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Thermodynamics and Statistical Mechanics of the Ideally Polarisable Electrode Gibbs Isotherm and Surface Tension

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Abstract

A definition of the ideally polarisable electrode which allows a general statistical mechanical treatment is given, comparisons with the usual thermodynamic approach being made. It is shown that, with this definition, the system behaves as a pure capacitance to an imposed alternating potential of sufficiently low frequency. The equilibrium states of the system are described by the grand canonical distribution. Thermodynamic functions, given in terms of the grand canonical partition function, can be computed in molecular terms: In particular, general expressions for the surface tension and the pressure are obtained, and compared to those proposed by various authors. The separation of the pressure into electrical and nonelectrical parts is analyzed. Expressions are given for the electrochemical potentials of charged and of dipolar species. With these microscopic definitions, the Gibbs adsorption isotherms and the Lippmann equation are derived. For several simple models, including that of Gouy and Chapman for an ionic solution and a metal electrode, these relations are explicitly considered. The inadmissibility, in a coherent model, of reducing the solvent to a medium of fixed dielectric constant, is emphasized.

Introduction

The ideally polarisable electrode (IPE) is the simplest electrochemical system. In spite of its ideality, it is possible to approach it experimentally, at least in a limited range of potential, in the mercury drop electrode. Because of this, the system has been the subject of many studies, which are summarized and discussed in the standard works on electrochemistry [1--4].

From thermodynamic reasoning, one can show that certain quantities characteristic of the interface, such as the electrode charge or the amounts of adsorbed substances, are accessible through studies of the surface tension of the IPE as a function of parameters like the potential difference across the system or the chemical potentials of the various components. On the other hand, several authors have attempted to define the surface tension σ directly, in terms of the mechanical equilibrium of the interface [5--10]. Various expressions have [End of page 151] been proposed for σ . In a study of the interface between an electrolytic solution and its vapor, Buff [11] showed that the thermodynamic and mechanical approaches yield the same microscopic expression for σ . Our study of the IPE is in part along these lines.

In the first part of this work, we define precisely the system and its surroundings (measurement cell). Subsequently, we derive the Gibbs adsorption isotherm by statistical mechanical methods (grand partition function). This procedure affords microscopic definitions of the various intensive quantities which characterize the interface. Subsequently, we compare the expression for the surface tension with those proposed in the literature.

(1) Definition of the Ideally Polarisable Electrode

Grahame [12,13] defines the ideally polarisable electrode (IPE) as a system having the property that change in the electric potential difference across it does not give rise to a continuous current in the circuit to which the system is connected. We will make this definition more precise in order to use it in our statistical mechanical treatment.

We will consider that we have planar symmetry for the IPE. The electrode or interface is supposed to be placed inside a larger system, referred to as the measurement cell. The system of the interface, which we are to study, is included between two planes, $z = a$ and $z = b$ (see Fig. 1). Its properties are uniform in the directions normal to the z axis, and vary uniformly along this axis, from $z = a$ to $z = b$. At these boundaries, the properties are supposed to be uniform and isotropic. In the most common case, the mercury-aqueous solution interface, the properties at $z = a$ would be those of bulk liquid mercury and those at $z = b$ would be those of the homogeneous solution. The area of our system, normal to the z -axis, is represented by A .

In our earlier work, we defined the IPE as an interface in which there exists a surface $z = \Sigma$ on which the density of all chemical species remains zero, and which separates two regions having no chemical species in common. This definition is identical to that proposed by Parsons and Devanathan [14], and indeed

[End of page 152] reproduces correctly the electrical Properties attributed to the IPE as we now see. Suppose that the interface, subjected to a time-independent potential difference, reaches a stationary state. The conduction current is

$$I_c = \sum_i n_i e_i \bar{v}_i \quad (1)$$

where n_i , e_i , and $\bar{v}_i$ represent the density, charge, and average velocity of particles of the i -th species. The Maxwell equations guarantee that the electric current $I = I_c + \partial D / \partial t$ is conserved along the circuit; since $\partial D / \partial t$ vanishes for a stationary state, I_c is itself conserved. But $n_i = 0$ for $z = \Sigma$, so that I_c vanished for $z = \Sigma$, and, being conservative, it vanishes everywhere. In ref. 7 it was shown that this model leads to purely capacitive behavior when the potential across the interface is varied sinusoidally and adiabatically. However, we shall replace this model below by another, which is more coherent with the statistical mechanical approach.

Where the interface is that between a liquid metal and an aqueous solution, the two parts of the system defined by the surface Σ may be referred to as the metal side ($z < \Sigma$) and the solution side ($z > \Sigma$) of the interface. The regions I and II of Fig. 1, which are not part of the system, correspond to the homogeneous solution. In the model for the interface developed by Gibbs and used in the thermodynamic treatments, there is no interfacial region, the interface being represented by a mathematical surface, on either side of which the properties are those of the homogeneous phases I or II (metal, solution). One can show [4] that the thermodynamic relations are independent of the position of this mathematical surface. Obviously, it is impossible to discuss the spatial distribution of the chemical species within the framework of such a model (this is one of the reasons that encouraged us to build a statistical mechanical treatment). In order to calculate the surface charge in Gibbs' model, one must be able to assign each charged chemical species to one side or the other of the interface. This requires that no charged species be common to the two phases separated by the interface. This condition is shared by our model, which, treating the interface as a three dimensional system, is capable of considering the distribution of matter within the interface.

It does not seem that the existence of a surface Σ where n_i vanishes for all i can be made consistent with the fluctuations in n_i and other quantities inherent in a statistical mechanical treatment. Therefore, we will now redefine the IPE using less restrictive conditions. In fact, the essential feature which differentiates the IPE from other interfaces is the absence of chemical reactions which can transform a charged component of region I to a charged component of region II, or vice versa. We thus define our IPE by the following conditions:

(1) The two regions located at the boundaries of the interface ($z = a$, $z = b$) have no common charged components.

(2) No chemical reactions may take place between the charged components. The components will be taken as charged and dipolar molecular species. We will have more to say about their choice below.

If there are no chemical reactions capable of creating or destroying molecules of species i , we can write the equation of continuity for this species

$$\frac{\partial n_i(z, t)}{\partial t} + \frac{\partial (n_i \bar{v}_i)}{\partial z} = 0 \quad (2)$$

[End of page 153] (all properties are uniform in the directions normal to z). The electric current, conserved around the circuit, is

$$I = I_c + \partial D / \partial t \quad (3)$$

with I_c defined by (1) and D the electrical displacement. Since neither D nor n_i can depend on time for a stationary state, $I = I_c$ and $n_i \bar{v}_i$ is independent of z . According to condition (1), n_i vanishes at one boundary ($z = a$ or at $z = b$) for each i , so that $n_i \bar{v}_i$ vanishes everywhere for every charged species i . Therefore $I - I_c = 0$. The result of statistical mechanical fluctuations is that, while n_i is not exactly zero at the boundary, its value can become extremely small, and the same conclusion follows with respect to I : there is no current for a stationary state.

