# The Free Energy of an Electrical Double Layer

## DEREK Y. C. CHAN AND D. JOHN MITCHELL

*Department of Applied Mathematics, Research School of Physical Sciences, Australian National University, Canberra ACT 2600, Australia*

A general expression for the free energy of an electrical double layer is derived using thermodynamic considerations together with a minimum number of approximations. The result is valid for a wide class of adsorption isotherms for the potential determining ions. The interaction free energy due to the overlap of two double layers has a simple graphical interpretation. For two identical surfaces, interaction at constant surface potential (charge density) is readily seen to be the lower (upper) bound for the double layer repulsion.

## 1. INTRODUCTION

The concept of the free energy of an electrical double layer is of considerable importance in colloid and surface science. It is needed to understand phenomena ranging from the spreading pressure of charged monolayers to the electrostatic stabilization of colloidal particles. In spite of this there is still some confusion as to the appropriate expression for the free energy that is relevant to a particular problem. The aim of this communication is to provide a simple pedagogical derivation of a general expression for the surface free energy of an electrical double layer. The result is applicable to a very general class of adsorption isotherms of the potential determining ions. The approximations needed to derive this expression for the free energy are clearly stated, and this helps to delineate the range of validity of standard expressions for the double layer free energy.

From our expression of the free energy, it is possible to give a graphical representation of the free energy of interaction due to the overlap of two identical double layers. This graphical representation is then used to demonstrate that the double layer interaction under the assumption of constant surface potential or constant surface charge density is, respectively, the lower or upper bound for the double layer repulsion.

## 2. FREE ENERGY OF A DOUBLE LAYER

For simplicity, we consider the free energy of formation of a double layer in isolation. The cases involving more than one interface (for instance, in the interaction of two surfaces) require fairly straightforward generalizations (see Section 4).

As the standard or reference state we take a *neutral* surface, with no adsorbed ions, in contact with a reservoir of bulk electrolyte containing indifferent and potential determining ions of known fixed bulk chemical potentials. We shall consider the free energy change in forming a fully charged double layer from this reference state by the *adsorption* of potential determining ions. The situation in which the surface charge develops as a result of the dissociation of potential determining ions from ionizable surface groups into solution can also be treated by the present formalism. The minor modification required will be given in an illustrated example in the next section.

The change in surface free energy per unit area, $df$ when $d\Gamma$ moles per unit area of potential determining ions are transferred from the bulk solution to the surface is given by

193

$$df = (\mu^S - \mu^B)d\Gamma \qquad [2.1]$$

where $\mu^S$ and $\mu^B$ are respectively the electrochemical potential of the potential determining ion at the surface and in the bulk electrolyte. Equation [2.1] is simply the definition of $df$, and for convenience we have limited ourselves to only one species of potential determining ions. If the surface is inhomogeneous, the change in free energy for the whole surface can be obtained by integrating $df$ over the surface. The surface electrochemical potential $\mu^S$ can be *formally* written as

$$\mu^S = \bar{\mu}^S + q\psi_0 \qquad [2.2]$$

where $\psi_0$ is the mean electrostatic potential on the surface and $q$ is the charge of the potential determining ion. Combining [2.1] and [2.2] the free energy per unit area, $f$ can be written as

$$f = \int_0^{\sigma_0} \psi_0(\sigma)d\sigma + \int_0^{\Gamma_0} (\bar{\mu}^S - \mu^B)d\Gamma \qquad [2.3]$$

where the surface charge density is given by

$$\sigma_0 = q\Gamma_0 \qquad [2.4]$$

with $\Gamma_0$ being the equilibrium surface concentration of potential determining ion. Since [2.2] is just a definition of $\bar{\mu}^S$, [2.3] is still exact. The term $\int_0^{\sigma_0} \psi_0(\sigma)d\sigma$ can be identified as the *electrical* work done in creating the double layer (1). The second integral in [2.3] is therefore called the *chemical* part of the free energy.

