

The role of energy and entropy in the electrical double layer

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Abstract

The free energy of the electrical double layer is expressed as the sum of the electrical field energy, the contribution of the entropy of the distribution of ions and, where applicable, the chemical free energy due to the preference of potential determining ions for the surface. General expressions are derived without the use of a charging process. They are given for arbitrary geometry in a form that is easily adapted for computations. The Poisson-Boltzmann equation is assumed to be valid. It is shown that the results are equivalent to those obtained by the use of charging processes. A table is given in which the signs of the various contributions to the free energy of interaction of double layers are given. Two quantitative applications are treated, one showing that the entropy contributes more to the electrical free energy of a double layer than the field energy. In the second example the energy/entropy method is applied to calculate the interaction of particles with different surface potentials.

INTRODUCTION

Most authors have dealt with the free energy of double layers and their interaction with the aid of imaginary charging processes (see: Verwey and Overbeek [1], Overbeek [2]) or via the integration of the force of interaction (Langmuir [3] and Refs [1,2]). Only exceptionally has this free energy been treated as the sum of energy and entropy contributions, e.g., by Marcus [4], who considered the properties of polyelectrolytes, and by Jönsson et al. [5,6], who applied this method to amphiphile-water systems.

It may be of some interest to formulate energy and entropy separately, and show how this can be applied to the interaction of colloidal particles. Apart from offering an independent way of treating double layer free energies without the use of the always somewhat artificial charging process, it will stress the (sometimes overwhelming) importance of the entropy explicitly.

Three elements have to be considered: (1) The electrostatic energy of the surface charges and the bulk charges. (2) The entropy involved in the uneven

distribution of the ions. (3) The “chemical” (i.e., non-electrical) preference of the ions forming the surface charge for the surface over the bulk or the tendency to electrolytic dissociation of groups in the surface. This last contribution may be omitted in dealing with interactions in which the surface charge remains constant, as, e.g., in clays, where the crystal lattice carries a permanent charge, in completely dissociated polyelectrolytes, such as NaPMA, or in micelles such as NaDS, or in some cases of rapid interaction as in Brownian encounters, during which the surface charge cannot adapt rapidly enough.

Model, terminology and symbols

We consider particles of arbitrary size and shape embedded in an aqueous electrolyte solution. In order to avoid unessential complications we shall limit our treatment to purely diffuse double layers, obeying the Poisson–Boltzmann equation. The surface of the particles with surface elements dA carries a surface charge density, σ , and it has a potential, φ_0 . Different particles may have different values of σ and φ_0 . The electrolyte solution with volume elements, dV , has a charge density, ρ , and a potential, φ , that vary with position. It contains ions of types, i , with charge number, z_i (sign included), in mole fraction, x_i , and concentration, n_i ions per unit volume. The solvent, water, is indicated by the subscript, w . The system as considered is electroneutral and it contains positions far away from all particles, indicated as infinity (∞), where φ and all its spatial derivatives are zero, and concentrations and mole fractions are $n_{i\infty}$, $n_{w\infty}$, $x_{i\infty}$, $x_{w\infty}$ respectively.

Dimensionless potentials are defined as $\psi = e\varphi/kT$ and $\psi_0 = e\varphi_0/kT$. The dielectric constant of the solution is ϵ_r , the permittivity of the vacuum is ϵ_0 .

Furthermore, the Debye length, κ^{-1} , is defined through

$$\kappa^2 = \frac{\sum_i n_{i\infty} z_i^2 e^2}{\epsilon_r \epsilon_0 kT} \quad (1)$$

and finally

$$\sigma = -\epsilon_r \epsilon_0 \text{grad}_n \varphi \equiv -\epsilon_r \epsilon_0 (d\varphi/dn) \quad (2)$$

at the surface, where n is the normal on the surface, directed into the solution.

The energy

The electrostatic energy, U_{el} , can be described as the field energy in the solution, or, alternatively as the energy of the surface charges and bulk charges in the local potential field. The two descriptions can be transformed into one another by using Green’s theorem in the form

$$-\int_A a_0 \text{grad}_n b \, dA = \int_V (a \text{div grad } b + \text{grad } a \cdot \text{grad } b) \, dV \quad (3)$$

where a and b are scalar fields, vanishing at infinity and having values a_0 and b_0 at the surface A . grad_n is directed from the surfaces into the volume V . Furthermore Eqn (2) for the surface charge density and Poisson's equation, Eqn (4), for the bulk charge density are needed.

