, the relevant calculation methods are quite complex even for the easiest parallel plates with Verwey's approach. Based on the Debye-Hückel (DH) [10] linear approach of solving the PB equation, Hogg and Healy gave the interaction energy of parallel plates at very low potential [11]. From another extreme condition Langmuir simplified the PB equation [12] and Luo *et al.* further introduced the Langmuir approximation method to calculate the EDL interaction of parallel plates at very high potential [13]. Devereux and de Bruyn gave the numerical calculation method of the EDL interaction energy [14]. To our knowledge, apart from the numerical method of calculating the EDL interaction, the solutions obtained from the above two methods are

merely for those extreme conditions in which there are either very low potentials or very high ones. Moreover, the numerical method is difficult to be used to discuss the EDL interaction further because of the absence of a potential expression. Though those analytical and numerical results have provided more insight into the properties of the EDL, they have critical disadvantages of being very complex expressions or just lumping the numerical data together so that relative contributions from different terms can not be apparent. Since the EDL is very important both to scientific and technical fields, an analytical expression for the EDL interaction that suits the general potentials remains a worthwhile endeavor even in our modern age.

In fact, from the viewpoint of functional theory, the PB equation for any shape could be analytically solved without any restriction [15]. In order to calculate the EDL interaction we have done substantial preparation by introducing the iterative method in functional theory into the solution of different geometrical PB equations without any restriction [16-21]. In this work we will start the calculation of the EDL interaction based on the simple parallel plate model and also with the help of functional analysis theory, and show the advantages of the functional approach by comparing with the DH method and the Langmuir approximation, as well as the numerical calculation.

II. THE INTERACTION BETWEEN TWO PARALLEL PLATES AT THE EXTREME POTENTIALS

The PB equation of potential ψ in the EDL of a particle is expressed as [9]

$$\nabla^2\psi = -\frac{\rho}{\varepsilon} \quad (1)$$

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where ∇^2 is the Laplacian operator, ρ is the volume charge density, and ε is the dielectric constant of medium. For an infinite flat plate, in the case of the z - z type ion-pairs, the corresponding PB equation is

$$\frac{d^2\psi}{dx^2} = \frac{2n_0ze}{\varepsilon} \sinh\left(\frac{ze\psi}{kT}\right) \quad (2)$$

where e is the elemental electric charge, n_0 is the concentration of ions far away from the particle, z is the valence of the ionic species in solution, k is the Boltzmann's constant, and T is the absolute temperature.

Under the very low potential condition (namely the DH approximation), Eq.(2) reduces to

$$\begin{aligned} \frac{d^2\psi}{dx^2} &\approx \kappa^2\psi \quad (3) \\ \kappa^2 &= \frac{2 \times 10^3 e^2 cz^2 N_A}{\varepsilon kT} \end{aligned}$$

where c is the concentration of ions (mol/L) and N_A is the Avogadro's constant. Eq.(3) yields

$$\psi_{\text{DH}} = A_1 \cosh \kappa x + A_2 \sinh \kappa x \quad (4)$$

where A_1 and A_2 are constants to be evaluated.

For the general case of two dissimilar plates with an apart distance h , Eq.(4) must satisfy the boundary conditions $\psi = \psi_a$ at $x=0$, and $\psi = \psi_b$ at $x=h$, where ψ_a and ψ_b are the surface potentials of respective plates A and B . Under the boundary conditions, Eq.(4) becomes

$$\psi_{\text{DH}} = \psi_a \cosh \kappa x + \frac{\psi_b - \psi_a \cosh \kappa h}{\sinh \kappa h} \sinh \kappa x \quad (5)$$

The interaction energy V between two EDLs is equal to the difference in free energies of the double layer system when the plates are brought together from infinity to distance h [9]. Thus

$$V = \Delta G = G_h - G_\infty \quad (6)$$

where G_h and G_∞ are the free energies of the double layer system when the plates are separated by distances of h and infinity respectively.

