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## The Lippmann Equation and the Ideally Polarizable Electrode

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The Lippmann equation for the ideally polarizable interface is normally derived by thermodynamics, using the Gibbs dividing surface. Therefore, the quantities appearing in the Lippmann equation can have no reference to the actual charge distribution in the interfacial region. For example, the quantity referred to as surface charge is actually a sum of surface excesses, rather than the integral of a true charge density. In this article we derive, by statistical mechanical methods, the Lippmann equation for a model at the molecular level, thus giving a precise physical definition to all quantities which appear. First, we derive the conditions for mechanical equilibrium for a system (the interface between metal and solution) in which an electric field is present, and whose properties are inhomogeneous and anisotropic. From the balance of forces, we obtain equations for the surface tension in terms of the pressure, electric field, electric charge density, and electric polarization at each point within the system. Considering a spherically symmetric system (mercury drop), we then proceed to a direct calculation of the change in the surface tension produced by a change in the potential drop across the interface, maintaining thermal equilibrium, constant temperature, and the pressure and chemical composition in homogeneous regions (on the boundaries of the interfacial region). Since an ideally polarizable interface does not permit charge transport across it, we introduce a surface within the interface on which the charge density is always zero. This surface serves to divide the interfacial region into two parts, thus allowing the surface charge to be defined as the integral of the charge density over the metal side of the interface. Only the solution side is treated by statistical mechanics. Boltzmann distributions for charged and polarizable species (solute and solvent) are used to guarantee thermal equilibrium. The Lippmann equation is obtained (a) considering only ions and supposing a dielectric constant equal to that of vacuum and (b) considering ions and molecules in thermal equilibrium, and a dielectric constant varying from point to point and changing with field. Finally, the response of our system to an imposed alternating potential is considered. A direct calculation of the impedance shows that it behaves, in the low-frequency limit, as a pure capacitance, and that the value of this capacitance is the derivative of the previously defined surface charge density with respect to the potential drop across the interface.

### I. Introduction

The Lippmann equation and the concept of the capacity of the double layer have long been of fundamental importance in electrochemistry, and continue to play an important role in modern developments.<sup>1,2</sup> Nevertheless, there are a certain number of ambiguities connected with these concepts which do not seem to have been adequately clarified in the literature.

The Lippmann equation is concerned with the surface tension of the interface between an ideally polarizable electrode and an ionic solution. (Recently, an extension of the equation to a reversible electrode has been given.<sup>1</sup>) According to this equation, the change in surface tension, divided by the change in the potential drop across the interface, gives the negative of the surface charge density (charge per unit area) of the electrode, if certain parameters are held constant. Keeping the Helmholtz (parallel-plate condenser) model of the double layer in mind, this permits the identification of (a) the second derivative of the surface tension with potential and (b) the capacity of the double layer obtained from impedance measurements. Thus a connection is made between the two principal methods for obtaining information on double layer structure.

A number of proofs of the Lippmann equation have been given, all by thermodynamic methods.<sup>3</sup> The use of thermodynamics gives the equation great generality, but at the same time means that the actual forces and interactions which determine the surface tension and its variation with potential are not considered. Correspondingly, the exact interpretation of the quantities appearing in the equation is not specified, but must await the use of a model. This can lead to problems in the interpretation of experimental results; for example, it is sometimes necessary<sup>1,4</sup> to distinguish between the "free" surface charge and the "thermodynamic" surface charge—it is the latter which enters the Lippmann equation.

When the Gibbs dividing surface is used for the derivation of the Lippmann equation, one can say nothing about the location of the charge or the distribution of the potential in the interface, since there is no interfacial region in the Gibbs picture. In particular, the charge of the double layer is not defined geometrically; the total charge is zero, so that each position of the Gibbs dividing surface leads to a different geometrically defined charge  $+Q$  on one side and a charge  $-Q$  on the other. The charge appearing in the Lippmann equation is actually a combination of Gibbs surface excesses. Of course, thermodynamically derived results constitute necessary conditions which must be obeyed by any particular model, and are useful in discussion<sup>1,5</sup> of such models.

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In this article, we consider several models for the ideally polarizable electrode and derive the Lippmann equation from statistical mechanical considerations, without recourse to thermodynamics. This allows the unambiguous definition, in terms of microscopic properties, of all the quantities which appear. Surprisingly, no derivation of this kind seems to have been presented in the literature, in spite of the long history of the Lippmann equation. Thermodynamic reasoning is universally used, followed by interpretation in terms of models.

We consider two descriptions of the "solution:" ions located in a region of dielectric constant  $\epsilon_0$  (corresponding to a gas, a fused salt, or a plasma), and ions located in a region of dielectric constant  $\epsilon$ , which may vary from point to point. The electrode (metal side of the double layer) is taken as an external source of potential; a variation in its charge leads to variations in the potential drop across the "solution" and in the surface tension. Further discussion of the models is given in section II. For each model of the solution, we derive the laws of mechanical equilibrium from purely microscopic considerations, employing Newton's laws for the coulombic interactions between the particles of which the atoms and molecules are composed. From the equilibrium conditions an equation for the surface tension is deduced. This is done for the case of dielectric constant  $\epsilon_0$  (only ions present) in section III, and for the case of dielectric constant  $\epsilon$  (ions and polarizable species present) in section V. The change in the surface tension and its ratio to the change in potential drop are computed directly. Then the Lippmann equation is derived in the two cases (sections IV and VI).

It is universal to refer<sup>2,6</sup> to the derivative of the surface charge density with respect to the potential drop across the double layer as the differential capacity of the double layer. In the case of the simple Helmholtz (parallel-plate condenser) model,<sup>2</sup> this quantity is evidently the capacity, in the sense of the impedance. However, it does not seem to have been shown in the literature that the ideally polarizable electrode actually behaves, to an alternating imposed voltage, as a capacitive circuit element.

In section VII, we show in general that, for sufficiently low frequency  $\omega$  of the alternating voltage, the ideally polarizable electrode presents an impedance of  $(i\omega C)^{-1}$ , where the capacitance  $C$  is the derivative of the electrode charge with respect to the potential drop across the interface. In conjunction with the results of the preceding sections, this means that the second derivative of the surface tension with respect to the potential drop is indeed identical with the capacity obtained from impedance measurements. This fact is well established experimentally by the work of Frumkin,<sup>7</sup> Cachet,<sup>8</sup> and others.

Section VIII contains a summary of our results and some discussion. We believe that the work presented here can be important in giving significance at the microscopic (*i.e.*, molecular) level to some of the macroscopic (*i.e.*, thermodynamic) laws of electrochemistry.

## II. Models Employed

A number of previous workers<sup>9</sup> have discussed electrocapillary phenomena in statistical mechanical terms. The review of Ono and Kondo<sup>10</sup> contains particularly valuable discussions of such work. In summary, it may be said that these authors attempt a more rigorous and general treatment than we present here, and consequently arrive at more complicated and mathematical results. We attempt to

emphasize physical concepts and thus work with simplified models.

We do not attempt, for example, to treat the entire system of solvated ions, metal ions, electrons, solvent molecules, etc., but define at the outset the separation of the system into two phases. The existence of a surface of separation is fundamental to our definition of the ideally polarizable electrode: for there to be no charge transfer across the interface, it suffices that there be a surface on which the charge density always vanishes. We identify this surface as the surface which separates the phases.