$$\text{div grad } \varphi = -\rho / \epsilon_r \epsilon_0 \quad (4)$$

Then

$$\begin{aligned} U_{\text{el}} = \text{field energy} &= \frac{\epsilon_r \epsilon_0}{2} \int_V (\text{grad } \varphi)^2 \, dV = (\text{with Green's theorem}) \\ &= -\frac{\epsilon_r \epsilon_0}{2} \int_A \varphi_0 (\partial \varphi / \partial n)_{\text{surf}} \, dA - \frac{\epsilon_r \epsilon_0}{2} \int_V \varphi \text{div grad } \varphi \, dV = \\ [\text{with Eqns (2) and (4)}] &= +\frac{1}{2} \int_A \sigma \varphi_0 \, dA + \frac{1}{2} \int_V \rho \varphi \, dV \end{aligned} \quad (5)$$

The relation between the potential, the charges and the space coordinates has to be obtained by solving the Poisson-Boltzmann equation, Eqn (6), with the relevant boundary conditions at the surfaces and at infinity.

$$\begin{aligned} \text{div grad } \varphi &= -\frac{\rho}{\epsilon_r \epsilon_0} = -\frac{\sum_i z_i e n_i}{\epsilon_r \epsilon_0} = -\frac{\sum_i z_i e n_{i0} \exp(-z_i e \varphi / kT)}{\epsilon_r \epsilon_0} = \\ (\text{for a single } z\text{-}z \text{ electrolyte}) &= +\frac{2ze n_0}{\epsilon_r \epsilon_0} \sinh z\psi = \\ &\kappa^2 \left(\frac{kT}{ze} \sinh z\psi \right) \end{aligned} \quad (6)$$

The entropy

The entropy difference, ΔS , between the ion distribution in the double layer and the same ions and solvent molecules in the solution at $\varphi=0$ is given for dilute electrolyte solutions by

$$\begin{aligned}
\Delta S &= -k \int_V \left\{ \sum_i n_i \ln \frac{x_i}{x_{i0}} + n_w \ln \frac{1 - \sum_i x_i}{1 - \sum_i x_{i0}} \right\} dV \cong \\
&\quad -k \int_V \left\{ \sum_i \left(n_i \ln \frac{n_i}{n_{i0}} - n_i + n_{i0} \right) \right\} dV \\
&= +k \int_V \left\{ \sum_i n_{i0} [z_i \psi \exp(-z_i \psi) + \exp(-z_i \psi) - 1] \right\} dV \quad (7)
\end{aligned}$$

In the last transformation the Boltzmann relation has been applied. With the aid of

$$\rho = \sum_i z_i e n_i = -\epsilon_r \epsilon_0 \operatorname{div} \operatorname{grad} \varphi$$

and

$$\begin{aligned}
\int_0^\psi \epsilon_r \epsilon_0 \operatorname{div} \operatorname{grad} \varphi \, d\psi &= - \int_0^\psi \rho \, d\psi = \int_0^\psi \sum_i n_{i0} e \exp(-z_i \psi) \, d(-z_i \psi) \\
&= \sum_i n_{i0} e \{ \exp(-z_i \psi) - 1 \}
\end{aligned}$$

Eqn (7) can be transformed into

$$-T\Delta S = +\epsilon_r \epsilon_0 \int_V \varphi \operatorname{div} \operatorname{grad} \varphi \, dV - \epsilon_r \epsilon_0 \int_V dV \int_0^\varphi \operatorname{div} \operatorname{grad} \varphi \, d\varphi \quad (8)$$

The electric free energy

The Helmholtz free energy, F_{el} , of the electric double layer is found by combining U_{el} and $-T\Delta S$. F_{el} is equal to the Gibbs free energy, G_{el} , if the volume of the solution is not affected by the redistribution of the ions. Should the volume of the solution be affected by the charge distribution, a (small) $P\Delta V$ term has to be taken into account and G_{el} rather than F_{el} is the required quantity. See Fowler and Guggenheim [7] who have dealt with this point in connection with the ionic atmospheres in the Debye-Hückel theory of electrolytes. We shall neglect this fine point here and just consider incompressible systems. Then, with Eqns (5) and (8) we have

$$\begin{aligned}
F_{\text{el}} &= U_{\text{el}} - T\Delta S = \epsilon_r \epsilon_0 \int_V \left[\frac{(\text{grad } \varphi)^2}{2} + \varphi \text{div grad } \varphi - \int_0^\varphi \text{div grad } \varphi d\varphi \right] dV \\
&= \epsilon_r \epsilon_0 \int_V \left\{ \int_0^\varphi \text{grad } \varphi d(\text{grad } \varphi) + \int_0^\varphi \varphi d(\text{div grad } \varphi) \right\} dV \quad (9)
\end{aligned}$$