Verwey and Overbeek have shown that when surface potential is constant and small [9], the free energy of a single flat is given by: $G = -\sigma\psi_c/2$, where σ is the surface charge density, and ψ_c is the surface potential of flat particle. Thus, G_h , the free energy of the double layer system, is equal to the sum of free energies of separate layers

$$G_h = -\frac{1}{2}(\sigma_a\psi_a + \sigma_b\psi_b) \quad (7)$$

where σ_a and σ_b are the surface charge densities of the single layers. The surface charge density at a plane surface is given by

$$\sigma = -\varepsilon \left(\frac{d\psi}{dx} \right)_{x=0} \quad (8)$$

Thus σ_a and σ_b can be obtained, and then substituted into Eq.(7) to get

$$G_h = \frac{\kappa\varepsilon}{2} [2\psi_a\psi_b\text{csch}\kappa h - (\psi_a^2 + \psi_b^2) \coth \kappa h] \quad (9)$$

It follows from Eq.(9) that as the separation of the plates is large

$$G_\infty = -\frac{\kappa\varepsilon}{2}(\psi_a^2 + \psi_b^2) \quad (10)$$

Thus, from Eq.(6)

$$\begin{aligned} V_{\text{DH}} &= \frac{\kappa\varepsilon}{2} [(\psi_a^2 + \psi_b^2)(1 - \coth \kappa h) \\ &\quad + 2\psi_a\psi_b\text{csch}\kappa h] \quad (11) \end{aligned}$$

In the case of another extreme condition, in particular, at very high potential, the Langmuir method was used to calculate the interaction energy by Luo *et al.*, and Eq.(2) was simplified to [12]

$$\frac{d^2\psi}{dx^2} \approx \frac{kT\kappa^2}{ze} \exp\left(\frac{ze}{kT}\psi\right) \quad (12)$$

The potential in the minimum of two parallel plates ψ_{min}^L was obtained from Eq.(12), the repulsive force per unit area P and the free interaction energy V per unit area [9] were respectively expressed as

$$\begin{aligned} \psi_{\text{min}}^L &= 2\frac{kT}{ze} \ln \left\{ 2\pi \left[\kappa h + 2 \exp\left(-\frac{ze\psi_a}{2kT}\right) \right. \right. \\ &\quad \left. \left. + 2 \exp\left(-\frac{ze\psi_b}{2kT}\right) \right]^{-1} \right\} \quad (13) \end{aligned}$$

$$P = \varepsilon\kappa^2 \left(\frac{kT}{e}\right)^2 \left[\cosh\left(\frac{ze\psi_{\text{min}}^L}{kT}\right) - 1 \right] \quad (14)$$

$$V = \int_h^\infty p dh \quad (15)$$

where ψ_{min}^L is the potential in the minimum of two parallel plates.

From Eqs.(13)-(15), the interaction energy V_L between two parallel plates was obtained [13]

$$\begin{aligned} V_L &= \varepsilon\kappa \left(\frac{kT}{e}\right)^2 \left[2\pi^2 \left(\frac{1}{\kappa h + m} - \frac{1}{2\pi + m} \right) \right. \\ &\quad \left. - \frac{(\kappa h + m)^3 - (2\pi + m)^3}{24\pi^2} + (\kappa h - 2\pi) \right] \quad (16) \end{aligned}$$

where $m = 2 \exp\left(-\frac{ze\psi_a}{2kT}\right) + 2 \exp\left(-\frac{ze\psi_b}{2kT}\right)$.

III. APPLICATION OF FUNCTIONAL THEORY IN THE CALCULATION OF THE INTERACTION ENERGY BETWEEN TWO PARALLEL PLATES

According to the functional analysis theory, for a set C composed of continuous functions (ψ, ϕ, \dots) that

have at least second-order derivatives in an open interval (a, b) , where a and b are two different real numbers, a norm of ψ is defined by [22-24]

$$\|\psi\| = \max_{a < r < b} |\psi(r)| \quad (17)$$

Then it is easy to prove that any functions in this set can satisfy the following axioms of norm. That is, if $\psi, \phi \in C$, then

$$\begin{aligned} \|\psi\| &\geq 0 \\ \|\psi + \phi\| &\leq \|\psi\| + \|\phi\| \\ \|\lambda\psi\| &= |\lambda| \|\psi\| \quad (\lambda \text{ is a real}) \end{aligned} \quad (18)$$

and the set C forms a Banach space B . If \hat{P} is such an operator that acts on this space and results in an identical function when it operates on the function ψ in this space

$$\psi = \hat{P}\psi \quad (19)$$

and if \hat{P} also satisfies the Lipschitz condition [25,26]