Now let us consider the effects of a potential drop

$$U = U_s + U_0 e^{i\omega t}$$

imposed across the system. Let ω tend to zero. The adiabatic theorem of statistical mechanics then states that the system always remains in an equilibrium state, so that its properties at each instant depend only on the values of the thermodynamic variables at that same instant. Let $(\partial n_i^e / \partial U) \Delta U$ represent the difference between the values of $n_i(z)$ for two equilibrium states, for which the potential drops across the interface differ by ΔU , and, similarly, $(\partial D^e / \partial U) \Delta U$ is the difference in $D(z)$. The adiabatic theorem may be written:

$$\partial D(z, t) / \partial t = [\partial D^e(z) / \partial U] (dU/dt) \quad (4a)$$

$$\partial n_i(z, t) / \partial t = [\partial n_i^e(z) / \partial U] (dU/dt) \quad (4b)$$

The equation of continuity (2) may be integrated using (4b) to yield:

$$\begin{aligned} n_i \bar{v}_i(z) &= n_i \bar{v}_i(O_i) + \int_{O_i}^z (-\partial n_i / \partial t) dz \\ &= \int_{O_i}^z (-\partial n_i^e / \partial U) dz (dU/dt) \end{aligned}$$

We may choose, as the origin of integration O_i , the boundary of the system ($z = a$ or $z = b$) for which $n_i = 0$. The current I (eqn. 3) may be written

$$I_c + (\partial D / \partial t) = [\sum_i e_i \int_{O_i}^z (-\partial n_i^e / \partial U) dz + (\partial D^e / \partial U)] (dU/dt)$$

The value of the expression in square brackets is characteristic of the equilibrium states of the system and is independent of t ; since the current is conserved along the circuit, it is also independent of z . The impedance is

$$Z = \frac{U_0 e^{i\omega t}}{I} = \left[i\omega \left(-\sum_i e_i \frac{\partial}{\partial U} \int_{O_i}^z n_i dz + \frac{\partial D}{\partial U} \right) \right]^{-1}$$

which represents a pure capacitance. **[End of page 154]**

In the homogeneous regions of the cell which are adjacent to the IPE, the conduction current must obey Ohm's law. Thus the electric field E vanishes there for a stationary state. We will choose a and b far away enough from the regions of inhomogeneity so that

$$E(a) = E(b) = 0$$

The electric field, where it does exist, is always in the z direction. Applying Gauss' theorem to the closed surface which includes our system shows that the total charge of the interface must vanish. If we denote by q_A and q_B respectively the charges carried by the ions of the interface which are also found in homogeneous regions I and II, we have

$$q_A + q_B = 0 \quad (5)$$

The quantities q_A and q_B may also be defined geometrically, by dividing the interface by a plane $z = d$, with d between a and b but otherwise arbitrary. Equation (5) will still hold, but the quantities q_A and q_B themselves will have different values.

Having divided the system geometrically into two parts, $a < z < d$ and $d < z < b$, one could treat each separately by statistical mechanical methods. In such a treatment, one would neglect correlations between particles not on the same side of the dividing plane. Each half of the interface would become part of the surroundings of the other. Many models of the interface are in fact of this kind, treating only the solution side and using the metal side simply as an external source of electric field.

The IPE is connected by the measurement cell to a system which can make the IPE undergo various transformations. Their definition is important, because the behavior of the IPE depends on the properties of this system. For example, to study the perturbation of an electrolytic solution by an electric field, one must choose appropriate electrodes to be coupled to the solution: depending on the electrodes, there may or may not be a current across the solution. In the present case, we will suppose the IPE to be coupled to a reversible electrode, as in the thermodynamic description, so that charge may be brought into the system from the surroundings, or removed.

In particular, let us consider two non-polarisable electrodes in regions I and II, connected through a battery, which is capable of introducing a quantity of

[End of Page 155] electric charge in one of the two regions, simultaneously subtracting the same quantity of charge from the other (Fig. 2). Since there is no barrier to the passage of charge within regions I and II, the charge must appear within the interfacial region, on either side of the interface: q_A will become $q_A + \delta q$ and q_B become $q_B - \delta q$. Therefore, the transformation imposed by the surroundings is a change in the charge density of the electrode. For such a change to occur, there must be a difference between the e.m.f. of the battery and the potential drop $U = Vb - Va$; charge will be transferred in the direction tending to reduce this difference to zero.

(2) Gibbs Adsorption Isotherm

Our statistical mechanical treatment will be within the framework of classical mechanics. Let u_{ij} represent the interaction potential between particles of species i and j . This potential may include: the Coulombic interaction $e_i e_j / 4 \pi \epsilon_0 r_{ij}$ between charges e_i and e_j separated by a distance r_{ij} , a repulsive interaction at small distances, and a non-central potential due to dipole moments of one or both particles i and j . Because of this last possibility, we write

$$u_{ij} = u_{ij}(x_{ij}, y_{ij}, z_{ij}, \Omega_i, \Omega_j) \quad (6)$$

where Ω_i and Ω_j give the orientations of the dipole moments of i and j . The charged species are supposed to be spherical and without internal degrees of freedom. We have assumed that all interactions involve two-body potentials.

For the calculation of average values of the quantities which characterize the interface we will use the grand canonical distribution [15,16]. Let there be different α chemical species in the interface, which is at equilibrium at temperature T . Then the probability density for n particles (n_1 of species 1, n_2 of species 2, etc.) is given by

$$\rho_{n_1 \dots n_\alpha}^{(n)} = \frac{1}{\Theta} \sum_{N_1=n_1}^{\infty} \dots \sum_{N_\alpha=n_\alpha}^{\infty} \left(\prod_{s=1}^{\alpha} \frac{z_s^{N_s}}{(N_s - n_s)!} \right) \int e^{-\beta U(N)} dR_{n+1} \dots dR_N d\Omega_{n+1} \dots d\Omega_N \quad (7)$$

In this equation, z_s is the activity of species s , $U(N)$ is the potential energy of the system

$$U(N) = \sum_{i=1}^N \sum_{j>1}^N u_{ij} \quad (8)$$

and

$$n = \sum_{i=1}^{\alpha} n_i, \quad N = \sum_{i=1}^{\alpha} N_i$$

The integrations in (7) are over the positions (R_i) and the orientations (Ω_i) of the particles numbered from $n+1$ to N . Finally, Θ is the grand partition function: [End of page 156]

$$\Theta = \sum_{\substack{N_1=0 \\ \vdots \\ N_\alpha=0}}^{\infty} \left(\prod_{s=1}^{\alpha} \frac{z_s^{N_s}}{N_s!} \right) \int e^{-\beta U(N)} dR_1 \dots dR_N d\Omega_1 \dots d\Omega_N \quad (9)$$

As noted previously, the α species appearing in (7)–(9) are ions, electrons and molecules, not neutral solutes (salts). Their activities or chemical potentials are governed by the environment of the system, i.e., regions I and II, and we will suppose these may be varied through the measurement cell. Because these regions are electrically neutral, it is in reality possible to regulate only certain combinations of activities or chemical potentials, those corresponding to neutral species formed by associating positively and negatively charged species. The number of neutral species can obviously be greater than the number of charged species, but the possibility of "chemical reactions" of the type

reduces the number of independently variable activities. For example, with two positive ions and two negative ions, four neutral associations or salts are possible, but there exists one chemical reaction, reducing the number of independently variable activities to three. Adding an "electrical variable", we recover four variable parameters, equal in number to the number of charged species. With n_+ positively charged species and n_- negatively charged species, we obtain n_+n_- neutral associations and $(n_+ - 1)(n_- - 1)$ independent chemical reactions, leaving $n_+ + n_- - 1$ independent activities. Adding the electrical variable, we have the number of charged species, $n_+ + n_-$.

By simple transformations it may be shown that Θ obeys

$$kT \log \Theta = TS + \sum_{i=1}^{\alpha} \bar{N}_i \tilde{\mu}_i - U = \sum_{j=1}^h x_j X_j \quad (10)$$

Here, S is the statistical entropy, $\bar{N}_i$ the mean number of particles of species i , and $\tilde{\mu}_i$ the corresponding conjugate variable. The quantity U obeys:

$$dU = - \sum_{j=1}^h X_j dx_j + \sum_{i=1}^{\alpha} \tilde{\mu}_i d\bar{N}_i + T dS \quad (11)$$

In eqns. (10) and (11) the k quantities x_j are the external forces, with conjugate variables X_j defined by

$$X_j = \frac{1}{\beta} \left(\frac{\partial \log \Theta}{\partial x_j} \right)_{\beta, \tilde{\mu}_i, x_i} \quad (12)$$

Imposing a transformation at constant T , one obtains, using (10) and (11), a Gibbs-Duhem type relation which represents the Gibbs isotherm in its general form:

$$\sum_{i=1}^{\alpha} \bar{N}_i d\tilde{\mu}_i = \sum_{j=1}^h x_j dX_j \quad (13)$$

[End of page 157] It is possible to calculate all the quantities appearing in this relation from themicroscopic (molecular) point of view.