In a large class of models for the adsorption of potential determining ions, $\bar{\mu}^S$, the chemical part of the surface electrochemical potential is assumed to depend *only* on the amount of ions adsorbed and does not depend *explicitly* on the surface potential $\psi_0$. Thus we *assume*

$$\bar{\mu}^S = \bar{\mu}^S(\Gamma), \qquad [2.5]$$

so that all electrostatic contributions to the surface electrochemical potential, $\mu^S$, are described by the term $q\psi_0$, [2.2], while $\bar{\mu}^S$ contains nonelectrostatic contributions, e.g., excluded volume effects, dispersion interactions etc. Consequently with [2.5], the free energy per unit area becomes

$$f = \int_0^{\sigma_0} \psi_0(\sigma)d\sigma + \int_0^{\Gamma_0} (\bar{\mu}^S(\Gamma) - \mu^B)d\Gamma. \quad [2.6]$$

In order to carry out the first integral in [2.6] we need to know the functional form of $\psi_0(\sigma)$. This is obtained from the surface potential–surface charge relationship that is given by the distribution of charges in the diffuse double layer. For example, if the nonlinear Poisson–Boltzmann equation is employed to describe the diffuse layer at a flat surface we will have the result

$$\psi_0(\sigma) = \psi_0^D(\sigma)$$

$$= (2kT/e) \sinh^{-1} (2\pi e\sigma/\kappa\epsilon kT). \quad [2.7]$$

A different model for the diffuse layer will yield a different function $\psi_0^D(\sigma)$—the superscript D denotes a potential–charge relationship that follows from the ionic distribution in the diffuse double layer.

In evaluating the second integral in [2.6] we recall that $\mu^B$, the bulk electrochemical potential of the adsorbing ions is assumed to be constant. The functional form of $\bar{\mu}^S(\Gamma)$ required in [2.6] is provided by the isotherm chosen to describe the adsorption of potential determining ions. Since the amount of charge adsorbed is

$$\sigma = q\Gamma \qquad [2.8]$$

we can define a function $\psi_0^S(\sigma)$ by

$$q\psi_0^S(\sigma) = -[\bar{\mu}^S(\Gamma) - \mu^B]$$

$$= -[\bar{\mu}^S(\sigma/q) - \mu^B]. \quad [2.9]$$

Equation [2.9] may now be regarded as a "surface equation of state" which says that if the amount of adsorbed charge is $\sigma$ then the surface potential must have the value $\psi_0^S(\sigma)$ if the system is to remain at equilibrium. Equations [2.7] and [2.9] provide two equations for two quantities—the surface charge and the surface potential. Equilibrium is given by the obvious requirement

$$\psi_0^D(\sigma_0) = \psi_0^S(\sigma_0) \qquad [2.10]$$

which for a planar double layer in the Poisson–Boltzmann approximation gives

$$(2kT/e) \sinh^{-1} (2\pi e \sigma_0 / \kappa \epsilon kT)$$

$$= -\frac{1}{q} [\bar{\mu}^S(\sigma_0/e) - \mu^B]. \qquad [2.11]$$

Using [2.8] and [2.9] we can write [2.6] in the compact form

$$f = \int_0^{\sigma_0} [\psi_0^D(\sigma) - \psi_0^S(\sigma)]d\sigma. \qquad [2.12]$$

The two terms in the free energy expression have simple graphical representations. Such representations are useful in illustrating the interaction free energy between double layers (see later). We represent the function $\psi_0^D(\sigma)$ due to the diffuse layer ([2.7] or equivalent) by the line OD in Fig. 1. The function $\psi_0^S(\sigma)$ can be represented in the following manner. We can assume without loss of generality that the potential determining ion and hence $\psi_0$ and $\sigma_0$ are positive. Using the fact that $\mu^B$ is a constant, the thermodynamic condition $(\partial \bar{\mu}^S/\partial \Gamma) > 0$ implies that the function $\psi_0^S(\sigma)$ must be a curve with *negative* slope. This is represented by the line SS'. The point of intersection X, cf. [2.10], determines the *equilibrium* value of the surface potential and surface charge as indicated by the points P and Q in Fig. 1. The first integral in [2.12] corresponds to the area of the shaded region bounded by the figure QOX in Fig. 1. The second integral in [2.12] corresponds to the *negative* of the area of the hatched region
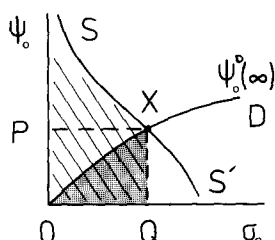
bounded by the figure OQXS. The free energy per unit area of the double layer is given by the negative of the area bounded by the figure OXS.