The integrations from 0 to φ are to be understood in the sense that at $\varphi=0$ all surfaces are uncharged and the potential is zero everywhere, whereas at $\varphi=\varphi_0$ all surfaces have their final surface potential φ_0 , not necessarily the same for all surfaces. The Poisson–Boltzmann equation, Eqn (6), remains valid at all stages. To show this more explicitly we introduce an integration variable, α , going from 0 to 1 for the whole system and the surface potentials change from 0 to φ_0 when α goes from 0 to 1. Then

$$\begin{aligned}
F_{\text{el}} &= \epsilon_r \epsilon_0 \int_V \left\{ \int_{\alpha=0}^1 \text{grad } \varphi \frac{\partial(\text{grad } \varphi)}{\partial \alpha} d\alpha + \int_{\alpha=0}^1 \varphi \frac{\partial(\text{div grad } \varphi)}{\partial \alpha} d\alpha \right\} dV \\
&= \epsilon_r \epsilon_0 \int_V \left\{ \int_0^1 \left(\text{grad } \varphi \text{grad } \frac{\partial \varphi}{\partial \alpha} + \varphi \text{div grad } \frac{\partial \varphi}{\partial \alpha} \right) d\alpha \right\} dV = \\
&\text{with Green's formula} = \epsilon_r \epsilon_0 \int_A \int_0^1 \varphi_{\text{surf}} \left(-\frac{\partial}{\partial n} \frac{\partial \varphi}{\partial \alpha} \right)_{\text{surf}} d\alpha dA \\
&= -\epsilon_r \epsilon_0 \int_A \int_{\alpha=0}^1 \varphi_{\text{surf}}(\alpha) d\left(\frac{\partial \varphi(\alpha)}{\partial n} \right) dA = + \int_A \int_{\sigma=0}^{\sigma \text{ final}} \varphi_{\text{surf}} d\sigma dA \quad (10)
\end{aligned}$$

and this is the same expression as found with the imaginary charging process, in which σ goes from zero to its final value.

Not only can Eqn (10) be derived from Eqn (9), but the reverse is also possible. The only requirements are that, during the charging process implied in $\int \varphi_{\text{surf}} d\sigma$, the solution part of the double layer is in thermodynamic and, thus, also in electric equilibrium. Poisson's law must be obeyed at all stages, there must be a well-defined relation, $\rho = \rho(\varphi)$ between the local charge density and the local potential, but this relation may deviate from the Boltzmann relation, $\rho = \sum z_i e n_i = \sum z_i e n_{i0} \exp(-z_i \psi)$ as used in the transformation of Eqn (7) into Eqn (8).

Therefore, it follows that the relation, implied in Eqns (8) and (9),

$$-T\Delta S = - \int_V dV \int_0^\varphi \varphi d\rho \quad (8a)$$

remains valid, even when the entropy deviates from Eqn (7) and the ion concentration distribution deviates from the Boltzmann relation, and thus Eqn (8a) has a wider validity than the derivation of Eqn (8) from Eqn (7) might seem to imply.

An independent method to derive Eqn (8a) is to state that during the charging process, $\int \varphi_{\text{surf}} d\sigma$, the solution part of the double layer arranges itself automatically, i.e., with zero contribution to the free energy, and thus the change in entropy and the electrical work done just compensate one another or

$$F_{\text{elec, solution}} = \int dV \int_0^\varphi \varphi d\rho - T\Delta S = 0$$

The chemical free energy

F_{el} and $\int \varphi_{\text{surf}} d\sigma$ in Eqns (9) and (10) cover only the electrostatic energy and the entropy of the ions as mentioned in the introduction. When the surface charge, composed of one or more types of ions, j , is in equilibrium with these ions in the solution by adsorption (or by dissociation), the free energy also contains the "chemical" term, F_{chem}

$$F_{\text{chem}} = \int_A dA \int_0^{\Gamma_{\text{final}}} \left\{ \sum_j \Delta\mu_j d\Gamma_j \right\} = \int_A dA \left\{ \sum_j \Delta\mu_j \Gamma_j \right\} \quad (11)$$

where Γ_j is the amount of j adsorbed per unit area and $\Delta\mu_j$ is the difference in chemical potential of j between the surfaces and the solution. The second equality in Eqn (11) is valid when $\Delta\mu_j$ is independent of Γ_j , e.g., because the chemical potential of the potential determining ions, j , in the surface is determined by and equal to the chemical potential of these same ions in the substrate of the surface, as with metals, sparingly soluble oxides or salts. Since at equilibrium the electrochemical potentials have to be equal between surface and solution,