(3) Surface Tension, Pressure, and Chemical Potential

In the grand canonical representation of the system, the numbers of particles of the different chemical species are not fixed; only mean values are known. In contrast, the external parameters x_j have exact values. Within the physical interface, which is infinite in the directions normal to the inhomogeneity, we consider a system of volume V and of area A in these directions, V being equal to $(b - a)A$. The quantities A and V are independent variables: Green [17] has shown how one can define changes of variables which alter V leaving A constant, or vice versa. The two mechanical variables A and V will be considered as external forces, and their conjugate variables denoted by σ and p are referred to as surface tension and pressure.

According to (12) the surface tension σ is given by:

$$\sigma = \frac{1}{\beta} \left(\frac{\partial \log \Theta}{\partial A} \right)_{\beta, \tilde{\mu}_i, p} \quad (14)$$

To make explicit the dependence of Θ on A we replace the coordinates X_i, Y_i, Z_i of particle i by reduced coordinates X'_i, Y'_i, Z'_i defined by

$$X_i = A^{1/2} X'_i \quad (15)$$

$$Y_i = A^{1/2} Y'_i \quad (15)$$

$$Z_i = VA^{-1} Z'_i$$

When A is changed, keeping V constant, the vectors between the centers of gravity of the particles are changed, but not their orientations. Using (15), the calculation required to derive σ according to (14) reduces to differentiating u_{ij} with respect to A keeping constant $X'_i, Y'_i, Z'_i, \Omega_i$, and $X'_j, Y'_j, Z'_j, \Omega_j$. We have

$$\frac{\partial u_{ij}}{\partial A} = \frac{1}{2A} \left[\frac{\partial u_{ij}}{\partial X_{12}} X_{12} + \frac{\partial u_{ij}}{\partial Y_{12}} Y_{12} - 2 \frac{\partial u_{ij}}{\partial Z_{12}} Z_{12} \right]$$

Since the X and Y coordinates play equivalent roles, σ becomes

$$\sigma = \frac{1}{2} \sum_{s=1}^{\alpha} \sum_{r=1}^{\alpha} \int_{Z_1=a}^b dZ_1 \int \left(\frac{\partial u_{sr}}{\partial X_{12}} X_{12} - \frac{\partial u_{sr}}{\partial Z_{12}} Z_{12} \right) \rho_{sr}(Z_1 R_{12} \Omega_1 \Omega_2) dR_{12} d\Omega_1 d\Omega_2 \quad (16)$$

Here and in what follows, we use ρ_{sr} to represent $\rho_{n_1 \dots n_{\alpha}}^{(2)}$ with $n_s = 1, n_r = 1, n_t (t \neq r, s) = 0$; ρ_s represents $\rho_{n_1 \dots n_{\alpha}}^{(2)}$ with $n_s = 1, n_t (t \neq s) = 0$.

By a procedure analogous to the above, the pressure may be calculated. This quantity, which is the variable conjugate to V , requires a change of V with A held constant and thus a change in $(b \rightarrow a)$. According to (12) it is defined as

$$p = \frac{1}{\beta} \left(\frac{\partial \log \Theta}{\partial V} \right)_{\beta, \tilde{\mu}_i, A}$$

[End of page 158] Using (15) we find

$$p = \frac{1}{V} \int dR_1 \left[\sum_{s=1}^{\alpha} \frac{1}{\beta} \rho_s(Z_1) - \sum_{s=1}^{\alpha} \sum_{r=1}^{\alpha} \frac{1}{2} \int \frac{\partial u_{rs}}{\partial Z_{12}} Z_{12} \rho_{rs}(Z_1 R_{12} \Omega_1 \Omega_2) dR_{12} d\Omega_1 d\Omega_2 \right] \quad (17)$$

where $\rho_s(Z_1)$ is the density of particles of species s at Z_1 . The term $\beta^{-1} \rho_s(Z_1)$ arises because, with $dX_i dY_i dZ_i$ constant, the volume element $dX_i dY_i dZ_i$ depends on V (but not on A). Equation (17) defines the pressure normal to the interface as the mean value of the quantity in square brackets. This quantity is not itself the pressure, however, because its value is only approximately independent of Z_1 , whereas the mechanical equilibrium condition requires that the normal pressure be the same everywhere in the interface (for all Z_1 , since it is clearly independent of X_1 and Y_1). In Appendix 1 we show (eqns. A4 and A5) that the quantity

$$p_N = \sum_{s=1}^{\alpha} \frac{1}{\beta} \rho_s(Z_1) - \frac{1}{2} \sum_{s=1}^{\alpha} \sum_{r=1}^{\alpha} \int \frac{\partial u_{rs}}{\partial Z_{12}} Z_{12} dR_{12} d\Omega_1 d\Omega_2 \sum_{m=1}^{\infty} \frac{1}{m!} (-R_{12} \cdot \nabla_1)^{m-1} \rho_{rs}(Z_1 R_{12} \Omega_1 \Omega_2) \quad (18)$$

obeys the two conditions

$$dp_N/dZ_1 = 0 \quad \text{and} \quad pV = \int dR_1 p_N(Z_1)$$

This permits the identification of p_N with the normal pressure at the interface. For a homogeneous phase, one may write

$$p_N = p = \sum_{s=1}^{\alpha} \frac{1}{\beta} \bar{\rho}_s - \frac{1}{2} \sum_{s=1}^{\alpha} \sum_{r=1}^{\alpha} \int \frac{\partial u_{rs}}{\partial Z_{12}} Z_{12} dR_{12} d\Omega d\Omega_2 \bar{\rho}_{rs}(R_{12} \Omega_1 \Omega_2) \quad (19)$$

where $\rho_s(Z_1)$ and $\rho_{rs}(Z_1 R_{12} \Omega_1 \Omega_2)$ have been replaced by $\bar{\rho}_s$ and $\bar{\rho}_{rs}(R_{12} \Omega_1 \Omega_2)$, which are independent of Z_1 .

For the calculation of $\bar{\mu}_i$ we use the method proposed by Buff and Stillinger [16] for the case of central forces in the solution-vapor interface. Consider the particle numbered 1, which is of species s . Letting ξ be the parameter giving the coupling of particle 1 to the rest of the system, we find that $\rho_s(Z_1 \Omega_1 \xi)$, the probability of finding 1 at Z_1 with orientation Ω_1 , obeys the integral equation [15,16]

$$\partial \rho_s(Z_1 \Omega_1 \xi) / \partial \xi = -\rho_s(Z \Omega \xi) \partial \log \Theta(\xi) / \partial \xi - \beta \sum_{r=1}^{\alpha} \int u_{1r} \rho_{sr}(Z_1 R_{12} \Omega_1 \Omega_2) dR_{12} d\Omega_2 \quad (20)$$

Integrating over ξ from 0 to 1, we find

$$\begin{aligned} \log \rho_s(Z_1 \Omega_1, \xi = 1) &\equiv \log \rho_s(Z_1 \Omega_1) = \log \frac{\rho_s(Z_1 \Omega_1, \xi = 0) \Theta(\xi = 0)}{\Theta(\xi = 1)} \\ &- \beta \sum_{r=1}^{\alpha} \int_0^1 d\xi \int u_{1r} \frac{\rho_{sr}(Z_1 R_{12} \Omega_1 \Omega_2 \xi)}{\rho_s(Z_1 \Omega_1 \xi)} dR_{12} d\Omega_2 \end{aligned} \quad (21)$$

[End of page 159] Using eqn. (A8) of Appendix 2, we may write (21) in the form

$$\beta \tilde{\mu}_s = \log \rho_s(Z_1 \Omega_1) + \log \Lambda^3 + \sum_{r=1}^{\alpha} \beta \int_0^1 d\xi \int u_{1r} \frac{\rho_{sr}(Z_1 R_{12} \Omega_1 \Omega_2 \xi)}{\rho_s(Z_1 \Omega_1 \xi)} dR_{12} d\Omega_2 \quad (22)$$

Equation (22) defines $\tilde{\mu}_s$ for charged or polar species as well as for electrically neutral and spherical molecules. Note that the parameter ξ plays an unsymmetric role in this equation, affecting only particle 1 of species s .