The expression for the free energy of a double layer given by Verwey and Overbeek (1) involves the further assumption that $\bar{\mu}^S(\Gamma)$, the chemical part of the surface electrochemical potential, is independent of $\Gamma$, the amount of potential determining ions adsorbed (2). Setting $\bar{\mu}^S(\Gamma)$ = constant is equivalent to setting $\psi_0^S(\Gamma) = \psi_0$, a constant (see Eq. [2.9]) so that from [2.12] the free energy of the double layer becomes

$$f = \int_0^{\sigma_0} \psi_0(\sigma)d\sigma - \sigma_0\psi_0$$

$$= -\int_0^{\psi_0} \sigma_0(\psi)d\psi. \qquad [2.13]$$

Thus [2.13] which is sometimes known as the constant potential result is appropriate only if $\bar{\mu}^S$ is assumed to be a constant (2). This condition can be represented in Fig. 1 by replacing the curve SS' by an appropriate horizontal line.

### 3. IONIZABLE SURFACE GROUPS— AN ILLUSTRATIVE EXAMPLE

Consider a surface bearing surface groups which can undergo the following dissociation reaction

$$-A^-H^+ \rightleftharpoons -A^- + H^+ \qquad [3.1]$$
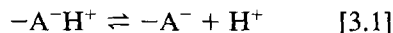
characterized by the intrinsic dissociation constant $K$. Let $\Gamma_S$ be the total number per unit area of ionizable groups and $\Gamma_H$ the amount of $H^+$ adsorbed. Assuming a mass action reaction, the surface charge density is given by

$$\sigma_0 = e(\Gamma_H - \Gamma_S)$$

$$= \frac{-e\Gamma_S}{[1 + (H/K) \exp(-e\psi_0^S/kT)]} \qquad [3.2]$$

where $H$ is the concentration of $H^+$ in bulk. Equation [3.2] can be written as



FIG. 1. A graphical representation of the free energy of formation of an electric double layer.

$$e\psi_0^S = kT \ln H$$

$$- \left[ kT \ln K + kT \ln \left( \frac{\Gamma_H}{\Gamma_S - \Gamma_H} \right) \right]$$

$$= \mu_B - \bar{\mu}^S(\Gamma_H). \qquad [3.3]$$

If we take the reference state to be the neutral surface in which all surface groups are fully associated, the free energy of formation of the double layer is then

$$f = \int_0^{\Gamma_S - \Gamma_H} (\mu^B - \mu^S) d(\Gamma_S - \Gamma_H)$$

$$= \int_0^{\sigma_0} \psi_0(\sigma) d\sigma + \int_{\Gamma_H}^{\Gamma_S} (\mu^B - \bar{\mu}^S) d\Gamma_H$$

$$= \int_0^{\sigma_0} \psi_0(\sigma) d\sigma + \int_{\Gamma_H}^{\Gamma_S} \left[ kT \ln (H/K) \right.$$

$$\left. - kT \ln \left( \frac{\Gamma_H}{\Gamma_S - \Gamma_H} \right) \right] d\Gamma_H$$

$$= \int_0^{\sigma_0} \psi_0(\sigma) d\sigma - \sigma_0\psi_0 - kT\Gamma_S \ln (\Gamma_S/\Gamma_H)$$

$$= - \int_0^{\psi_0} \sigma_0(\psi) d\psi + kT\Gamma_S \ln (1 - \sigma_0) \qquad [3.4]$$

where $\alpha_0$ is the fraction of surface groups which is dissociated at equilibrium. This result agrees with that obtained earlier by a direct calculation (2).

## 4. INTERACTION FREE ENERGY

The interaction free energy $V(L)$ is the change in the total free energy as the interacting surfaces are brought together from infinity to some separation $L$. That is

$$V(L) = \sum_i \int dA_i(f_L^i - f_\infty^i) \qquad [4.1]$$

where the summation is over the interacting surfaces and the free energy of each surface is obtained by an integration $\int dA_i$ over the free energy per unit area, $f$. For the interaction between two identical surfaces, [4.1] reduces to

$$V(L) = 2 \int dA(f_L - f_\infty)$$

$$= 2 \int dA\Delta f(L). \qquad [4.2]$$

From [2.12], the interaction free energy per unit area, $\Delta f(L)$ is given by

$$\Delta f(L) = \int_0^{\sigma_0(L)} [\psi_0^D(\sigma, L) - \psi_0^S(\sigma)] d\sigma$$

$$- \int_0^{\sigma_0(\infty)} [\psi_0^D(\sigma, \infty) - \psi_0^S(\sigma)] d\sigma. \qquad [4.3]$$

In [4.3], we have indicated all explicit dependences on the separation $L$. The diffuse layer potential–charge relationship, $\psi_0^D$ is obviously a function of $L$. However, we have assumed that the adsorption isotherms at each surface do not depend explicitly on separation.