The system is taken as spherically symmetric, since the experimental measurements of electrocapillarity, to which our theoretical results are always implicitly referred, involve the mercury drop. Thus, the metal phase is found in the region  $r < r_\Sigma$  and the solution phase in the region  $r > r_\Sigma$ . The interface region extends from the surface  $r = r_i$  to the surface  $r = r_e$ , where  $r_i < r_\Sigma < r_e$  and all properties are homogeneous for  $r < r_i$  and  $r > r_e$ .

The interactions within the metal phase are never considered. This does not imply the region  $r < r_\Sigma$  does not contribute to the surface tension or to the potential drop across the interface. We are not interested in the calculation of the surface tension itself, but in the calculation of the change in the surface tension which accompanies a change in the potential drop, with the aim of indicating the physical effects which must be taken into consideration to produce the Lippmann equation. Thus, we assume that the contributions of the region  $r < r_\Sigma$  to the surface tension and to the potential drop are independent of the potential drop. The potential difference between  $r_\Sigma$  and  $r_i$  will be independent of the overall potential drop if the charge distribution within the metal phase remains unchanged. This is the case, for example, if the charge of the metal is on the surface (in which case the potential difference between  $r_\Sigma$  and  $r_i$  vanishes).

We consider explicitly the ions and atoms of the solution, interacting with each other and with the electrode or metal phase. The distribution of these ions and atoms is supposed to be determined by a Boltzmann-like distribution function. We suppose that the potential of the metal acting on an atom or ion of the solution is the sum of an electrostatic part of a "chemical" part. The former is the interaction of a charged or polarizable particle with a charged sphere; it depends on the total charge of the sphere but not on how this charge is distributed.

The second contribution is a potential  $W_i(r)$  ( $r > r_\Sigma$ ) which may be different for each species, thus taking into account specific chemical effects. Since  $r_\Sigma$  divides the metal phase from the solution phase,  $W_i$  for charged species should approach infinity as  $r$  approaches  $r_\Sigma$ . It is reasonable to suppose that the chemical force due to the electrode dies off rapidly with  $r$ , so that  $W_i$  has become constant for  $r > r_e$ . We make no other assumption as to the behavior of  $W_i$  between  $r_\Sigma$  and  $r_e$  (it may be totally repulsive or contain an attractive part, corresponding to adsorption). However, we assume that  $W_i$  is independent of the charge of the electrode. This assumption has been commonly accepted as a realistic one by physical chemists;<sup>3a,c,11</sup> it is at the root of the division of the electrochemical potential into electrical and chemical parts.

When the charge of the electrode is changed, we assume that the atoms and ions of the solution rearrange themselves to form a new state of equilibrium, *i.e.*, a canonical distribution obtains before and after the change. However,

since overall electroneutrality must be maintained, the systems before and after the change are different, containing different numbers of particles. In conformity with the role of the electrode as an external source of potential, all its properties, including the value of  $r_\Sigma$ , are supposed to be unchanged.

Within this general framework, two models for the solution phase are considered. First, in sections III and IV, we consider ions in a medium of dielectric constant  $\epsilon_0$  (vacuum). There is no polarization of the medium. This is appropriate to ions in the gas phase (plasma) or a molten salt. The only electrostatic interactions are the attractions and repulsions between point charges. Short-range interionic interactions may be considered to be included in the pressure. It will be assumed that the change in the pressure which accompanies a change in the potential drop across the interface may be approximated by the change in kinetic pressure,  $\Sigma n_i kT$ . This means that the contribution of the short-range interactions to the pressure change is supposed to be relatively unimportant. This assumption is parallel to the assumption that the potentials of chemical force  $W_i(r)$  are independent of potential drop.

In sections V and VI we include the effect of polarizable atoms, which give a dielectric constant  $\epsilon$  different from  $\epsilon_0$ . These atoms represent the solvent. It should be noted that we use the word "atom" in a general way, to include molecules, ions, etc. The polarization at each point is given by  $(\epsilon - \epsilon_0)E$ , where  $E$  is the electric field at this point. The value of  $\epsilon$  may differ from point to point, because the number of polarizable atoms differs (electrostriction) or because the polarizability per atom differs (saturation). The latter effect may be less important than the former.<sup>12</sup> Interactions between ions and solvent atoms which are not electrostatic in character may be included in the model, provided that their effects on the change of pressure are unimportant compared to the change of kinetic pressure.

### III. Balance of Forces for Interacting Ions

In this section, we calculate conditions for mechanical equilibrium between molecular entities composed of charged particles which interact according to Coulomb's law. Each molecular entity is charged but nonpolarizable. Of course, it is necessary to imagine additional short-range interactions to ensure stability of the system. From the laws of mechanical equilibrium we derive an expression for the surface tension.

The formalism we employed was used by Mazur<sup>13</sup> in a discussion of the electromagnetic properties of matter from a statistical mechanical point of view. The "atoms," numbered by an index  $k$ , are composed of point particles of masses  $m_{ki}$  and charges  $e_{ki}$ , located at positions  $\mathbf{R}_{ki}$ . The position of the constituent particle, numbered by  $ki$ , relative to the center of gravity  $\mathbf{R}_k$  of the atom  $k$ , is denoted by  $\mathbf{r}_{ki}$ , where

$$\mathbf{r}_{ki} = \mathbf{R}_{ki} - \mathbf{R}_k = \mathbf{R}_{ki} - \sum_i^{(k)} m_{ki} \mathbf{R}_{ki} / m_k \quad (1)$$

and  $m_k = \sum_i m_{ki}$ . Let  $f$  represent the statistical distribution function in phase space, so that the average value of a dynamical quantity  $\alpha$  is given by  $\langle \alpha f \rangle$ , the fences indicating integration over the phase space. In particular, the probability per unit volume of finding the center of gravity of the  $k$ th atom at point  $\mathbf{R}$  at time  $t$  is given by  $\langle \delta(\mathbf{R}_k - \mathbf{R}) f \rangle$ , where  $\delta$  is the Dirac delta function. Thus the number density of atoms at point  $\mathbf{R}$  at time  $t$  is

$$\rho_n(\mathbf{R}, t) = \sum_k \langle \delta(\mathbf{R}_k - \mathbf{R}) f \rangle \quad (2)$$

and the charge density at point  $\mathbf{R}$  at time  $t$  is

$$\rho(\mathbf{R}, t) = \langle \sum_{ki} e_{ki} \delta(\mathbf{R}_k - \mathbf{R}) f \rangle = \langle \sum_k e_k \delta(\mathbf{R}_k - \mathbf{R}) f \rangle \quad (3)$$

where  $e_k = \sum_i e_{ki}$ .