$$\Delta\mu_j + z_j e \varphi_0 = 0 \quad (12)$$

With this expression and with $\sigma = \sum_j z_j e \Gamma_j$, Eqn (11) is transformed into

$$F_{\text{chem}} = - \int_A \sigma \varphi_0 dA \quad (13)$$

With application of Eqn (2) and Green's theorem, Eqn (3), this can also be written as

$$F_{\text{chem}} = -\epsilon_r \epsilon_0 \int_V dV [\varphi \operatorname{div} \operatorname{grad} \varphi + (\operatorname{grad} \varphi)^2] \quad (14)$$

Splitting of the chemical free energy, F_{chem} , into energy and entropy contributions cannot be done a priori, but requires experimental input, e.g., in the form of the heat (enthalpy) of adsorption or as the temperature dependence of the point of zero charge ($\sigma=0$).

If the surface contains a limited number of adsorption or dissociation sites, the entropy due to the distribution of the charges among these sites can be calculated, as already shown by Payens [8] in 1955, by Chan and Mitchell [9] and, very recently, by Stigter and Dill [10], but the entropy part contained in the standard free energy of adsorption or dissociation is just as inaccessible a priori as when $\Delta\mu_j$ is independent of the surface charge.

The total free energy

The total free energy, F_{tot} , is found as the sum of F_{el} [Eqn (9)] and F_{chem} [Eqn (14)]

$$F_{\text{tot}} = F_{\text{el}} + F_{\text{chem}} = -\epsilon_r \epsilon_0 \int_V dV \left[\frac{(\operatorname{grad} \varphi)^2}{2} + \int_0^\varphi \operatorname{div} \operatorname{grad} \varphi d\varphi \right] \quad (15)$$

or alternatively as the sum of Eqns (10) and (13)

$$F_{\text{tot}} = \int_A \int_{\sigma=0}^{\sigma \text{ final}} \varphi_{\text{surf}} d\sigma dA - \int_A \varphi_{\text{surf}} \sigma dA = - \int_A \int_{\varphi_{\text{surf}}=0}^{\varphi_0 \text{ final}} \sigma d\varphi_{\text{surf}} dA \quad (16)$$

In the derivation given in Eqn (10) we demonstrated the relation between the energy/entropy method and the charging process in which the surface is charged.

Similarly Eqn (15) for F_{tot} can also be found with the use of the Debye-Hückel type charging process, in which the charge of all ions in the system is gradually increased from zero to the final values. Proof of this statement is given in the Appendix.

What is the use of this approach?

In the first place the Eqns (5) for U_{el} , (7) and (8) for $-T\Delta S$, (9) for F_{el} , (14) for F_{chem} and (15) for F_{total} have been derived without the use of charging processes. They form suitable starting points for computations, assuming that

the potential ϕ is known as a function of the spatial coordinates after solution of the Poisson–Boltzmann equation.

Furthermore, U_{el} and $-T\Delta S$ are both positive. They work together and are obviously of the same order of magnitude. The driving force for the formation of the double layer is the negative chemical free energy or the given presence of a fixed surface charge density, σ .

Finally in the interaction between particles with a double layer, $[F_{el} - F_{el}(\infty)]$ at constant surface charges or $[F_{tot} - F_{tot}(\infty)]$ at constant surface potentials, where ∞ means that the particles are far apart, we shall find examples in which the interaction is mainly due to the entropy, other examples where it is mainly due to F_{chem} , but only very few where the energy, U_{el} , makes a sizable contribution to the final effect. Actually, in most cases the energy of interaction and the free energy of interaction differ even in sign.

As an illustration we present a table (Table 1) in which the signs of the various contributions to the interaction are given for a number of typical cases. We shall not go into all the details of the table. The main effects should be obvious enough. In a following paper a series of examples will be worked out quantitatively. In a later section of the present paper two quantitative applications are presented.