Let us define g_{sr} by the equation:

$$\rho_{sr}(Z_1 R_{12} \Omega_1 \Omega_2 \xi) = \rho_s(Z_1 \Omega_1 \xi) \rho_r(Z_2 \Omega_2) g_{sr}(Z_1 R_{12} \Omega_1 \Omega_2 \xi) \quad (23)$$

We will further put $g_{sr} = 1 + (g_{sr} - 1)$ to separate (22) into two parts, contributions of the form

$$\mu'_s = \sum_{r=1}^{\alpha} \int_0^1 d\xi \int (u_{1r}^S + u_{1r}^L) \rho_r(Z_2 \Omega_2) dR_{12} d\Omega_1 d\Omega_2 \quad (24)$$

and contributions

$$\begin{aligned} \mu''_s &= \beta^{-1} \log[\rho_s(Z_1 \Omega_1) \Lambda^3] + \sum_{r=1}^{\alpha} \int_0^1 d\xi \int (u_{1r}^S + \\ &+ u_{1r}^L) \rho_r(Z_2 \Omega_2) [g_{sr}(Z_1 R_{12} \Omega_1 \Omega_2 \xi) - 1] dR_{12} d\Omega_1 d\Omega_2 \end{aligned} \quad (25)$$

The interaction potential between particle 1 and a particle of species r has been written as a sum of short-range (u_{1r}^S) and long-range (u_{1r}^L) contributions. The integration over R_{12} in (25) is limited to small distances in any case because of the presence of $g_{sr} - 1$; the other term in μ''_s is purely local in character. Both u^S and u^L contribute to the integral (24) in non-uniform regions. In homogeneous and isotropic media, short-range forces contribute to μ'_s ; the homogeneity implies local electrical neutrality which prevents interactions involving nearby charges from contributing, while the isotropicity means that the average dipole moment and field at any point in such a medium is zero. However, the long range of electrostatic interactions means that distant charges may have to be considered; as we will see, they enter in the electrostatic potential, which is constant in such a region.

If particle 1 is an ion, the Coulombic contribution to (24) will be $\rho_1 V(Z_1)$, $V(Z_1)$ being the mean value of the electrostatic potential at Z_1 , due to the other particles of the system. On the other hand, if 1 is a molecule having a permanent dipole moment of magnitude m_1 , (24) will give $-m_1(\Omega_1) \cdot E(Z_1)$, with $E(Z_1)$ being the mean electric field at Z_1 .

$$E(Z_1) = -\nabla_{Z_1} V(Z_1) \quad (26)$$

For a charged particle in the interface we have, therefore,

$$\beta \tilde{\mu}_s = \log \rho_s(Z_1) + \log \Lambda^3 + \sum_{r=1}^{\alpha} \beta \int_0^1 d\xi \int u_{sr}^S \frac{\rho_{sr}(Z_1 R_{12} \Omega_2 \xi)}{\rho_s(Z_1 \xi)} dR_{12} d\Omega_2$$

[End of page 160]

$$+ \sum_{r=1}^{\alpha} \beta \int_0^1 d\xi \int u_{sr}^L \rho_r(Z_2 \Omega_2) [g_{sr}(Z_1 R_{12} \Omega_2 \xi) - 1] dR_{12} d\Omega_2 + \beta e_s V(Z_1) \quad (27)$$

The quantity $\tilde{\mu}_s$, consistently with common usage, should be called the electrochemical potential, and the term "chemical potential" should be applied to the quantity $\tilde{\mu}_s - e_s V(Z_1)$, which we will denote by $\mu_s(Z_1)$. In an equilibrium state, the electrochemical potential must be independent of position:

$$\tilde{\mu}_s(Z_1) = \tilde{\mu}_s = \text{constant} \quad (28)$$

On a boundary of the (IPE) system we will have

$$\tilde{\mu}_s = \mu_s(s) + e_s V(s) \quad (29)$$

where $V(s)$ is the electrostatic potential within the homogeneous phase which contains the constituent s . By virtue of the homogeneity, the phase is an equipotential region. The quantity $\mu_s(s)$ is the chemical potential of s at the boundary and in the adjacent homogeneous phase. As we have remarked in the preceding Section, it is only on the boundaries of the system that one can regulate μ_s , by regulation of the composition of the homogeneous phase: μ_s will depend only on local conditions.

By manipulations similar to the above one may calculate the electrochemical potential $\tilde{\mu}_s$ of a dipolar species. The electrochemical potential in this case is written:

$$\tilde{\mu}_s = \mu_s(Z_1, \Omega_1) - m_1(\Omega_1) \cdot E(Z_1) \quad (30)$$

where μ_s represents $\log p_s(Z_1, \Omega_1) + \log \Lambda^3$ plus the contribution of shortrange forces and correlations. The electrochemical potential must be independent of Z_1 and also of the orientation Ω_1 for an equilibrium state, but its two parts obviously depend separately on Z_1 and Ω_1 . On the boundary of the system, the electric field vanishes and $\mu_s = \tilde{\mu}_s$, the chemical potential. We emphasize that μ_s depends on Z_1 within the inhomogeneous region, for charged or polar species, due to the dependence of μ_s' on Z_1 .

Now we may write eqn. (13):

$$\sum_{s=1}^{\alpha} \bar{N}_s d\mu_s + \sum_{s=1}^{\alpha} \bar{N}_s e_s dV(s) = V dp - A d\sigma \quad (31)$$

where $V(s)$ is the potential in the homogeneous phase for which p_s is not zero. Using (5) and the definition

$$q_A = \sum_s \bar{N}_s e_s$$

with the sum being over chemical species found on the A-side of the interface (in phase I) and a similar definition for q_s we have the Gibbs isotherm in the usual form:

$$A d\sigma = V dp - \sum_{s=1}^{\alpha} \bar{N}_s d\mu_s + q_A dV_{ab} \quad (32)$$

[End of page 161] Here

$$V_{ab} = V(a) - V(b)$$

and we have used the fact that $q_B = -q_A$. It is possible to modify eqn. (32) by the substitution of the chemical potentials of the electrically neutral solutes for those of the ions.

Thus, we have recovered the Gibbs isotherm in the familiar form, starting from the grand canonical distribution. In this way, all the quantities appearing in the equation are defined in microscopic or molecular terms. We now proceed to compare the expression for the surface tension with others found in the literature.

(4) Comparison Between Expressions for the Surface Tension

Let us for a moment limit ourselves to central forces. Then we may write

$$\frac{\partial u_{sr}}{\partial X_{12}} = \frac{\partial u_{sr}}{\partial R_{12}} \frac{\partial R_{12}}{\partial X_{12}} = \frac{X_{12}}{R_{12}} \frac{\partial u_{sr}}{\partial R_{12}} \quad (33)$$

and the surface tension, eqn. (16), becomes

$$\sigma = \frac{1}{2} \sum_{s=1}^{\alpha} \sum_{r=1}^{\alpha} \int_a^b dZ_1 \int_V \frac{\partial u_{sr}}{\partial R_{12}} \frac{X_{12}^2 - Z_{12}^2}{R_{12}} \rho_{sr}(Z_1, R_{12}) dR_{12} \quad (34)$$

The expression (34) appears often in the literature.