Following Mazur, we derive the equilibrium of forces by calculating the time rate of change of the translational momentum density  $\rho_m \mathbf{v}$ , where the mass density is

$$\rho_m(\mathbf{R}, t) = \langle \sum_{ki} m_{ki} \delta(\mathbf{R}_k - \mathbf{R}) f \rangle = \langle \sum_k m_k \delta(\mathbf{R}_k - \mathbf{R}) f \rangle \quad (4)$$

and the mean velocity is

$$\mathbf{v} = \langle \sum_k m_k \mathbf{R}_k \delta(\mathbf{R}_k - \mathbf{R}) f \rangle / \langle \sum_k m_k \delta(\mathbf{R}_k - \mathbf{R}) f \rangle \quad (5)$$

We obtain

$$\partial(\rho_m \mathbf{v}) / \partial t = -\nabla_R \cdot (\rho_m \mathbf{v} \mathbf{v} + \mathbf{p}_K) + \sum_k \langle m_k \ddot{\mathbf{R}}_k \delta(\mathbf{R}_k - \mathbf{R}) f \rangle \quad (6)$$

where

$$\mathbf{p}_K = \langle \sum_k m_k (\dot{\mathbf{R}}_k - \mathbf{v})(\dot{\mathbf{R}}_k - \mathbf{v}) \delta(\mathbf{R}_k - \mathbf{R}) f \rangle$$

is the kinetic pressure tensor. At thermal equilibrium,  $\mathbf{p}_K = nkT$  times the unit tensor, where  $n$  is the number of atoms per unit volume. We consider a system in static equilibrium, so that  $\mathbf{v} = 0$ , and  $\partial(\rho_m \mathbf{v}) / \partial t = 0$ . Our treatment is purely classical, and considers explicitly only the coulombic interactions between the particles of which the atoms are composed. We thus introduce *ad hoc* a contribution to the pressure tensor which is due to exchange forces, van der Waals forces, and other interactions which cannot be explained by classical electrostatics. Denoting it by  $\mathbf{p}_S$ , and setting eq 6 equal to zero, we have

$$0 = -\nabla_R \cdot (\mathbf{p}_K + \mathbf{p}_S) + \langle \sum_k m_k \ddot{\mathbf{R}}_k \delta(\mathbf{R}_k - \mathbf{R}) f \rangle \quad (7)$$

The electrostatic force  $\mathbf{F}_k = m_k \ddot{\mathbf{R}}_k$  may be considered as including a contribution of an external electric field  $\mathbf{E}^{\text{ext}}$  and a contribution of the other particles. In general

$$m_k \ddot{\mathbf{R}}_k = \sum_i m_{ki} \ddot{\mathbf{R}}_{ki} = \sum_i e_{ki} \mathbf{E}^{\text{ext}}(\mathbf{R}_{ki}) - \sum_{i,j}^{(i \neq k)} \nabla_{ki} (4\pi\epsilon_0)^{-1} e_{ki} e_{ij} |\mathbf{R}_{ki} - \mathbf{R}_{ij}|^{-1} \quad (8)$$

The quantities  $\mathbf{R}_{ki}$  may be expanded in a Taylor series in  $\mathbf{r}_{ki}$ . In this section, we consider only zero-order terms, which corresponds to taking into account only the interactions between the total charges of the atoms. Then

$$m_k \ddot{\mathbf{R}}_k = e_k \mathbf{E}^{\text{ext}}(\mathbf{R}_k) - (4\pi\epsilon_0)^{-1} \nabla_k \sum_i^{(i \neq k)} e_k e_i |\mathbf{R}_k - \mathbf{R}_i|^{-1}$$

where  $e_k = \sum_i e_{ki}$  and (see eq 3)

$$\begin{aligned} \nabla_R \cdot (\mathbf{p}_K + \mathbf{p}_S) &= \langle \sum_k \mathbf{E}^{\text{ext}}(\mathbf{R}_k) e_k \delta(\mathbf{R}_k - \mathbf{R}) f \rangle + \\ &(4\pi\epsilon_0)^{-1} \int \langle \sum_{k,l} e_k e_l (-\nabla_k |\mathbf{R}_k - \mathbf{R}_l|^{-1}) \delta(\mathbf{R}_k - \mathbf{R}) \times \\ &\delta(\mathbf{R}_l - \mathbf{R}') f \rangle d\mathbf{R}' = \mathbf{E}^{\text{ext}}(\mathbf{R}) \rho(\mathbf{R}) - (4\pi\epsilon_0)^{-1} \times \\ &\int \nabla_R |\mathbf{R} - \mathbf{R}'| \langle \sum_k e_k \delta(\mathbf{R}_k - \mathbf{R}) \sum_l e_l \delta(\mathbf{R}_l - \mathbf{R}') f \rangle d\mathbf{R}' \quad (9) \end{aligned}$$

The last quantity in fences is a sum of two-particle distribution functions. We write the two-particle distribution function for particles  $k$  and  $l$  as a product of one-particle distribution functions multiplied by a correlation factor

$$\langle \delta(\mathbf{R}_k - \mathbf{R}) \delta(\mathbf{R}_l - \mathbf{R}') f \rangle = \langle \delta(\mathbf{R}_k - \mathbf{R}) f \rangle \langle \delta(\mathbf{R}_l - \mathbf{R}') f \rangle (1 + h_{kl}(\mathbf{R}, \mathbf{R}')) \quad (10)$$

The correlation function  $h_{kl}(\mathbf{R}, \mathbf{R}')$  depends on  $\mathbf{R}'$  and on  $\mathbf{R} - \mathbf{R}'$ , approaching zero as  $|\mathbf{R} - \mathbf{R}'|$  approaches infinity. Thus the last term in (9) is

$$-(4\pi\epsilon_0)^{-1} \sum_{k,l} \int \nabla_{\mathbf{R}} |\mathbf{R} - \mathbf{R}'|^{-1} e_k e_l \langle \delta(\mathbf{R}_k - \mathbf{R}) f \rangle \times \\ \langle \delta(\mathbf{R}_l - \mathbf{R}') f \rangle (1 + h_{kl}(\mathbf{R}, \mathbf{R}')) d\mathbf{R}' = \sum_k e_k \rho^{(k)}(\mathbf{R}) \times \\ \sum_l \int \mathbf{E}_l(\mathbf{R}, \mathbf{R}') d\mathbf{R}' - (4\pi\epsilon_0)^{-1} \int \nabla_{\mathbf{R}} |\mathbf{R} - \mathbf{R}'|^{-1} \times \\ \sum_k e_k \rho^{(k)}(\mathbf{R}) \sum_l \int e_l \rho^{(l)}(\mathbf{R}') h_{kl}(\mathbf{R}, \mathbf{R}') d\mathbf{R}'$$

where  $\mathbf{E}_l(\mathbf{R}, \mathbf{R}')$  is the average electric field at  $\mathbf{R}$  due to particles  $l$  at  $\mathbf{R}'$ . Since this quantity, summed over  $l$  and integrated over  $\mathbf{R}'$ , is the average electric field at  $\mathbf{R}$  due to particles in the system, we may combine it with  $\mathbf{E}^{\text{ext}}(\mathbf{R})$  to obtain the total electric field at  $\mathbf{R}$ ,  $\mathbf{E}(\mathbf{R})$ . Now eq 9 becomes

$$\nabla_{\mathbf{R}}(\mathbf{p}_K + \mathbf{p}_S) = \mathbf{E}(\mathbf{R}) - (4\pi\epsilon_0)^{-1} \times \\ \int \nabla_{\mathbf{R}} |\mathbf{R} - \mathbf{R}'|^{-1} \sum_{k,l} e_k e_l \rho^{(k)}(\mathbf{R}) \rho^{(l)}(\mathbf{R}') h_{kl}(\mathbf{R}, \mathbf{R}') d\mathbf{R}'$$