TABLE 1

Sign of the various contributions to the free energy of interaction (+ is repulsion, - is attraction) between two particles with double layers

Parameters that are kept constant		Contributions due to ^a							
		U_{el}	$-T\Delta S$	F_{el}	F_{chem}	F_{tot}			
$\phi_{01} = \phi_{02}$		-	-	-	⊕	+			
$\sigma_1 = \sigma_2$		-	⊕	+	n.a.	n.a.			
$\phi_{02} > \phi_{01} > 0$	} {	}	}	large separation	-	-	⊕	+	
$\phi_{02} < \phi_{01} < 0$				small separation	+	-	+	⊖	-
$\sigma_2 > \sigma_1 > 0$	} {	}	}	large separation	-	⊕	+	n.a.	
$\sigma_2 < \sigma_1 < 0$				small separation	-	⊕	+	n.a.	n.a.
$\phi_{02} > 0 > \phi_{01}$	} {	}	}	large separation	+	+	+	⊖	-
$\phi_{02} < 0 < \phi_{01}$				small separation	+	-	+	⊖	-
$\phi_{02} = -\phi_{01}$	} {	}	}	large separation	+	+	+	⊖	-
				small separation	+	-	+	⊖	-
$\sigma_2 > 0 > \sigma_1$	} {	}	}	large separation	⊖	⊖	-	n.a.	n.a.
$\sigma_2 < 0 < \sigma_1$				small separation	-	⊕	+	n.a.	n.a.
	} {	}	}	large separation	⊖	⊖	-	n.a.	n.a.
$\sigma_2 = -\sigma_1$				small separation	⊖	⊖	+	n.a.	n.a.

^aThe main contributions to the interaction for the various cases are indicated by circles around the + or - signs. Only with constant charges of opposite signs does the energy of interaction, U_{el} , play a significant supporting role.

U_{el} is a free energy

The field energy, U_{el} , is only a pure energy in the primitive model, in which the solvent is considered as a structureless medium with a dielectric constant, ϵ_r . The molecules of the solvent, however, are ordered by the electric field and therefore U_{el} is a free energy, containing both energy and entropy contributions. In water the entropy part is quite large, as is well known from the application of the theory of Debye and Hückel to the heat of dilution of electrolyte solutions.

Since the electrical free energy of a double layer with surface charge density, σ , can be written:

$$\frac{F_{el}}{A} = \frac{f(\sigma^2)}{2\epsilon_r \epsilon_0 \kappa} \quad \text{and} \quad \kappa \epsilon_r = \text{const}(\epsilon_r/T)^{1/2} \quad (17)$$

the energy of the double layer, U_{dl} , becomes

$$U_{dl} = F_{el} - T \frac{\partial F_{el}}{\partial T} = \frac{f(\sigma^2)}{4\epsilon_r \epsilon_0 \kappa} \left(1 + \frac{T}{\epsilon_r} \frac{\partial \epsilon_r}{\partial T} \right) \quad (18)$$

and the entropy contribution, $-TS_{dl}$, to the free energy is

$$-TS_{dl} = T \frac{\partial F_{el}}{\partial T} = \frac{f(\sigma^2)}{4\epsilon_r \epsilon_0 \kappa} \left(1 - \frac{T}{\epsilon_r} \frac{\partial \epsilon_r}{\partial T} \right) \quad (19)$$

Now for water at 25°C (T/ϵ_r) ($\partial \epsilon_r / \partial T$) = -1.35 and this results in U_{dl} being much smaller and of different sign from U_{el} and $-TS_{dl}$ being more than twice $-T\Delta S$.

Nevertheless, the values for F_{el} calculated with primitive model equations for U_{el} and $-T\Delta S$ are correct.

APPLICATIONS

We shall now discuss a few applications showing how the free energy of the double layer and of double layer interaction is composed quantitatively from energy and entropy contributions.

Single flat double layer

For a unit area of a single flat double layer in a 1-1 electrolyte of concentration n

$$U_{el} = \frac{\epsilon_r \epsilon_0}{2} \int_{x=0}^{\infty} \left(\frac{d\varphi}{dx} \right)^2 dx = \frac{\epsilon_r \epsilon_0}{2} \int_{\varphi=\varphi_0}^{\varphi=0} \left(\frac{d\varphi}{dx} \right) d\varphi \quad (20)$$

where x is the coordinate perpendicular to the surface. For this case the Poisson–Boltzmann equation is easily solved, giving as the first integral

$$\frac{d\varphi}{dx} = -2\kappa \frac{kT}{e} \sinh \frac{e\varphi}{2kT} \quad (21)$$

and

$$U_{el} = 2\epsilon_r \epsilon_0 \kappa \left(\frac{kT}{e} \right)^2 \left(\cosh \frac{e\varphi_0}{2kT} - 1 \right) \quad (22)$$

For $-T\Delta S$ we start with Eqn (7) that we rewrite as:

$$-T\Delta S = 2nkT \int_{x=0}^{\infty} (\psi \sinh \psi - \cosh \psi + 1) dx \quad (23)$$