Returning to the general case, we introduce the expression (19) for the pressure into eqn. (16). The result,

$$\sigma = \int_a^b dZ_1 \left[p - \sum_{s=1}^{\alpha} kT \rho_s(Z_1) + \int_V \frac{1}{2} \sum_{s=1}^{\alpha} \sum_{r=1}^{\alpha} \frac{\partial u_{sr}}{\partial X_{12}} X_{12} \rho_{sr}(Z_1 R_{12} \Omega_1 \Omega_2) \right. \\ \left. \times dR_{12} d\Omega_1 d\Omega_2 \right] \quad (35)$$

is identical to that derived [20] directly from considerations of mechanical equilibrium. In eqn. (18), we have defined a normal pressure p_N whose mean value is p , and which is equal to the pressure in the homogeneous phases (Appendix 1). One can similarly define a tangential pressure

$$p_T(Z_1) = kT \sum_{s=1}^{\alpha} \rho_s(Z_1) - \frac{1}{2} \sum_{s=1}^{\alpha} \sum_{r=1}^{\alpha} \int \frac{\partial u_{sr}}{\partial X_{12}} X_{12} \sum_{m=1}^{\infty} \frac{1}{m!} (-R_{12} \cdot \nabla_1)^{m-1} \times \rho_{sr}(Z_1 R_{12} \Omega_1 \Omega_2) dR_{12} d\Omega_1 d\Omega_2 \quad (36)$$

Only the leading term in the sum over m survives an integration over the volume of the interface. Using the expressions for p_N and p_T , the surface tension can be written in the well-known form [18--20]

$$\sigma = \int_a^b dZ [p - p_T(Z)] dZ = \int_a^b dZ [p_N(Z) - p_T(Z)] \quad (37)$$

It is interesting to note that the mean electric field, which is normal to the interface, does not appear explicitly in (18) and (36).

Sanfeld and Defay [21] and more recently Hurwitz and d'Alkaine [6] and other authors [7--10] have attempted to make explicit the contribution of the mean electric field E to σ . Their approaches involve considerations of mechanical equilibrium within the interface, and generally suppose that the surface tension can be separated into two parts: one given by the expression that would hold in the absence of electric field, and another including the terms depending explicitly on the electric field [23]. As has been noted by Hurwitz and d'Alkaine [6], such an approach is not truly microscopic. The absence of a field would change ρ_{sr} and hence the contribution of short-range forces to the pressures. The expressions given above are consistent with mechanical equilibrium in the interface and with the thermodynamic equations generally used to describe interfaces. None of our expressions requires the explicit appearance of the electric field. It is, however, possible to make the field appear explicitly.

In the tangential pressure (36) we keep only the term for $m = 1$, make the separation of μ_{sr} into short-range and long-range parts, μ_{sr}^s and μ_{sr}^L . μ_{sr}^L referring to the electrostatic part. As done previously, we write $\rho_s \rho_r (g_{sr} - 1 + 1)$ for ρ_{sr} and isolate the long-range term:

$$\begin{aligned} p_T(Z_1) &= kT \sum_{s=1}^{\alpha} \rho_s(Z_1) - \frac{1}{2} \sum_{s=1}^{\alpha} \sum_{r=1}^{\alpha} \int \frac{\partial u_{sr}^s}{\partial X_{12}} X_{12} \rho_{sr}(Z_1 R_{12} \Omega_1 \Omega_2) dR_{12} d\Omega_1 d\Omega_2 \\ &\quad - \frac{1}{2} \sum_{s=1}^{\alpha} \sum_{r=1}^{\alpha} \int \frac{\partial u_{sr}^L}{\partial X_{12}} X_{12} \rho_s(Z_1 \Omega_1) \rho_r(Z_2 \Omega_2) [\rho_{sr}(Z_1 R_{12} \Omega_1 \Omega_2) - 1] \\ &\quad dR_{12} d\Omega_1 d\Omega_2 \\ &\quad - \frac{1}{2} \sum_{s=1}^{\alpha} \sum_{r=1}^{\alpha} \int \frac{\partial u_{sr}^L}{\partial X_{12}} X_{12} \rho_s(Z_1 \Omega_1) \rho_r(Z_2 \Omega_2) dR_{12} d\Omega_1 d\Omega_2 \quad (38) \\ &= \tilde{p}_T(Z_1) - \frac{1}{2} \sum_{s=1}^{\alpha} \sum_{r=1}^{\alpha} \int \frac{\partial u_{sr}^L}{\partial X_{12}} X_{12} \rho_s(Z_1 \Omega_1) \rho_r(Z_2 \Omega_2) dR_{12} d\Omega_1 d\Omega_2 \end{aligned}$$

In the last integral we may carry out an integration by parts (Appendix 3) and write

$$p_T(Z_1) - \tilde{p}_T(Z_1) = \frac{1}{2} \sum_{s=1}^{\alpha} \sum_{r=1}^{\alpha} \int u_{sr}^L \rho_s(Z_1 \Omega_1) \rho_r(Z_2 \Omega_2) dR_{12} d\Omega_1 d\Omega_2 \quad (39)$$

If s represents a charged species,

$$\int d\Omega_2 \sum_{r=1}^{\alpha} u_{sr}^L \rho_r(Z_2 \Omega_2) = \sum_r' \frac{e_s e_r}{R_{12}} \rho_r(Z_2) + \sum_r'' e_s \frac{\bar{\mu}_r(Z_2) \cdot R_{21}}{R_{12}^2} \rho_r(Z_2)$$

with the sum Σ_r' including all charged species r and the sum Σ_r'' including all dipolar species r ; $\bar{\mu}_r(Z_2)$ is the mean dipole moment of particles of species r at the point Z_2 and $\rho_r(Z_2)$ their density at this point. We may similarly divide Σ , [End of page 163] into Σ_s' and Σ_s'' . Integrating over R_{12} , we find

$$\begin{aligned} & \int \sum_{s=1}^{\alpha} \sum_{r=1}^{\alpha'} u_{sr}^L \rho_s(Z_1) \rho_r(Z_2 \Omega_2) dR_{12} d\Omega_2 = \\ & = \sum_{s=1}^{\alpha'} e_s \rho_s(Z_1) \int dR_{12} \left[\frac{\rho(Z_2)}{R_{12}} + \frac{P(Z_2) \cdot R_{12}}{R_{12}^3} \right] = \rho(Z_1) V(Z_1) \end{aligned}$$

with $P = \sum' \bar{\mu}_r \rho_r$ being the electric polarisation at the point Z_1 . If s is a dipolar species,

$$\begin{aligned} & \int dR_{12} d\Omega_2 \sum_{r=1}^{\alpha} u_{sr}^L \rho_r(Z_2 \Omega_2) = \\ & = \int dR_{12} \left[\sum_r' \frac{\mu_s(Z_1 \Omega_1) \cdot R_{12} e_r \rho_r(Z_2)}{R_{12}^3} \right. \\ & \quad \left. + \sum_r'' \mu_s(Z_1 \Omega_1) \cdot \left(\frac{\bar{\mu}_r(Z_2)}{R_{12}^3} - 3 R_{12} \frac{\bar{\mu}_r(Z_2) \cdot R_{12}}{R_{12}^5} \right) \rho_r(Z_2) \right] \end{aligned}$$

The quantity in square brackets is $E(Z_1)$, the electric field, and

$$\int d\Omega_1 \sum_{s=1}^{\alpha} \mu_s(Z_1 \Omega_1) \rho_s(Z_1 \Omega_1) = P(Z_1)$$

Thus, (39) may be written:

$$p_T(Z_1) - \tilde{p}_T(Z_1) = \frac{1}{2} [\rho(Z_1) V(Z_1) - P(Z_1) \cdot E(Z_1)] \quad (40)$$

with the second member being just the electrostatic energy of the system.