$$\|\hat{P}\psi - \hat{P}\phi\| \leq \alpha \|\psi - \phi\| \quad (\psi, \phi \in B) \quad (20)$$

where α is called Lipschitz constant, then beginning with any function ψ_0 (where $\psi_0 \in B$), one can get

$$\psi_{j+1} = \hat{P}\psi_j \quad (j = 0, 1, 2 \dots) \quad (21)$$

$$\lim_{j \rightarrow \infty} \psi_j(r) = \psi(r) \quad (22)$$

where $\psi(r)$ is the real solution of equation

$$\psi(r) = \hat{P}\psi(r) \quad (23)$$

and $\psi_n(r)$ is generally called an approximate solution of Eq.(21) in the n th iteration.

It is easy to prove that for any solution of PB equation of a particle, the norm of $\psi(r)$ expressed in Eq.(17) can be defined and it can also satisfy the axioms of norm in Eq.(18), therefore, $\psi(r) \in B$. The corresponding operator is constructed according to the functional theory and Eq.(2) as

$$\hat{P} = \frac{kT}{ze} \sinh^{-1} \left(\frac{ze}{kT\kappa^2} \frac{d^2}{dx^2} \right) \quad (24)$$

In order to obtain the solution of Eq.(2), by appointing ψ_{DH} obtained from DH method as the initial function ψ_0 in the iterative method, and substituting Eq.(24) into Eq.(21), one can get

$$\begin{aligned} \psi_1 &= \hat{P}\psi_{DH} \\ &= \frac{kT}{ze} \sinh^{-1} \left\{ \frac{ze}{kT\kappa^2} \frac{d^2}{dx^2} \left[\psi_a \cosh \kappa x \right. \right. \\ &\quad \left. \left. + \frac{\psi_b - \psi_a \cosh \kappa h}{\sinh \kappa h} \sinh \kappa x \right] \right\} \\ &= \frac{kT}{ze} \sinh^{-1} \left\{ \frac{ze}{kT} \left[\psi_a \cosh \kappa x \right. \right. \\ &\quad \left. \left. + \frac{\psi_b - \psi_a \cosh \kappa h}{\sinh \kappa h} \sinh \kappa x \right] \right\} \end{aligned} \quad (25)$$

Further by substituting Eq.(25) into Eq.(8), and combining Eq.(7), one can obtain the free energy of the plates with a distance h apart

$$G_h = \frac{\varepsilon\kappa}{2} \left[\frac{\psi_b \operatorname{csch} \kappa h - \psi_a \coth \kappa h}{\sqrt{1 + (ze\psi_a/kT)^2}} \psi_a \right. \\ \left. - \frac{\psi_b \coth \kappa h - \psi_a \operatorname{csch} \kappa h}{\sqrt{1 + (ze\psi_b/kT)^2}} \psi_b \right] \quad (26)$$

Thus

$$G_\infty = -\frac{\varepsilon\kappa}{2} \left[\frac{\psi_a^2}{\sqrt{1 + (ze\psi_a/kT)^2}} + \frac{\psi_b^2}{\sqrt{1 + (ze\psi_b/kT)^2}} \right] \quad (27)$$

From Eqs.(6), (26), and (27), the interaction energy V_f with functional method can be figured out as

$$V_f = \frac{\kappa\varepsilon}{2} \left[\frac{\psi_a(\psi_a + \psi_b \operatorname{csch} \kappa h - \psi_a \coth \kappa h)}{\sqrt{1 + (ze\psi_a/kT)^2}} \right. \\ \left. + \frac{\psi_b(\psi_b + \psi_a \operatorname{csch} \kappa h - \psi_b \coth \kappa h)}{\sqrt{1 + (ze\psi_b/kT)^2}} \right] \quad (28)$$

For convenience, Eq.(25) can further be expressed as

$$\psi_{f1} = \frac{kT}{ze} \sinh^{-1} \left\{ \frac{ze}{kT} \cdot \left[\frac{\psi_b - \psi_a \exp(\kappa h)}{\exp(-\kappa h) - \exp(\kappa h)} \exp(-\kappa x) \right. \right. \\ \left. \left. + \frac{\psi_a \exp(-\kappa h) - \psi_b}{\exp(-\kappa h) - \exp(\kappa h)} \exp(\kappa x) \right] \right\} \quad (29)$$