Using Eqn (21) we transform Eqn (23) into

$$\begin{aligned} -T\Delta S &= -\frac{2nkT}{\kappa} \int_{\varphi=\varphi_0}^{\varphi=0} \frac{\psi \sinh \psi - \cosh \psi + 1}{\sinh(\psi/2)} d\left(\frac{\psi}{2}\right) \\ &= 2\epsilon_r \epsilon_0 \kappa \left(\frac{kT}{e} \right)^2 \int_{\varphi=\varphi_0}^{\varphi=0} [\sinh(\psi/2) - \psi \cosh(\psi/2)] d(\psi/2) \\ &= 2\epsilon_r \epsilon_0 \kappa \left(\frac{kT}{e} \right)^2 [3 - 3 \cosh(\psi_0/2) + \psi_0 \sinh(\psi_0/2)] \end{aligned} \quad (24)$$

Equations (22) and (24) add up nicely to give the well-known value for F_{el}

$$\begin{aligned} F_{el} &= \int_{\varphi=0}^{\varphi=\varphi_0} \varphi d\sigma = \text{with Eqns (2) and (21)} \\ &= 2\epsilon_r \epsilon_0 \kappa \left(\frac{kT}{e} \right)^2 \left[2 - 2 \cosh\left(\frac{\psi_0}{2}\right) + \psi_0 \sinh\left(\frac{\psi_0}{2}\right) \right] \end{aligned} \quad (25)$$

In the limit of small surface potentials

$$\begin{aligned} F_{el}(\varphi_0 \rightarrow 0) &= \epsilon_r \epsilon_0 \kappa \left(\frac{kT}{e} \right)^2 \frac{\psi_0^2}{2} \equiv \frac{P}{2} \psi_0^2 = \frac{\sigma^2}{2\epsilon_r \epsilon_0 \kappa}; \\ U_{el} &\rightarrow \frac{F_{el}}{2} \text{ and } -T\Delta S \rightarrow \frac{F_{el}}{2} \end{aligned} \quad (26a)$$

whereas for very high surface potentials

$$F_{\text{el}}(\varphi_0 \rightarrow \infty) = P \exp(\psi_0/2) \left\{ \psi_0 - 2 \dots \right\} = 2\sigma \frac{kT}{e} \left(\ln \frac{\sigma kT}{eP} - 1 \right) \quad (26b)$$

$$U_{\text{el}}(\varphi_0 \rightarrow \infty) = F_{\text{el}} \frac{1 - 2e^{-\psi_0/2}}{\psi_0 - 2 + 4e^{-\psi_0/2}} \text{ and } -T\Delta S = F_{\text{el}} \frac{\psi_0 - 3 + 6e^{-\psi_0/2}}{\psi_0 - 2 + 4e^{-\psi_0/2}}$$

In words: at low potentials energy and entropy contribute equally to the free energy of the double layer, whereas at high potentials the entropy ($-T\Delta S$) contributes more than half, in the limit nearly all of F_{el} .

Two particles interacting at constant, but different surface potentials

As a second application we consider the interaction between two parallel flat surfaces of unit area at constant surface potentials φ_{01} and φ_{02} (which may be high) in a 1-1 electrolyte of concentration n . The distance between the surfaces is H , the distance from the left hand surface is x . The free energy of interaction, F_{inter} is $F_{\text{tot}}[H, \text{Eqn (15)}] - F_{\text{tot}}(H \rightarrow \infty)$. So

$$F_{\text{inter}}(\text{per unit area}) = -\epsilon_r \epsilon_0 \int_0^H \left[\frac{1}{2} \left(\frac{d\varphi}{dx} \right)^2 + \int_0^\varphi \frac{d^2\varphi}{dx^2} d\varphi \right] dx - F_{\text{tot}}(H \rightarrow \infty) \quad (27)$$

When H is finite, the Poisson-Boltzmann equation, Eqn (28), cannot be solved explicitly, but a first integration is possible, leading to Eqn (29)

$$\frac{d^2\varphi}{dx^2} = \kappa^2 \frac{kT}{e} \sinh \frac{e\varphi}{kT} \quad (28)$$

$$\frac{e}{kT\kappa} \frac{d\varphi}{dx} = \frac{d\psi}{d(\kappa x)} = \pm (2 \cosh \psi - 2b)^{1/2} \quad (29)$$

where $b = \cosh \psi_{\text{min}}$ if ψ has a minimum between $x=0$ and $x=H$, otherwise $-\infty < b < \cosh \psi_{01}$, when we choose $0 < \psi_{01} < \psi_{02}$.