The last term may be written as

$$-(4\pi\epsilon_0)^{-1} \nabla_{\mathbf{R}} \int |\mathbf{R} - \mathbf{R}'|^{-1} \sum_{k,l} e_k e_l \rho^{(k)}(\mathbf{R}) \rho^{(l)}(\mathbf{R}') \times \\ h_{kl}(\mathbf{R}, \mathbf{R}') d\mathbf{R}' + (4\pi\epsilon_0)^{-1} \int |\mathbf{R} - \mathbf{R}'|^{-1} \sum_l e_l \rho^{(l)}(\mathbf{R}') \times \\ \nabla_{\mathbf{R}} \left[ \sum_k e_k \rho^{(k)}(\mathbf{R}) h_{kl}(\mathbf{R}, \mathbf{R}') \right] d\mathbf{R}' \equiv -\nabla_{\mathbf{R}} \mathbf{p}_U + \mathbf{F}^*(\mathbf{R})$$

Finally

$$\nabla_{\mathbf{R}} \cdot (\mathbf{p}_K + \mathbf{p}_U + \mathbf{p}_S) = \mathbf{E}(\mathbf{R}) \rho(\mathbf{R}) + \mathbf{F}^*(\mathbf{R}) \quad (11)$$

Of the three contributions to the pressure tensor,  $\mathbf{p}_K$  and  $\mathbf{p}_U$  are isotropic. The contribution due to short-range forces is anisotropic, even if the forces themselves are central, because it involves the two-particle distribution function. If the forces are extremely short range (hard spheres, in the limit) the anisotropy disappears. The force  $\mathbf{F}^*(\mathbf{R})$  is also anisotropic; in fact, it has only one nonvanishing component, in the radial direction, in the case of spherical symmetry. In a homogeneous medium,  $\mathbf{F}^*$  and  $\mathbf{p}_U$  vanish. We note that  $\mathbf{F}^*$  is intrinsically due to interparticle correlations and cannot be expressed in general as the gradient of a pressure since  $\nabla \times \mathbf{F}^*$  is not zero.

In what follows, we shall neglect  $\mathbf{F}^*$  (however see Appendix, eq A6). This is apparently done by other authors who write the equations for mechanical equilibrium in terms of macroscopic or average quantities. We use the remaining expression

$$\nabla \cdot \mathbf{p} = \mathbf{E}(\mathbf{R}) \rho(\mathbf{R}) \quad (12)$$

to express the condition of mechanical equilibrium in the presence of an electric field. We consider the spherically symmetric region between a sphere of radius  $r_i$  and a sphere of radius  $r_e$ .  $\mathbf{E}$  is necessarily in the radial direction, while  $\mathbf{p}$  has at each point two independent components,  $p_N$  along the radial direction and  $p_T$  in all perpendicular directions. The properties of the system are homogeneous for

$r < r_i$  and  $r > r_e$ , and vary continuously from  $r_i$  to  $r_e$ . Our first goal is to derive a convenient expression for the surface tension in terms of the pressure and electric field at each point in the system.

We have first the experimental definition of the surface tension (Laplace equation):

$$p_i - p_e = 2\sigma/r_\sigma \quad (13)$$

Here,  $p_i$  and  $p_e$  are the (isotropic) pressures for  $r_i$  and  $r_e$ ,  $\sigma$  is the surface tension, and  $r_\sigma$  the radius of the surface of tension. Another expression for  $\sigma$  and  $r_\sigma$  is obtained by noting that the three-dimensional interfacial region is supposed to behave as a geometric surface of radius  $r_\sigma$ ,  $r_i < r_\sigma < r_e$ , on which the surface tension acts. This means that, instead of taking into account the actual values of  $p_N$  and  $p_T$  at each point in the interface, we may consider that our system consists of a homogeneous bulk phase with pressure  $p_i$  and corresponding values of other properties for  $r < r_\sigma$ , a homogeneous bulk phase with pressure  $p_e$  and corresponding values of other properties for  $r > r_\sigma$ , and a tension  $\sigma$  acting at  $r_\sigma$ .

In the Appendix we show that the volume force  $\mathbf{E}\rho$  is equivalent, in the case of spherical symmetry, to a surface force, *i.e.*, the integral of  $\mathbf{E}\rho$  over any volume is equal to the integral of the normal component of a fictitious pressure over the surface bounding the volume. In particular, one can use the force laws which obtain in the absence of field, provided one replaces  $p_T$  by  $p_T + \frac{1}{2}\epsilon_0 E^2$  and  $p_N$ , the radial component of the pressure, by  $p_N - \frac{1}{2}\epsilon_0 E^2$  (see eq A4). Now we consider the part of the interfacial region contained between the half-plane  $\phi = 0$  and the half-plane  $\phi = \alpha$ , where  $\phi$  is the polar angle. In calculating the work done in increasing  $\alpha$  by  $d\alpha$ , a virtual displacement which maintains the symmetry of the system, we may use the exact description of the forces in terms of  $p_N$  and  $p_T$  or the description in terms of  $\sigma$  and  $r_\sigma$ . Equating the two, we obtain the desired equation for  $\sigma$  and  $r_\sigma$ .

The normal force acting on the area between the circles  $r$  and  $r + dr$  and between the rays  $\theta$  and  $\theta + d\theta$  ( $\theta =$  azimuthal angle) is  $p_T(r)r = dr d\theta$  and the distance moved by these points during the displacement is  $r \sin \theta d\alpha$ . Thus, replacing  $p_T$  by  $p_T + \frac{1}{2}\epsilon_0 E^2$ , as indicated above, the work done in increasing  $\alpha$  by  $d\alpha$ , including the effect of the electric field, is

$$W = \int_0^\pi d\theta \int_{r_i}^{r_e} dr (p_T(r) + \frac{1}{2}\epsilon_0 E^2) r^2 \sin \theta d\alpha \quad (14)$$

If we consider the system as having a pressure  $p_i$  for  $r < r_\sigma$ , a pressure  $p_e$  for  $r > r_\sigma$ , and a tension  $\sigma$  at  $r = r_\sigma$ , the work is

$$W = \int_0^\pi d\theta \left[ \int_{r_i}^{r_\sigma} dr p_i r^2 \sin \theta + \int_{r_\sigma}^{r_e} dr p_e r^2 \sin \theta - \sigma r_\sigma^2 \sin \theta \right] d\alpha \quad (15)$$

since  $\sigma$  is a tension. Equating the expressions for  $W$  and rearranging, we find

$$\sigma r_\sigma^2 = \int_{r_i}^{r_\sigma} (p_i - p_T - \frac{1}{2}\epsilon_0 E^2) r^2 dr + \int_{r_\sigma}^{r_e} (p_e - p_T - \frac{1}{2}\epsilon_0 E^2) r^2 dr \quad (16)$$

This equation has also been derived by Sanfeld and others<sup>14</sup> using other arguments.

Other equations are possible, but (16) has several advan-

tages for our purposes. We are interested in calculating the change in  $\sigma$  which accompanies a change in potential, keeping interior and exterior pressures, temperature, and other parameters constant. The explicit appearance of  $p_i$  and  $p_e$  in (16) makes it easy to ensure that they are held constant when  $\sigma$  is changed. A second advantage is the way in which  $r_\sigma$  enters (16). When  $\sigma$  changes,  $r_\sigma$  will certainly change as well, and the calculation of  $\Delta r_\sigma$  would be troublesome. As we will see below, use of (16) makes such a calculation unnecessary.

We now proceed to the calculation of  $\Delta\sigma$  and the change in  $U$ , the potential drop across the double layer, leading to the Lippmann equation. In the Lippmann equation, as derived thermodynamically, pressure, temperature, and chemical potentials of bulk phases are held constant in calculation of  $\Delta\sigma/\Delta U$ . Our derivation will give a precise sense to these conditions.