For Eq.(29), the derivative of ψ_{f1} must vanish at an interior point. Let this point be $x=s$, namely $\left(\frac{d\psi_{f1}}{dx} \right)_{x=s} = 0$. Thus

$$\begin{aligned} \frac{d\psi_{f1}}{dx} &= \left\{ \frac{-\kappa[\psi_b - \psi_a \exp(\kappa h)]}{\exp(-\kappa h) - \exp(\kappa h)} \exp(-\kappa x) \right. \\ &\quad \left. + \frac{\kappa[\psi_a \exp(-\kappa h) - \psi_b]}{\exp(-\kappa h) - \exp(\kappa h)} \exp(\kappa x) \right\} \\ &\quad \cdot \left\{ 1 + \left(\frac{ze}{kT} \right)^2 \left[\frac{\psi_b - \psi_a \exp(\kappa h)}{\exp(-\kappa h) - \exp(\kappa h)} \exp(-\kappa x) \right. \right. \\ &\quad \left. \left. + \frac{\psi_a \exp(-\kappa h) - \psi_b}{\exp(-\kappa h) - \exp(\kappa h)} \exp(\kappa x) \right]^2 \right\}^{-1/2} \\ &= 0 \end{aligned} \quad (30)$$

From the above equation

$$x = s = \frac{1}{2\kappa} \ln \frac{\psi_b - \psi_a \exp(\kappa h)}{\psi_a \exp(-\kappa h) - \psi_b} \quad (31)$$

Substituting Eq.(31) into Eq.(29), one can acquire the potential in the minimum of two dissimilar parallel plates ψ_{\min}^f with the functional method

$$\psi_{\min}^f = \frac{kT}{ze} \sinh^{-1} \left\{ \frac{ze}{kT} \left[\frac{\psi_b - \psi_a \exp(\kappa h)}{\exp(-\kappa h) - \exp(\kappa h)} \right] \cdot \exp \left(-\frac{1}{2} \ln \frac{\psi_b - \psi_a \exp(\kappa h)}{\psi_a \exp(-\kappa h) - \psi_b} \right) + \frac{\psi_a \exp(-\kappa h) - \psi_b}{\exp(-\kappa h) - \exp(\kappa h)} \cdot \exp \left(\frac{1}{2} \ln \frac{\psi_b - \psi_a \exp(\kappa h)}{\psi_a \exp(-\kappa h) - \psi_b} \right) \right\} \quad (32)$$

The high surface potential usually appears in the colloidal solution of high concentration and high valence of the ionic species. Meanwhile, κh is usually greater, and so, $\exp(\kappa h) \gg 1$, $\exp(-\kappa h) \ll 1$. Substituting these conditions into Eq.(32)

$$\psi_{\min}^f = \frac{kT}{ze} \sinh^{-1} \left[\frac{2ze\sqrt{\psi_a\psi_b}}{kT} \exp \left(-\frac{\kappa h}{2} \right) \right] \quad (33)$$

From Eqs.(33) and (14), the repulsive force P_f with functional method can be obtained as

$$P_f = \frac{k^2 T^2 \varepsilon \kappa^2}{e^2} \left(\sqrt{1 + \frac{4e^2 \exp(-\kappa h) z^2 \psi_a \psi_b}{k^2 T^2}} - 1 \right) \quad (34)$$

Substituting Eq.(34) into Eq.(15), one can get the interaction energy V_f with functional method.

Figure 1, 2, and 3 respectively give some comparisons of the interaction energies at very low, very high, and moderate potentials among the methods, namely V_{DH} (DH approximation), V_L (Langmuir approximation), V_n (numerical method [14]) and V_f (functional method). From the figures, one can obtain that even at very low or very high potentials, for which DH and Langmuir methods are merely suitable (Figs.1 and 2), the functional method is still dominantly superior to those two methods.

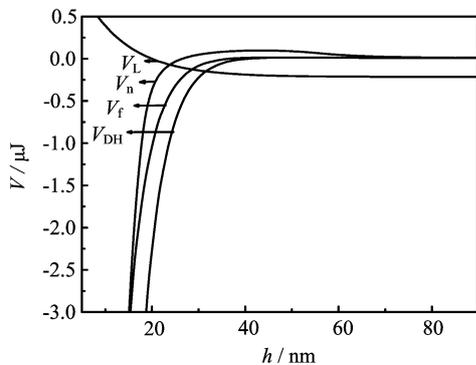


FIG. 1 Comparison among V_f , V_{DH} , V_L , and V_n at low potential in the case: $\psi_a=46$ mV, $\psi_b=0.3$ mV, $z=1$, $c=1$ mmol/L, $T=298.16$ K, $\varepsilon=6.954 \times 10^{-10}$ c/(V m).