The relation between b (or ψ_{min}) and H is given by

$$\kappa H = \int_{\psi_{\text{min}}}^{\psi_{01}} \frac{d\psi}{(2 \cosh \psi - 2 \cosh \psi_{\text{min}})^{1/2}} + \int_{\psi_{\text{min}}}^{\psi_{02}} \frac{d\psi}{(2 \cosh \psi - 2 \cosh \psi_{\text{min}})^{1/2}} \quad (30a)$$

or, when there is no minimum in ψ

$$\kappa H = \int_{\psi_{01}}^{\psi_{02}} \frac{d\psi}{(2 \cosh \psi - 2b)^{1/2}} \quad (30b)$$

With the use of Eqns (28) and (29) $F_{\text{tot}}(H)$ can be transformed into

$$F_{\text{tot}}(H) = -\epsilon_r \epsilon_0 \kappa \left(\frac{kT}{e} \right)^2 \left\{ \int_{\psi_{\min}}^{\psi_{01}} \left(2 \cosh \psi - 2 \cosh \psi_{\min} \right)^{1/2} d\psi + \int_{\psi_{\min}}^{\psi_{02}} \text{similar} + \left(\cosh \psi_{\min} - 1 \right) \kappa H \right\} \quad (31a)$$

or, without a minimum in ψ

$$F_{\text{tot}}(H) = -\epsilon_r \epsilon_0 \kappa \left(\frac{kT}{e} \right)^2 \left\{ \int_{\psi_{01}}^{\psi_{02}} \left(2 \cosh \psi - 2b \right)^{1/2} d\psi + \left(b - 1 \right) \kappa H \right\} \quad (31b)$$

The two types of integrals occurring in the equations for κH and F_{tot} can be transformed into elliptic integrals [11,12], but they can be dealt with more easily by numerical integration.

$F_{\text{tot}}(H \rightarrow \infty)$ is simply the sum of two separate double layer free energies and is known or, if desired, is easily found from Eqn (31a) with $\psi_{\min} = 0$

$$F_{\text{tot}}(H \rightarrow \infty) = -\epsilon_r \epsilon_0 \kappa \left(\frac{kT}{e} \right)^2 \left\{ 4 \cosh \frac{\psi_{01}}{2} + 4 \cosh \frac{\psi_{02}}{2} - 8 \right\} \quad (32)$$

By choosing a series of suitable values of ψ_{\min} or b , respectively, and calculating for each of these κH [Eqn (30)] and F_{inter} [Eqns (27), (31) and (32)], a plot of F_{inter} against κH can be made.

With the use of Derjaguin's Eqn (33) [13] the free energy of interaction, F_{inter} , between two spheres with radii a_1 , and a_2 , surface potentials ψ_{01} and ψ_{02} and shortest distance between the surfaces, H_0 can be found with a straightforward numerical integration

$$F_{\text{inter, spheres}} = \frac{2\pi a_1 a_2}{a_1 + a_2} \int_{H_0}^{\infty} F_{\text{inter}}(\psi_{01}, \psi_{02}, H) dH \quad (33)$$

In Fig. 1 results of this program are shown for two typical cases together with results obtained with the linear approximation [$\sinh(e\varphi/kT)$ in Eqn (28) replaced by $e\varphi/kT$] as treated in 1966 by Hogg et al. [14]. It is remarkable how good the linear approximation is, even at surface potentials of 50 and 100 mV.

It should be mentioned that Derjaguin [15] in 1954 has treated the interaction of particles with different surface potentials based on the force (not the free energy) of interaction, both for high and for low surface potentials.

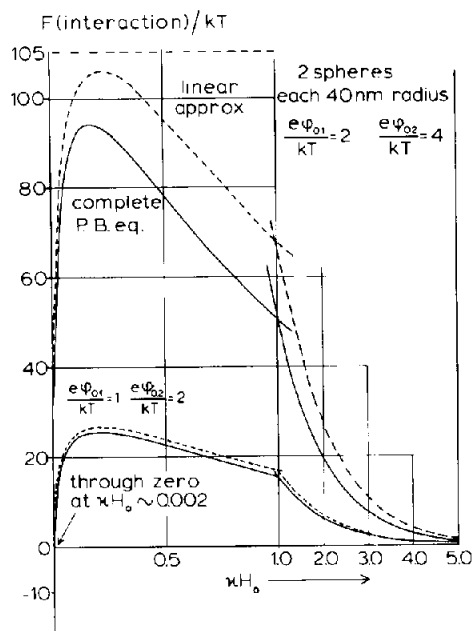


Fig. 1. Free energy of interaction of two spherical particles each with a radius of 40 nm in units kT at 25 °C. The upper two curves refer to dimensionless surface potentials 2 and 4 (51.4 and 102.8 mV, respectively) the lower two curves refer to $\psi_{01}=1$ and $\psi_{02}=2$. During the interacting the surface potentials remain constant. Drawn lines refer to use of the complete Poisson-Boltzmann equation, broken lines to the linear approximation. H_0 is the distance between the surfaces on the line connecting the centers of the spheres.