Inserting (40) into (37), we find a new expression for σ . If we carry out an integration by parts, using the fact that the electric field vanishes on the bound, aries of the system, we find

$$\sigma = \int_a^b [p - \tilde{p}_T(Z) - \frac{1}{2} E^2(Z)] dZ \quad (41)$$

This is the expression used in ref. 5 [7--12]. In the expression for $p_N(Z)$ we can define a quantity $\tilde{p}_N(Z)$ analogously to $\tilde{p}_T(Z)$, and thus find the other expressions proposed by other workers [5,21]. A change in the definition $\tilde{p}_T(Z)$ in (41) can transform it into the form of ref. 6. Obviously, a large number of equivalent expressions can be obtained for σ by such rewritings. It must be underlined, however, that definitions of $\tilde{p}_N(Z)$ and $\tilde{p}_T(Z)$ are different in each case. Only a general microscopic approach, such as that discussed here, allows the unambiguous definition of all the terms appearing in an expression for σ . Furthermore, the quantities $\tilde{p}_N(Z)$ and $\tilde{p}_T(Z)$ can be more or less sensitive to the electrical conditions, according to their definitions. Although it is not evident from the way (41) is written, a change in the state of the system which changes the electric field will probably change $\tilde{p}_N(Z)$ as well. [End of page 164]

(5) Discussion: Lippmann Equation

By considering the ideally polarisable electrode as an open system, enclosed in surroundings whose variation can modify its composition, we have shown that the system obeys an equation which is formally identical to the thermodynamic relation given by Gibbs. Now, however, all the quantities appearing in the equation are defined in microscopic terms. The thermodynamic definition of the surface tension is identical to the general mechanical definition.

In principle, one could use the present formalism to calculate all the thermodynamic parameters characterizing the interface starting from the interaction potentials u_{ij} . In practice, such an approach is too difficult now and for some time in the future, and we must have recourse to models. In this respect, the formalism we have presented imposes a certain number of constraints on such models. As previously emphasized [9], all such models, once the u_{ij} are fixed, are models for the correlation functions u_{ij} .

Once one has given an approximate formula for the distribution of matter in the IPE, one can calculate the surface charge q_A and q_B directly, by integration. However, eqn. (32) shows that the surface charge can also be obtained from the Lippmann equation,

$$q_A = A(\partial \sigma / \partial V_{ab})_{T, p, \bar{\mu}} \quad (42)$$

when the statistical mechanical formulas are used to calculate σ and the other thermodynamic quantities. In refs. 8 and 9 it was shown that a model like the Gouy-Chapman model can lead to a contradiction between the two values

for q_A . In this model, applied to an n -valent electrolyte in a solvent of dielectric constant ϵ , the density of the ions is given by

$$n_i = n_{ie} e^{\pm qV/kT}, \quad i = 1, 2$$

Here, q is the ionic charge, n_{ie} the density of species i in the homogeneous phase, and V the electrical potential, which obeys the Poisson equation:

$$\frac{d}{dZ} \left(\epsilon \frac{dV}{dZ} \right) = -\rho = n_1 q + n_2 (-q)$$

This model treats only the solution side of the interface, from $Z = 0$ to $Z = b$. The solution to the above equations leads to [24]

$$\frac{qV}{kT} = 2 \log \frac{1 + e^{-KZ} \tanh(qU/4kT)}{1 - e^{-KZ} \tanh(qU/4kT)}$$

with $K^2 = 2 q^2 n_{ie} / \epsilon kT$ and U the potential drop across the solution side of the interface. A direct calculation of the surface charge leads [8] to

$$q_B = \int_0^\infty \rho dZ = (4 kT n_{ie} / q) \sinh W \cosh W \quad (43)$$

with $W = qU/4kT$.

Now let us imagine a change of equilibrium state that alters U to $U + \Delta U$, holding constant n_{ie} , P , and other properties of the homogeneous solution phase. Since this model does not consider short-range forces, we may use (41). [**End of page 165**] to obtain the following expression for the change in surface tension:

$$\Delta\sigma = \Delta \int_0^\infty dZ [kT(n_{1e} + n_{2e} - n_1 - n_2) - \frac{1}{2} (dV/dZ)^2] dZ$$

(While n_{1e} and n_{2e} are unchanged, they have been left in the above expression so that the integral converges.) After several algebraic manipulations, we find

$$\begin{aligned} \Delta\sigma &= \Delta \int_0^\infty dZ \left[-16 kT n_{ie} \frac{e^{-2KZ} \tanh^2 W}{(1 - e^{-2KZ} \tanh^2 W)^2} - \frac{8 kTK^2}{q^2} \frac{e^{-2KZ} \tanh^2 W}{(1 - e^{-2KZ} \tanh^2 W)^2} \right] \\ &= \Delta \left(\left(\frac{-8 kT^2 K^2}{q^2} \right) \left(\frac{\epsilon + 1}{2K} \right) \frac{\tanh^2 W}{1 - \tanh^2 W} \right) \end{aligned}$$

According to the Lippmann equation,

$$q_B = - \frac{\Delta\sigma}{\Delta U} = \frac{4 k^2 T^2 K (\epsilon + 1)}{q^2} \frac{\Delta(\sinh^2 W)}{\Delta U} = \frac{2 kTK (\epsilon + 1)}{q} \sinh W \cosh W$$

which disagrees with (43), unless $\epsilon = 1$. For $\epsilon \neq 1$, an inconsistency in the model is indicated. As we have discussed elsewhere [8,10] the problem lies in the fact that the Gouy-Chapman model does not take into consideration the alteration in the distribution of solvent molecules, and hence of E , which must accompany the change of U . The fact that the Lippmann equation is verified when a formula for q other than (41) is used [25] does not remove the inconsistency.

From eqn. (32) one can also deduce laws of the form

$$\bar{N}_s = -A \left(\frac{\partial \sigma}{\partial \mu_s} \right)_{\mu_1, T, P, V_{ab}} \quad (44)$$

We will show that such relations are obeyed for a simple model of the interface, in which we neglect all the non-Coulombic forces and all the correlations $g_{rs} \rightarrow 1$. Making these assumptions, we derive from eqns. (22)--(30)

$$\beta \tilde{\mu}_s = \log[\rho_s(Z) \Lambda^3] + \beta e_s V(Z) \quad (45)$$

for charged particles and

$$\beta \tilde{\mu}_s = \log[\rho_s(Z, \Omega) \Lambda^3] - \beta \mathbf{m}_s \cdot \mathbf{E}(Z) \quad (46)$$

for dipolar molecules. Suppose we modify μ_1 , the chemical potential of particles of species 1, which are assumed charged. Equation (45) yields

$$\beta \Delta \tilde{\mu}_1 \rho_1(Z) = \Delta \rho_1(Z) + \beta e_1 \rho_1(Z) \Delta V(Z) \quad (47a)$$

and, for other charged species,

$$\Delta\rho_s(Z) + \beta e_s \rho_s(Z) \Delta V(Z) = 0 \quad (47b)$$

For dipolar particles, we have

$$\Delta\rho_s(Z, \Omega) - \rho_s(Z, \Omega) m_s(\Omega) \cdot \Delta E(Z) = 0 \quad (48)$$

which, with integration over $\sim$ and summation over all s for polar molecules, [End of page 166] yields

$$\sum_{s \text{ polar}} \Delta\rho_s(Z) = P(Z) \cdot \Delta E(Z) \quad (49)$$

In a similar way, we get from eqns. (47)

$$\sum_{s \text{ charged}} \Delta\rho_s(Z) = -\beta\rho(Z)\Delta V(Z) + \beta\rho_1(Z)\Delta\mu_1 \quad (50)$$

With this model, the surface tension is simply

$$\sigma = \int (p - \beta^{-1} \sum_s \Delta\rho_s - \frac{1}{2} E^2) dZ$$

and its change is

$$\Delta\sigma = - \int (\beta^{-1} \sum_s \rho_s + E \Delta E) dZ \quad (51)$$

since the pressure is unchanged. Inserting (49) and (50) into (51) we find

$$\Delta\sigma = - \int [-\rho\Delta V + (E + P)\Delta E] dZ - \Delta\mu_1 \int \rho_1(Z) dZ \quad (52)$$

The first integral may be written using the electrical displacement D as follows:

$$\int_a^b (-\rho\Delta V + D\Delta E) dZ = [-\rho\Delta V]_a^b + \int_a^b \left[D \frac{d}{dz} (\Delta V) + D\Delta \left(\frac{-dV}{dZ} \right) \right] dZ \quad (53)$$

Since $\rho(a) = \rho(b) = 0$ and $d(\Delta V)/dZ = A(dV/dZ)$, this gives zero. The second integral of (52) is just $\bar{N}_1/A$. Thus this simple model of the interface is consistent with thermodynamic relations like (44). However, if one changes the model by replacing the solvent by a medium of uniform dielectric constant, as in the Gouy-Chapman model, it can be verified quickly that (44) will no longer be satisfied. Since the contribution of (49) will not be present, the electrical polarization will not appear in (52) and the first integral will no longer vanish. A consistent model of the interface necessitates some explicit consideration of the solvent.