#### IV. Lippmann Equation for Phase of Dielectric Constant $\epsilon_0$

We start from eq 16 and 13, which define  $\sigma$  and  $r_\sigma$ . For a change in the interface which maintains  $p_i$  and  $p_e$  constant, we have

$$\Delta\sigma r_\sigma^2 + 2\sigma r_\sigma \Delta r_\sigma = - \int_{r_i}^{r_e} \Delta(p_T + \frac{1}{2}\epsilon_0 E^2) r^2 dr + p_i r_\sigma^2 \Delta r_\sigma - p_e r_\sigma^2 \Delta r_\sigma$$

By virtue of (13), the terms in  $\Delta r_\sigma$  disappear, leaving

$$\Delta\sigma r_\sigma^2 = - \int_{r_i}^{r_e} \Delta p_T r^2 dr - \frac{1}{2}\epsilon_0 \Delta \int_{r_i}^{r_e} E^2 r^2 dr \quad (17)$$

The second integral may be written in terms of the electrostatic potential  $\psi$ :

$$-(4\pi)^{-1} \int \mathbf{E} \cdot \nabla \psi d\tau = -(4\pi)^{-1} \int \psi \mathbf{E} \cdot d\mathbf{S} + (4\pi)^{-1} \int \psi (\nabla \cdot \mathbf{E}) d\tau$$

Since  $\mathbf{E} = \hat{0}$  on the boundary surface (the spheres of radii  $r_i$  and  $r_e$ ), the surface integral vanishes. Using the Poisson equation, we have

$$\Delta\sigma r_\sigma^2 = - \int_{r_i}^{r_e} \Delta p_T r^2 dr - \frac{1}{2} \int_{r_i}^{r_e} \Delta(\psi \rho) r^2 dr \quad (18)$$

for a change maintaining  $p_i$  and  $p_e$  constant. By the definition of the ideally polarizable electrode (see section II), there is a surface, corresponding to  $r = r_\Sigma$ , on which the charge density vanishes:  $\rho(r_\Sigma) = 0$ . This surface also serves to divide the electrode or metal phase from the solution phase. Thus the electrode charge is obtained by integrating the charge density from  $r_i$  to  $r_\Sigma$  and the electrode surface charge density  $Q$  is obtained by dividing the electrode charge by  $4\pi r_\Sigma^2$ . Similarly the charge of the solution is obtained by integration of  $\rho$  from  $r_\Sigma$  to  $r_e$ . The charge density  $\rho$  is supposed to vanish for  $r \leq r_i$  and  $r \geq r_e$ . Since the electric field is zero at  $r = r_i$  and at  $r = r_e$ , we must have the electroneutrality condition

$$\int_{r_\Sigma}^{r_e} r^2 \rho dr = -Q r_\Sigma^2 \quad (19)$$

As discussed in section II, our model permits us, in calculating  $\Delta\sigma$  and  $\Delta U$ , to consider only the solution part. The change in  $U$  is produced by addition of charge to the metal phase, which produces a rearrangement of charge density in the solution, whose total charge must change to maintain electroneutrality. In summary, the electrode is considered

as a system of fixed properties, whose charge may be varied without changing its other properties.

We now have

$$\Delta\sigma r_\sigma^2 = - \int_{r_\Sigma}^{r_e} \Delta p_T r^2 dr - \frac{1}{2} \int_{r_\Sigma}^{r_e} (\Delta\psi \rho + \psi \Delta\rho) r^2 dr \quad (20)$$

If we take, as we may without loss of generality, the potential at  $r = r_\Sigma$  as zero, the potential at a point  $r > r_\Sigma$  is given by

$$\psi(r) = \frac{1}{\epsilon_0 r} \int_{r_\Sigma}^r \rho r'^2 dr - \frac{1}{\epsilon_0} \int_{r_\Sigma}^r r \rho dr - \frac{Q}{\epsilon_0} r_\Sigma + \frac{1}{\epsilon_0 r} Q r_\Sigma^2 \quad (21)$$

Since  $U$  is supposed to be the potential drop in going from the electrode to the homogeneous region of the solution

$$U = \int_{r_\Sigma}^{r_e} \frac{1}{\epsilon_0} \rho r dr + \frac{Q}{\epsilon_0} r_\Sigma \quad (22)$$

where (19) has been used. Now suppose that  $Q$  is changed to  $Q + \Delta Q$ , so that, at each point between  $r_\Sigma$  and  $r_e$ ,  $\rho$  changes to  $\rho + \Delta\rho$  and  $\psi$  changes to  $\psi + \Delta\psi$ . A direct calculation using eq 19, 21, and 22 yields

$$\int_{r_\Sigma}^{r_e} \psi \Delta\rho r^2 dr = U \Delta Q r_\Sigma^2 - \epsilon_0^{-1} \int_{r_\Sigma}^{r_e} dr \int_{r_\Sigma}^r dr' \Delta\rho(r') \rho(r) (r' r^2 - r r'^2)$$

and

$$\int_{r_\Sigma}^{r_e} \Delta\psi \rho r^2 dr = \int_{r_\Sigma}^{r_e} \psi \Delta\rho r^2 dr$$

In the calculation of  $\Delta p_T$ , we consider only the kinetic pressure contribution,  $nkT$ , assuming that the other contributions do not change appreciably with  $\Delta Q$ . Since the temperature is to be held constant during the change

$$\Delta p_T = kT \Delta n = kT \sum_i \Delta n_i(r)$$

where  $n_i(r)$  is the concentration of ion  $i$ . Thus we have

$$\Delta\sigma r_\sigma^2 = -kT \sum_i \int_{r_\Sigma}^{r_e} \Delta n_i r^2 dr - \int_{r_\Sigma}^{r_e} (\Delta\psi \rho) r^2 dr \quad (23)$$

In changing  $Q$  we are supposed to go from one equilibrium state to another, and to maintain the properties of the solution where it is homogeneous, corresponding to holding chemical potential constant. The equilibrium condition will be imposed by assuming Boltzmann distributions before and after the change in  $Q$ , with  $n_i(r_e)$  constant. Thus

$$n_i(r) = n_i(r_e) \exp(-[V_i(r) - V_i(r_e)]/kT) \quad (24)$$

The potential energy  $V_i(r)$  contains an electrostatic part  $q_i\psi(r)$  and a chemical part  $W_i(r)$  due to the electrode (see section II). Therefore, since  $n_i(r_e)$  is constant

$$\Delta n_i(r) = n_i(r_e) \exp(-[V_i(r) - V_i(r_e)]/kT) (-q_i/kT) (\Delta\psi(r) - \psi(r_e)) = n_i(r) (-q_i/kT) (\Delta\psi(r) + \Delta U)$$

We have used the fact that  $\psi(r_e) = -U$ . Substituting into (23)

$$\Delta\sigma r_\sigma^2 = \sum_i \int_{r_\Sigma}^{r_e} n_i q_i (\Delta\psi + \Delta U) r^2 dr - \int_{r_\Sigma}^{r_e} \Delta\psi \rho r^2 dr \quad (25)$$

Now  $\rho = \sum n_i q_i$ , so the first part of the "pressure" term cancels out the "electrostatic" term. The similarity of "kinetic pressure" and electrostatic terms has been discussed by Frenkel,<sup>9b</sup> who emphasized the dangers of neglecting one while changing the other.