CONCLUSIONS

Considering field energy and entropy separately forms a useful approach to problems involving the free energy of double layers and double layer interaction. It avoids the use of charging processes. It shows clearly the importance of entropy contributions and the relative lack of importance of the energy. It forms a good basis for formulating and computing double layer free energies. The equations so obtained are equivalent to those obtained by the Debye and Hückel type charging process [$d\lambda/\lambda$; see Appendix and Eqn (15)]. Especially when the Poisson-Boltzmann equation cannot be solved explicitly, as in most non-linearized cases the method is superior to the use of the charging process in which the surface is charged stepwise ($\int \phi_0 d\sigma$ or $-\int \sigma d\phi_0$).

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APPENDIX

In order to show the equivalence of the energy/entropy method and the Debye-Hückel type charging method we write [2]

$$F_{\text{tot}} = \int_0^1 \frac{d\lambda}{\lambda} \int_V \rho' \phi' dV + \int_0^1 \frac{d\lambda}{\lambda} \int_A \sigma' \phi'_0 dA + \int_0^1 \frac{d\lambda}{\lambda} \int_A \frac{\sigma'}{z_j e} \frac{\partial \Delta \mu'_j}{\partial \lambda} dA \quad (\text{A1})$$

The charging process involves charging all ions simultaneously in steps $z_j e d\lambda$ and also increasing the preference of the potential determining ions, j , for the surface, expressed as $\Delta \mu'_j = \mu'_j$ (surface) $- \mu'_j$ (solution). The primes indicate that the primed quantities are at the stage λ of the charging process. Equilibrium between surfaces and solution requires that at all stages

$$\Delta \mu'_j + z_j e \lambda \phi'_0 = 0 \quad (\text{A2})$$

At stage λ the Poisson-Boltzmann equation runs

$$\text{div grad } \phi' = -\frac{\rho'}{\epsilon_r \epsilon_0} = -\sum_i \frac{z_i e \lambda n_{i0}}{\epsilon_r \epsilon_0} \exp\left(-\frac{z_i e \lambda \phi'}{kT}\right) = \lambda f(\lambda \phi') \quad (\text{A3})$$

By introducing

$$\phi' d\lambda = \frac{\partial}{\partial \lambda} (\lambda \phi') d\lambda - \lambda \frac{\partial \phi'}{\partial \lambda} d\lambda \quad (\text{A4})$$

and applying Eqns (A2) and (A3), Eqn (A1) can be transformed into

$$F_{\text{tot}} = -\epsilon_r \epsilon_0 \int_V dV \int_{\lambda \phi' = 0}^{\lambda \phi' = \phi} f(\lambda \phi') d(\lambda \phi') + \epsilon_r \epsilon_0 \int_V dV \int_{\lambda=0}^{\lambda=1} \text{div grad } \phi' \frac{\partial \phi'}{\partial \lambda} d\lambda - \int_A dA \int_{\lambda=0}^{\lambda=1} \sigma' \frac{\partial \phi'_0}{\partial \lambda} d\lambda \quad (\text{A5})$$

Realizing that $f(\phi) = \text{div grad } \phi$, replacing $(\lambda \phi')$ by ϕ in the first integral, and combining the last two integrals by Green's theorem [Eqn (3)], while using Eqn (2) for σ' we find

$$F_{\text{tot}} = -\epsilon_r \epsilon_0 \int_V dV \left(\int_0^\phi \text{div grad } \phi d\phi + \int_{\lambda=0}^{\lambda=1} \text{grad } \phi' \frac{\partial}{\partial \lambda} (\text{grad } \phi') d\lambda \right) \\ = -\epsilon_r \epsilon_0 \int_V dV \left(\int_0^\phi \text{div grad } \phi d\phi + \frac{(\text{grad } \phi)^2}{2} \right) \quad (\text{A6})$$

which is identical to the form derived from energy and entropy and given in Eqn (15).

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