Figure 1 expresses that three curves V_{DH} , V_n , and V_f are coincident at lower potentials ψ_a and ψ_b at very long distance with the interaction energy about zero. But as the distance gets shorter, V_{DH} is gradually far away from V_n . However V_f is close to V_n in all distances and they even coincide at very short spacing. The reason is that the construction of Eq.(24) has surmounted the restriction of low potential condition, and the obtained first iteration solution ψ_1 is more precise than ψ_{DH} , so the calculated result of V_f is more exact than V_{DH} , and much closer to V_n . Since V_L is obtained under the other extreme condition (very high potential), it is reasonably apart from V_n and the same reason applies for V_{DH} in Fig.2.

In Fig.2 for higher values of ψ_a and ψ_b , V_L is lower than V_n in all distances, and except for very short spacing it is far from V_n , especially with the increase of distance. Meanwhile, V_f and V_{DH} agree with V_n well as the increase of distance. Indeed it is because the Langmuir approximation is based on the simplification of the one-dimensional PB equation that Eq.(16) is divergent when it is far from the particle, consequently the Langmuir approximation is just for the close spacing condition. But the functional method is more like the

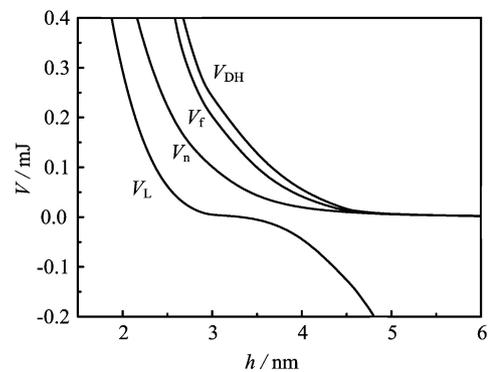


FIG. 2 Comparison among V_f , V_{DH} , V_L , and V_n at high potential in the case: $\psi_a=154$ mV, $\psi_b=128$ mV, $z=1$, $c=0.3$ mol/L, $T=298.16$ K, $\varepsilon=6.954 \times 10^{-10}$ c/(V m).

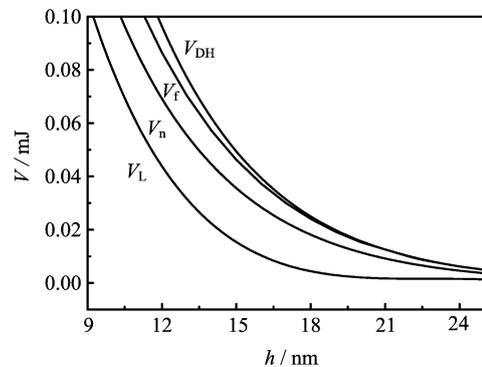


FIG. 3 Comparison among V_f , V_{DH} , V_L , and V_n at moderate potential in the case: $\psi_a=77$ mV, $\psi_b=67$ mV, $z=1$, $c=5$ mmol/L, $T=298.16$ K, $\varepsilon=6.954 \times 10^{-10}$ c/(V m).

numerical method as the distance increases. Besides, although the establishment of Eq.(19) is not related to the potential, for the chosen 0th iteration solution obtained at the very low potential, as a result, the curve of V_f is opposite to V_L , approaching V_n from the direction of higher than V_n (ipsilateral side with V_{DH}).

Comparison among V_L , V_{DH} , and V_f at moderate potential illustrated in Fig.3 also confirms V_f being the closest to V_n .

IV. CONCLUSION

The iterative method in functional theory can be used to calculate the interaction energy between two parallel plates. Since it can surmount the restriction of extreme potentials and has much more accurate and simple expression of interaction energy, undoubtedly it can be found to have important applications in the study of practical systems, such as emulsions and surfactant liquid crystal systems where moderate potentials are expected and the extreme potential supposition is invalid.

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