Equation 25 may now be written

$$\Delta \sigma r_\sigma^2 = \int_{r_\Sigma}^{r_e} \rho \Delta U r^2 dr = \Delta U (-Q r_\Sigma^2)$$

Now the effective thickness of the interfacial region is, in reality, always very small compared to its radius. For experiments with a mercury drop, the radius of the interface is of the order of 500  $\mu$ , while the thickness of the interfacial region is about 100  $\text{\AA}$ . Since  $r_\sigma$  and  $r_\Sigma$  both lie within the interfacial region, their values are essentially equal. Thus  $\Delta \sigma = -Q \Delta U$ ; the Lippmann result is proved.

## V. Balance of Forces in the Presence of a Polarizable Medium

In this section we consider the possibility of having net dipole moments on some molecules. Returning to eq 7 and 8, we retain terms through second order in the  $\mathbf{r}_{ki}$  in the Taylor series expansions, and, following Mazur, neglect quadrupole moments. The electric dipole moment of molecule  $k$  is defined as

$$\boldsymbol{\mu}_k = \sum_i e_{ki} \mathbf{r}_{ki} \quad (26)$$

We now have

$$m_k \ddot{\mathbf{R}}_k = e_k \mathbf{E}^{\text{ext}}(\mathbf{R}_k) + \boldsymbol{\mu}_k \cdot \nabla_k \mathbf{E}^{\text{ext}}(\mathbf{R}_k) - \nabla_k \times \sum_{l \neq k} (e_l e_k V_{kl} + e_l \boldsymbol{\mu}_k \cdot \mathbf{U}_{kl} + e_k \boldsymbol{\mu}_l \cdot \mathbf{U}_{lk} + \boldsymbol{\mu}_k \boldsymbol{\mu}_l : \mathbf{T}_{kl}) \quad (27)$$

where we have introduced the following abbreviations:

$$V_{kl} \equiv (4\pi\epsilon_0)^{-1} |\mathbf{R}_k - \mathbf{R}_l|^{-1}$$

$$\mathbf{U}_{kl} \equiv (4\pi\epsilon_0)^{-1} \nabla_k |\mathbf{R}_k - \mathbf{R}_l|^{-1}$$

$$\mathbf{T}_{kl} \equiv (4\pi\epsilon_0)^{-1} \nabla_k \nabla_l |\mathbf{R}_k - \mathbf{R}_l|^{-1}$$

We must now calculate, for insertion in eq 7

$$\langle m_k \mathbf{R}_k \delta(\mathbf{R}_k - \mathbf{R}) f \rangle = \mathbf{E}^{\text{ext}}(\mathbf{R}) + \mathbf{P} \cdot \nabla_R \mathbf{E}^{\text{ext}}(\mathbf{R}) - \sum_{k,l} \int d\mathbf{R}' [e_k e_l \langle \nabla_R V_{kl} \delta(\mathbf{R} - \mathbf{R}_k) \delta(\mathbf{R}' - \mathbf{R}_l) f \rangle + e_l \langle \nabla_R \boldsymbol{\mu}_k \cdot \mathbf{U}_{kl} \delta(\mathbf{R} - \mathbf{R}_k) \delta(\mathbf{R}' - \mathbf{R}_l) f \rangle + e_k \langle \nabla_R \boldsymbol{\mu}_l \cdot \mathbf{U}_{lk} \delta(\mathbf{R} - \mathbf{R}_k) \delta(\mathbf{R}' - \mathbf{R}_l) f \rangle + \langle \nabla_R \boldsymbol{\mu}_k \boldsymbol{\mu}_l : \mathbf{T}_{kl} \delta(\mathbf{R} - \mathbf{R}_k) \delta(\mathbf{R}' - \mathbf{R}_l) f \rangle] \quad (28)$$

Here  $\mathbf{P}$  is the electric dipole moment per unit volume,

$$\mathbf{P} = \left\langle \sum_k \boldsymbol{\mu}_k \delta(\mathbf{R} - \mathbf{R}_k) f \right\rangle$$

*i.e.*, the polarization.

As in section III, we may separate terms corresponding to local properties from terms corresponding to correlations. For example, the dipole moment of molecule  $k$  at point  $\mathbf{R}$ , for a given configuration of charges of other particles, is equal to its average value plus a fluctuation or correlation term. Similarly, the two-particle distribution functions are written as products of one-particle distribution functions and a correlation factor  $1 + h_{kl}(\mathbf{R}, \mathbf{R}')$  (eq 10). Some of the terms reflecting the correlations may be written as divergences of local pressure tensors as shown by Mazur<sup>13</sup> and interpreted as representing short-range forces. There remain terms which cannot be so written, as in

section II. Assuming that these can be ignored we have from (2)

$$\nabla_R \cdot \mathbf{p}' = \rho \mathbf{E}^{\text{ext}}(\mathbf{R}) + \mathbf{P} \cdot \nabla_R \mathbf{E}^{\text{ext}}(\mathbf{R}) + \rho \mathbf{E}^{(1)}(\mathbf{R}) + \mathbf{P} \cdot \nabla_R \mathbf{E}^{(1)}(\mathbf{R}) + \rho \mathbf{E}^{(2)}(\mathbf{R}) + \mathbf{P} \cdot \nabla_R \mathbf{E}^{(2)}(\mathbf{R}) \quad (29)$$

Here  $\nabla_R \mathbf{p}'$  includes all short-range terms which can be written as divergences, and

$$\mathbf{E}^{(1)}(\mathbf{R}) = -(4\pi\epsilon_0)^{-1} \nabla_R \int d\mathbf{R}' \rho(\mathbf{R}') |\mathbf{R} - \mathbf{R}'|^{-1}$$

$$\mathbf{E}^{(2)}(\mathbf{R}) = -(4\pi\epsilon_0)^{-1} \nabla_R \int d\mathbf{R}' \mathbf{P}(\mathbf{R}') \cdot \nabla_{R'} |\mathbf{R} - \mathbf{R}'|^{-1}$$

representing, respectively, the field at  $\mathbf{R}$  due to the ionic charges and the field at  $\mathbf{R}$  due to molecular dipoles.

Equation 29 may now be written

$$\nabla_R \cdot \mathbf{p} = \rho \mathbf{E}(\mathbf{R}) + \mathbf{P} \cdot \nabla_R \mathbf{E}(\mathbf{R}) \quad (30)$$

where  $\mathbf{E}(\mathbf{R}) = \mathbf{E}^{\text{ext}} + \mathbf{E}^{(1)} + \mathbf{E}^{(2)}$  is the total field at point  $\mathbf{R}$ . It must be remembered that certain contributions which are undeniably of electrostatic origin, but include the effect of correlations, have been included in the "pressure" term and others have been ignored. There is thus some arbitrariness in writing the electrical force as the right member of eq 30. Mazur<sup>13</sup> and Sanfeld<sup>14</sup> have discussed this point in detail, and emphasized that the balance of forces may be written in a number of apparently different ways; in each case the meaning of pressure is different.