The difference between the two integrals in [4.3] can be given a simple geometrical representation. This is done in Fig. 2. It is easy to deduce that for two identical surfaces the curve $\psi_0^D(\sigma, L)$ always lie *above* the curve for $\psi_0^D(\sigma, \infty)$. Thus the difference between the two integrals in [4.3] is represented by the area of the shaded region bounded by the figure ROX in Fig. 2.

From the above graphical representation, one can readily deduce the corresponding results for interactions under the assumptions of constant surface charge or surface potential. From [4.3], the interaction free energy per unit area at constant surface charge is given by the expression
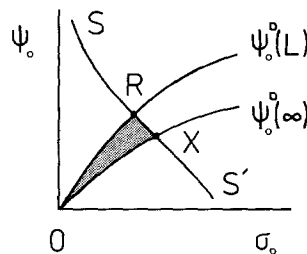


FIG. 2. A graphical representation of the interaction free energy per unit area under equilibrium adsorption of potential determining ions.
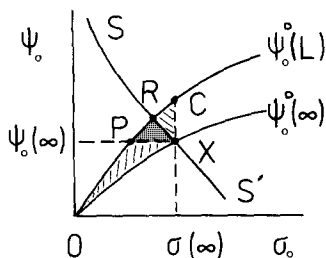
FIG. 3. A comparison of the interaction free energy per unit area under constant surface potential, constant surface charge, and adsorption equilibrium.

$$\Delta f^{\sigma}(L) = \int_0^{\sigma_0} [\psi_0^D(\sigma, L) - \psi_0^D(\sigma, \infty)]d\sigma \quad [4.4]$$

since $\sigma_0(L) = \sigma_0(\infty) = \sigma_0$, a constant. The graphical representation of $\Delta f^{\sigma}(L)$ is given in Fig. 3 where $\Delta f^{\sigma}(L)$ corresponds to the area bounded by the figure COX.

Similarly, from [4.3] the interaction free energy per unit area at constant surface potential is given by the expression

$$\Delta f^{\psi}(L) = \left\{ -\int_0^{\psi_0} \sigma_0(\psi, L)d\psi \right\}$$
$$- \left\{ -\int_0^{\psi_0} \sigma_0(\psi, \infty)d\psi \right\}. \quad [4.5]$$

The graphical representation of $\Delta f^{\psi}(L)$ corresponds to the area bounded by the figure POX.

The result for interactions under equilibrium adsorption of potential determining ions (Fig. 2) has been redrawn in Fig. 3. We can now clearly see that for the interaction between identical surfaces, the constant potential condition gives the lower bound for the double layer repulsion while the constant charge condition yields the upper bound. Furthermore, the constant charge or constant potential condition may be regarded as a special limit of interaction under equilibrium adsorption of potential determining ions.

Finally, we observe that the force between interacting surfaces is given by

$$F(L) = -\frac{\partial V(L)}{\partial L}. \quad [4.6]$$

Using [4.2] and [4.3] we find

$$F(L) = -2 \int dA \int_0^{\sigma_0(L)} \frac{\partial \psi_0^D(\sigma, L)}{\partial L} d\sigma. \quad [4.7]$$

There is no contribution from differentiation with respect to the upper limit ($\sigma_0(L)$) of the integral in [4.3] since at equilibrium

$$\psi_0^D(\sigma_0(L), L) = \psi_0^S(\sigma_0(L)). \quad [4.8]$$

Equation [4.7] simply states the fact that the force is only a function of the charge (or potential) of the surface and is independent of the charging process itself.

REFERENCES

1. Verwey, E. J. W., and Overbeek, J. Th. G., "Theory of the Stability of Lyophobic Colloids." Elsevier, Amsterdam, 1948.
2. Payens, Th. A. J., Philips Res. Rep. 10, 425 (1955).