Appendix 1

Let us write the relation (5) for a particle of type s , denoting by $\rho_s(Z_1\Omega_1)$ the probability of finding a particle of type s at R_1 with orientation Ω_1 . Differentiating the expression with respect to Z_1 , we obtain

$$\frac{1}{\beta} \frac{\partial \rho_s(Z_1\Omega_1)}{\partial Z_1} = \frac{1}{\Theta} \sum_{N_s=1}^{\infty} \sum_{\substack{N_t=0 \\ (t \neq s)}}^{\infty} \left(\prod_{s=2}^{\alpha} \frac{z_s^{N_s}}{N_s!} \right) \frac{z_1^{N_1}}{(N_1-1)!} \quad (A1)$$

$$\int \sum_{j=2}^N \left(-\frac{\partial u_{1j}}{\partial Z_1} \right) e^{-\beta U_N} dR_2 \dots dR_N d\Omega_2 \dots d\Omega_N$$

[End of page 167]

$$= \sum_{r=1}^{\alpha} \int \left(-\frac{\partial u_{sr}}{\partial Z_1} \right) \rho_{sr}(Z_1 R_{12} \Omega_1 \Omega_2) dR_{12} d\Omega_2$$

Integrating this equation over the angular variable Ω_1 yields

$$\frac{1}{\beta} \frac{\partial \rho_s(Z_1)}{\partial Z_1} = \sum_{r=1}^{\alpha} \int \left(-\frac{\partial u_{sr}}{\partial Z_1} \right) \rho_{sr}(Z_1 R_{12} \Omega_1 \Omega_2) dR_{12} d\Omega_1 d\Omega_2 \quad (A2)$$

It is easy to verify that (A2) is identical to the equation obtained from the mechanical equilibrium conditions on the forces (see, for example, ref. 7).

Now let us sum (A2) over the different types of particles, obtaining:

$$\frac{1}{\beta} \sum_{s=1}^{\alpha} \frac{\partial \rho_s(Z_1)}{\partial Z_1} = \sum_{s=1}^{\alpha} \sum_{r=1}^{\alpha} \int \frac{\partial u_{sr}}{\partial Z_{12}} \rho_{sr}(Z_1 R_{12} \Omega_1 \Omega_2) dR_{12} d\Omega_1 d\Omega_2 \quad (A3)$$

(we have used the fact that, since u_{sr} depends only on R_{12} , $\partial u_{sr}/\partial Z_1$ is the negative of $\partial u_{sr}/\partial Z_{12}$). Differentiating pN of eqn. (18) with respect to Z_1 we find, with the use of (A3),

$$\begin{aligned} \frac{dp_N}{dZ_1} &= \sum_{s=1}^{\alpha} \sum_{r=1}^{\alpha} \int \frac{\partial u_{sr}}{\partial Z_{12}} \rho_{sr}(Z_1 R_{12} \Omega_1 \Omega_2) dR_{12} d\Omega_1 d\Omega_2 \\ &\quad - \frac{1}{2} \sum_{s=1}^{\alpha} \sum_{r=1}^{\alpha} \int \frac{\partial u_{sr}}{\partial Z_{12}} dR_{12} d\Omega_1 d\Omega_2 Z_{12} \frac{\partial}{\partial Z_1} \sum_{m=1}^{\infty} \frac{1}{m!} (-R_{12} \cdot \nabla_1)^{m-1} \rho_{sr}(Z_1 R_{12} \Omega_1 \Omega_2) \\ &= \frac{1}{2} \sum_{s=1}^{\alpha} \sum_{r=1}^{\alpha} \int dR_{12} d\Omega_1 d\Omega_2 \frac{\partial u_{sr}}{\partial Z_{12}} [2 \rho_{sr}(Z_1 R_{12} \Omega_1 \Omega_2) \\ &\quad + \sum_{m=1}^{\infty} \frac{1}{m!} (-R_{12} \cdot \nabla_1)^m \rho_{sr}(Z_1 R_{12} \Omega_1 \Omega_2)] \end{aligned}$$

The sum over m is equal to $\rho_{sr}(Z_1 -Z_{12}, R_{12} \Omega_1 \Omega_2) - \rho_{sr}(Z_1 R_{12} \Omega_1 \Omega_2)$; the quantity $\rho_{sr}(Z_1 -Z_{12}, R_{12} \Omega_1 \Omega_2)$ may be replaced by $\rho_{rs}(Z_1, -R_{12} \Omega_1 \Omega_2)$ and, since $u_{sr} = u_{rs}$ and we are summing over both r and s , by $\rho_{sr}(Z_1, -R_{12} \Omega_1 \Omega_2)$. Then we have

$$\frac{dp_N}{dZ_1} = \frac{1}{2} \sum_{s=1}^{\alpha} \sum_{r=1}^{\alpha} \int dR_{12} d\Omega_1 d\Omega_2 \frac{\partial u_{sr}}{\partial Z_{12}} [\rho_{sr}(Z_1 R_{12} \Omega_1 \Omega_2) + \rho_{sr}(Z_1, -R_{12} \Omega_1 \Omega_2)]$$

By changing the integration variable from R_{12} to $-R_{12}$, noting that $\partial u_{sr}/\partial Z_{12} = -\partial u_{sr}/\partial(-Z_{12})$, one sees that contribution to the integral of the second term in square brackets gives the negative of that of the first, and

$$\begin{aligned} \frac{dp_N}{dZ_1} &= \frac{1}{2} \sum_{s=1}^{\alpha} \sum_{r=1}^{\alpha} \int dR_{12} d\Omega_1 d\Omega_2 \left[\frac{\partial u_{sr}}{\partial Z_{12}} \rho_{sr}(Z_1 R_{12} \Omega_1 \Omega_2) \right. \\ &\quad \left. - \frac{\partial u_{sr}}{\partial Z_{12}} \rho_{sr}(Z_1 R_{12} \Omega_1 \Omega_2) \right] = 0 \end{aligned} \quad (A4)$$

[End of page 168]

The sum over m in the expression (18) for P_N can be replaced by an integral, as shown by Harashima [18] and Irving and Kirkwood [26].