If we use (30) in the place of (12) to calculate the equilibrium condition for a volume of our system, we obtain

$$\int \mathbf{p} \cdot d\mathbf{S} = \int \rho \mathbf{E} d\tau + \int \mathbf{P} \cdot \nabla \mathbf{E} d\tau \quad (31)$$

Although the right side of (30) is not the gradient of a tensor, so that the volume integrals in (31) cannot in general be written as surface integrals, simplification is possible in the case of spherical symmetry. The vectors  $\mathbf{E}$  and  $\mathbf{P}$  are necessarily in the radial direction at each point in our system. Then, as shown in the Appendix (eq 7), the right side of (31) may be replaced by the integral over the surface of the normal component of a fictitious pressure. This means that we may calculate forces by ignoring the electric field terms and replacing  $p_T$  by  $p_T + \frac{1}{2}\epsilon_0 E_r^2$  and  $p_N$  by  $p_N + \frac{1}{2}(\epsilon_0 - \epsilon) E_r^2$ .

Again, we consider the volume and the fictitious displacement of section III. Equation 14 is unchanged, since only the tangential pressure enters. Therefore, eq 16 is unchanged. As previously, we now have to consider a change in  $U$  and the corresponding change in surface tension  $\sigma$ , while assuring that we pass from one state of equilibrium to another, maintaining constant the internal and external pressure, the temperature, and the composition of the two phases in homogeneous regions.

## VI. Lippmann Equation in the Presence of Polarization

We take as our point of departure eq 17. We assume no contributions from the region  $r < r_\Sigma$  so that our basic equation for the change in surface tension is

$$\Delta \sigma r_\sigma^2 = - \int_{r_\Sigma}^{r_e} \Delta p_T r^2 dr - \frac{1}{2} \epsilon_0 \int_{r_\Sigma}^{r_e} \Delta (E^2) r^2 dr \quad (32)$$

Now, the Poisson equation is

$$\nabla \cdot \mathbf{D} = \rho$$

where  $\mathbf{D} = \epsilon \mathbf{E}$  and the dielectric constant  $\epsilon$  at each point may depend on the electric field and on the position. The polarization is related to the field and the dielectric constant by

$$\mathbf{P} = (\epsilon - \epsilon_0)\mathbf{E}$$

The electric polarization at each point is proportional to the number of molecules per unit volume. The nature of these "molecules" is not specified, and their properties may be considered as depending on the chemical environment, in particular on the distance from the electrode. We have in mind, of course, induced polarization due to orientation of permanent dipole moments by an electric field.

As before, we take into account, in the calculation of  $\Delta p_T$ , only the change in the kinetic pressure. At constant temperature, this is  $\Delta nkT$ . Now, however, the total concentration  $n$  includes a contribution from solvent molecules, as well as from the ions. For simplicity, we assume that we may separate the two kinds of particles: the ions are nonpolarizable and the solvent molecules are not charged.

Thus

$$\Delta p_T = kT \left( \sum_i \Delta n_i + \Delta n_0 \right) \quad (33)$$

where the subscript 0 refers to the solvent. We assume, for all species, a Boltzmann distribution. For the ions we have eq 24, which led to

$$\Delta n_i(r) = n_i(r) (-q_i/kT) (\Delta\psi(r) + \Delta U) \quad (34)$$

The electrostatic energy of an orientable or polarizable molecule is given by

$$-\int_0^E \alpha E' dE'$$

where  $\alpha$  is the molecular electric polarizability and  $E$  the electric field. The molecules may of course be rotating species possessing permanent dipole moments. The value of  $\alpha$  may differ from point to point and may also depend on  $E'$  (dielectric saturation effect): it is well known that a strong enough electric field can essentially totally orient the solvent molecules, reducing their response to an additional imposed field and hence decreasing  $\alpha$ . The variation of  $\alpha$  with position is the electrostrictive effect: because the energy of a molecule decreases with field, such molecules tend to concentrate in regions of higher electric field. This means that the dielectric constant varies from point to point because the number of molecules changes. Thus in the equation

$$\epsilon - \epsilon_0 = n_0 \alpha \quad (35)$$

we assume that  $n_0$  follows a Boltzmann distribution

$$n_0/n_{0e} = \exp \left( - \left[ - \int_0^E \alpha E' dE' + W_0(r) \right] / kT \right)$$

Here  $n_{0e}$  is the concentration of solvent at  $r = r_e$  (where  $E = 0$ ), which is supposed to remain constant. The potential  $W_0$  is due to the electrode, and may include an attraction leading to adsorption, as well as a repulsive potential for  $r \cong r_\Sigma$ . However, we suppose  $W_0$  is independent of  $U$ , as in the case of the corresponding potential for the ions. This corresponds to a separation of "electrostatic" and "chemical" effects.

Now we may write

$$\Delta n_0 = n_{0e} \exp \left[ \left( \int_0^E \alpha E' dE' - W_0(r) \right) / kT \right] \times \Delta \left( \int_0^E \alpha E' dE' \right) / kT = n_0 (\alpha / kT) E \Delta E \quad (36)$$

Substituting into eq 33, we have

$$\Delta p_T = - \sum_i q_i n_i (\Delta\psi + \Delta U) + \frac{1}{2} n_0 \alpha \Delta(E^2) = -\rho (\Delta\psi + \Delta U) + \frac{1}{2} (\epsilon - \epsilon_0) \Delta(E^2)$$

This in turn is used in eq 32, giving

$$\Delta \sigma r_\sigma^2 = \int_{r_\Sigma}^{r_e} \rho \Delta\psi r^2 dr + \Delta U \int_{r_\Sigma}^{r_e} \rho r^2 dr - \frac{1}{2} \int_{r_\Sigma}^{r_e} (\epsilon - \epsilon_0) \Delta(E^2) r^2 dr - \frac{\epsilon_0}{2} \int_{r_\Sigma}^{r_e} \Delta(E^2) r^2 dr$$

The terms in  $\epsilon_0$  vanish, and

$$\Delta \sigma r_\sigma^2 = \int_{r_\Sigma}^{r_e} \rho \Delta\psi r^2 dr - \Delta U Q r_\Sigma^2 - \int_{r_\Sigma}^{r_e} \epsilon \mathbf{E} \cdot \Delta \mathbf{E} r^2 dr \quad (37)$$

The first integral in this equation may be treated by using Poisson's equation and integrating by parts

$$\int_{r_\Sigma}^{r_e} \rho \Delta\psi r^2 dr = (4\pi)^{-1} \int_{r_\Sigma}^{r_e} (\nabla \cdot \mathbf{D}) \Delta\psi d\tau = (4\pi)^{-1} \times \left[ \int_{r_\Sigma}^{r_e} d\mathbf{S} \cdot (\mathbf{D} \Delta\psi) - \int_{r_\Sigma}^{r_e} d\tau \nabla \cdot (\Delta\psi) \cdot \mathbf{D} \right] = - \int_{r_\Sigma}^{r_e} \Delta(-\mathbf{E}) \cdot \mathbf{D} r^2 dr$$

We have used the fact that  $\mathbf{D}$  vanishes at  $r = r_e$  while  $\psi$  and  $\Delta\psi$  vanish at  $r = r_\Sigma$ . Note that  $\Delta$  here signifies "the change in" and not the Laplacian.

Finally, eq 37 becomes

$$\Delta \sigma r_\sigma^2 = \int_{r_\Sigma}^{r_e} \Delta \mathbf{E} \cdot \mathbf{D} r^2 dr - \int_{r_\Sigma}^{r_e} \epsilon \mathbf{E} \cdot \Delta \mathbf{E} r^2 dr - \Delta U Q r_\Sigma^2$$

which may be rewritten

$$\Delta \sigma / \Delta U = -Q r_\Sigma^2 / r_\sigma^2 \cong -Q \quad (38)$$

Thus we again have the Lippmann equation.