To complete the identification of P_N with the pressure, one must show that its integral over R_1 is equal to pV , eqn. (17), i.e., that

$$\begin{aligned} \int_V dR_1 \sum_{s,r} \int \frac{\partial u_{rs}}{\partial Z_{12}} Z_{12} dR_{12} d\Omega_1 d\Omega_2 \sum_{m=1}^{\infty} \frac{1}{m!} (-R_{12} \cdot \nabla_2)^{m-1} \rho_{rs}(Z_1 R_{12} \Omega_1 \Omega_2) \\ = \int_V dR_1 \sum_{s,r} \int \frac{\partial u_{rs}}{\partial Z_{12}} Z_{12} dR_{12} d\Omega_1 d\Omega_2 \rho_{rs}(Z_1 R_{12} \Omega_1 \Omega_2) \end{aligned} \quad (A5)$$

The second member of (A5) is just the term in the sum for $m = 1$. For other values of m ,

$$\begin{aligned} \int_V dR_1 \sum_{s,r} \int \frac{\partial u_{rs}}{\partial Z_{12}} Z_{12} dR_{12} d\Omega_1 d\Omega_2 (-R_{12} \cdot \nabla_1)^{m-1} \rho_{rs}(Z_1 R_{12} \Omega_1 \Omega_2) \\ = A \sum_{s,r} \int \frac{\partial u_{rs}}{\partial Z_{12}} (-Z_{12})^2 dR_{12} d\Omega_1 d\Omega_2 (-R_{12} \cdot \nabla_1)^{m-2} [\rho_{rs}(b R_{12} \Omega_1 \Omega_2) \\ - \rho_{rs}(a R_{12} \Omega_1 \Omega_2)] \end{aligned}$$

Since all of the properties of the system are homogeneous and isotropic at $Z = a$ and $Z = b$, the last integral vanishes.

Appendix 2

In eqn. (21) the quantity $\rho_s(Z_1 \Omega_1 \xi = 0) \Theta(\sim = 0)/\Theta(\xi = 1)$ appears. Using the expression of eqn. (5) for $\rho_s(Z_1 \Omega)$ and putting $\xi = 0$, we may write the following expansion for $\rho_s(Z_1 \Omega_1 \xi = 0)$

$$\begin{aligned}\Theta(0)\rho_s(Z_1\Omega_1\xi=0) &= \frac{\xi_s^1}{0!} \prod_{r \neq s}^{\alpha} \frac{\xi_r^0}{0!} + \frac{\xi_s^2}{1!} \prod_{r \neq s}^{\alpha} \frac{\xi_r^0}{0!} \int dR_2 d\Omega_2 \\ &+ \dots + \frac{\xi_s^1}{0!} \sum_{r \neq s}^{\alpha} \frac{\xi_r^1}{1!} \prod_{t \neq r}^{\alpha} \frac{\xi_t^0}{0!} \int dR_2 d\Omega_2 \\ &+ \frac{\xi_s^2}{1!} \sum_{r \neq s}^{\alpha} \frac{\xi_r^1}{1!} \prod_{t \neq r}^{\alpha} \frac{\xi_t^0}{0!} \int dR_2 d\Omega_2 dR_3 d\Omega_3 e^{-\beta u_{23}} + \dots\end{aligned}$$

The partition function for $\sim = 1$ may be written

$$\Theta = \Theta(\xi = 1) = \prod_{r=0}^{\alpha} \frac{\xi_r^0}{0!} + \sum_{r=1}^{\alpha} \frac{\xi_r^1}{1!} \prod_{t \neq r}^{\alpha} \frac{\xi_t^0}{0!} \int dR_1 d\Omega_1 + \dots$$

[End of page 169]

$$\begin{aligned}&+ \sum_{r,t}^{(r \neq t)} \frac{\xi_r^1}{1!} \frac{\xi_t^1}{1!} \prod_{u \neq r}^{\alpha} \frac{\xi_u^0}{0!} \int dR_1 d\Omega_1 dR_2 d\Omega_2 e^{-\beta u_{12}} + \dots\end{aligned} \quad (A7)$$

A rearrangement of terms in (A6) and (A7) yields

$$+ \dots + \xi_s^1 \sum_{r \neq s}^{\alpha} \xi_r^1 \int dR_2 d\Omega_2 dR_3 d\Omega_3 e^{-\beta u_{23}} + \dots = \xi_s^1 \Theta(\xi = 1)$$

which leads to

$$\frac{\Theta(\xi = 0)\rho_s(Z_1\Omega_1\xi = 0)}{\Theta(\xi = 1)} = \frac{\exp(\beta \tilde{\mu}_s)}{\Lambda^3} \quad (A8)$$

since ξ_s is the activity of s [15]. The quantity Λ is given in terms of the mass of s and physical constants according to

$$\Lambda = h(2\pi m k_B T)^{-1/2} \quad (A9)$$

Appendix 3

In eqn. (38) we transform the integral by an integration by parts in X_{12} , using

$$\int \frac{\partial u_{sr}}{\partial X_{12}} X_{12} dX_{12} = |X_{12} u_{sr}| - \int u_{sr} dX_{12} \quad (A10)$$

In (A10) the integrated term is to be evaluated on the boundaries of the system: $X_{12} = \pm\infty$ $a < Z_2 < b$. If u_{sr} represents a charge-dipole or dipole-dipole interaction potential, $X_{12} u_{sr} \rightarrow 0$ as the boundaries tend to infinity, since u_{sr} varies as R_{12}^{-n} with $n > 1$. For the Coulombic charge-charge interaction potential,

$$\lim_{X_{12} \rightarrow \pm\infty} |X_{12} u_{sr}| = e_s e_r \quad (A11)$$

Now, unlike $P_N(Z)$, $P_T(Z)$ is not a priori a physical quantity, since only

$$(b-a)\bar{p}_T = \int_a^b p_T(Z_1) dZ_1$$

is defined, or enters our formulae. Because of this, (All) will always lead to a zero contribution to σ when the overall electrical neutrality of the interface is taken into account. This justifies the expression (39).

References

- 1 P. Delahay, Double Layer and Electrode Kinetics, Wiley-Interscience, 1965.
- 2 M.J. Spaarnay, The Electrical Double Layer, Pergamon Press, Oxford, 1972.
- 3 D.M. Mohilner, The Electrical Double Layer in Electroanalytical Chemistry, 1 (1966) 271.
- 4 J.O'M. Bockris and A.K.N. Reddy, Modern Electrochemistry, Plenum Press, New York, 1970.
- 5 A. Sanfeld, An Introduction to the Thermodynamics of Charged and Polarized Layers, Wiley-Interscience, London, 1968. [End of Page 170]
- 6 H.D. Hurwitz and C.V. d'Alkaine, J. Electroanal. Chem., 42 (1973) 77.
- 7 J.P. Badiali and J. Goodisman, J. Phys. Chem., 79 (1975) 223.
- 8 J. Goodisman, J. Chim. Phys., 72 (1975) 193.

- 9 J.P. Badiali and J. Goodisman, J. Electroanal. Chem., 65 (1975) 523.
- 10 J. Goodisman, J. Phys. Chem., 80 (1976) 2363.
- 11 F.P. Buff, J. Chem. Phys., 25 (1956) 196.
- 12 D.C. Grahame and R.B. Whitney, J. Chem.phys.
- 13 D.C. Grahame, Chem. Rev., 41 (1947) 441.
- 14 R. Parsons and M.A.V. Devanathan, Trans. Faraday Soc., (1953) 606. '
- 15 T.L. Hill, Statistical Mechanics, McGraw Hill, New York, 1956.
- 16 F.P. Buff and F.H. Stillinger, J. Chem. Phys., 25 (1956) 312.
- 17 H.S. Green, Proc. Roy. Soc., A189 (1947) 103.
- 18 A. Harashima, Advan. Chem. Phys., 1 (1958) 203.
- 19 Ono, Kondo, Handbuch der Physik, X (1960) 134.
- 20 J.G. Kirkwood and F.P. Buff, J. Chem. Phys., 17 (1969) 338.
- 21 A. Sanfeld and R. Defay, Electrochim. Acta, 12 (1967) 913.
- 22 H.S. Green, Molecula~ Theory of Fluids, North-Holland, Amsterdam, 1952.
- 23 R.M. Latanasion, N.H. McMillan and R.G. Lye, Corrosion Sci., 13 (1973) 387.
- 24 M.J. Spaarnay, The Electrical Double Layer, Pergamon, Oxford, 1972, Ch. 2.
- 25 K. Herzfeld, Phys. Z., 21 (1920) 28.
- 26 J.H. Irving and J.G. Kirkwood, J. Chem. Phys., 18 (1950) 817.

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