We emphasize that in the present case, where  $\epsilon$  differs from  $\epsilon_0$ , it was necessary to consider the distribution of solvent molecules and how it changes with  $U$ . As before, the anisotropy in the pressure tensor does not enter; indeed, we assume that the change in the kinetic pressure with  $U$  is more important than the change in the other contributions to pressure. By starting from a microscopic picture and using statistical mechanics, we were able to enumerate the changes contributing to the satisfaction of the Lippmann equation. The statistical mechanical treatment, in contrast to the thermodynamic one, allows explicit definition of the quantities entering the equations.

## VII. Capacity of the Ideally Polarizable Electrode

In this section, we consider the response of an ideally polarizable electrode to an imposed alternating potential, with a view to a direct calculation of the impedance. We recall that, as part of our definition of the ideally polarizable electrode, we used the existence of a surface on which  $\rho = 0$  (section II). We also wish to recall that the changes in  $\Delta\sigma$  and  $\Delta Q$  were supposed to be carried out in such a way that the system passes from one equilibrium state to another.

Let the potential  $U$  across the electrode be the steady potential  $U_s$  plus the alternating potential  $U_0 e^{i\omega t}$ . The effect of the alternating potential is to induce an alternating current, which, divided into  $U_0 e^{i\omega t}$ , yields the impedance. No continuous current is possible because no charge can pass the surface  $r = r_\Sigma$ . The current may be calculated at any point in the circuit, provided that one considers the total current, which is conserved. This current is



$$\mathbf{J} = \rho \mathbf{v} + \partial \mathbf{D} / \partial t \quad (39)$$

The term  $\rho \mathbf{v}$  represents the transport of charge with velocity  $\mathbf{v}$ ; the second term is the displacement current. On the surface  $r = r_\Sigma$ , only the displacement current is present.

We thus have to calculate  $\partial \mathbf{D}_\Sigma / \partial t$ . If the frequency  $\omega$  of the applied voltage is sufficiently small, we may invoke the adiabatic theorem,<sup>16</sup> which states that while the Hamiltonian is being changed, the system remains in a state of equilibrium at each instant. In a state of equilibrium, all properties of the system are determined by the external, macroscopic parameters. Therefore the value of  $\mathbf{D}_\Sigma$  at any time depends only on the value of the external parameters at that time, so that  $\mathbf{D}_\Sigma$  varies only by virtue of the variation of these parameters. If the pressure, temperature, composition at  $r_e$ , etc. are kept constant, there is only one parameter which varies, namely, the potential across the system.

The fact that  $\mathbf{D}_\Sigma$  varies with time only through the variation of  $U$  is expressed mathematically as

$$\frac{\partial \mathbf{D}_\Sigma}{\partial t} = \frac{\partial \mathbf{D}_\Sigma}{\partial U} \frac{dU}{dt} = \frac{\partial \mathbf{D}_\Sigma}{\partial U} U_0 i \omega e^{i \omega t}$$

Thus we have for the impedance

$$Z = \frac{U_0 e^{i \omega t}}{i \omega U_0 e^{i \omega t} (\partial \mathbf{D}_\Sigma / \partial U)} = \left( i \omega \frac{\partial \mathbf{D}_\Sigma}{\partial U} \right)^{-1} \quad (40)$$

The impedance is clearly that of a capacitance, the capacity being

$$C = \partial \mathbf{D}_\Sigma / \partial U$$

It will be remembered that this partial derivative is to be calculated by changing  $U$  in such a way that the system is always in a state of equilibrium.

Equation 40 establishes that, as  $\omega$  approaches zero, the ideally polarized electrode behaves as a true capacity toward the perturbation of the voltage across it by an alternating potential. If there is no matter on the surface  $r = r_\Sigma$ ,  $\mathbf{D}_\Sigma = E_\Sigma$ . In any case, Gauss's theorem permits us to show that  $\mathbf{D}_\Sigma = Q$ , where  $-Qr_\Sigma^2$  is the total charge of the solution.

Combining this result with that obtained previously, we have

$$C = \partial Q / \partial U = -\partial^2 \sigma / \partial U^2 \quad (41)$$

This result is familiar in electrochemistry but a general demonstration of the existence of the capacity of the ideally polarizable electrode seems not to have been presented.

### VIII. Conclusions

We have derived the Lippmann equation by a nonthermodynamic method, in terms of a specific physical model. We attempted in our model and in our derivation to simulate the actual experimental conditions for which the validity of the Lippmann equation is demonstrated (spherical electrode, solution of constant composition, etc). This does not seem to have been done previously.

Our proof is quite different from the usual thermodynamic one, and it gives an explicit physical meaning to all quantities entering the equation. This is not true when the equation is derived thermodynamically. For example, the charge per unit area of the electrode  $Q$  appears<sup>3</sup> as a combination of Gibbs surface excesses, which are invariant to the position of the Gibbs dividing surface. Clearly, this surface can play no role in separating the solution from the metal phase. One has to invoke a specific model which as-

signs charged species to one side of the interface or the other. No spatial separation between the components of the solution and metal phases is implied by the thermodynamic treatment.

Furthermore, the thermodynamic treatment can say nothing about how the charged species are actually distributed in the interfacial region or about how they interact. By introducing a model we come to grips directly with the structure of the interfacial region. Correspondingly, we are forced to consider the existence of a physical surface which divides the solution phase from the metal phase. However a natural way of introducing such a surface is given by the model itself. An ideally polarizable electrode does not allow the passage of a steady-state current between the region outside the interface and the region inside. This can be assured if  $\rho$  vanishes at some point in the circuit, *i.e.*, on a surface  $r = r_\Sigma$ . The surface on which the charge density vanishes is a natural one for dividing up the charge of the system. The charge density for  $r < r_\Sigma$  is assigned to the metal and that for  $r > r_\Sigma$  to the solution.

In addition to the surface  $r = r_\Sigma$  on which  $\rho$  vanishes, our models involve charged and polar entities (ions and molecules). It is clear that these entities may be relatively complex. We require simply that the charge density at any point be expressible in terms of densities of ions at that point and that the polarization of the medium be expressible in terms of the densities of molecules and the electric field at that point. We have furthermore introduced, for the density of each chemical species, a Boltzmann distribution with a potential energy consisting of independent electrical and chemical parts, the electrical part depending on the total electrical potential or field at a point. Actually, the assumption of a Boltzmann distribution is not necessary, since we have used only the equation for the relative change of concentration with a change in electric potential or electric field. Our assumption, strictly speaking, is that the change in concentration at a given point depends essentially on the change of the electrical condition (eq 34 and 36). The Boltzmann distribution with independent chemical and electrical parts is sufficient, but not necessary, for this purpose.

This brings us to an important point; because we are interested in calculating the change in the surface tension rather than the surface tension itself, we were able to arrive at a concrete and explicit result. A number of physical quantities, which are difficult to calculate in a reasonable way, do not enter, since they may be reasonably supposed to be unimportant to the change of surface tension. That our model is insufficient for calculation of the surface tension itself becomes evident in the following example.

Using eq 13 to eliminate  $p_i$  from eq 16 we have

$$\frac{\sigma}{3} \left( r_\sigma^2 + \frac{2r_i^3}{r_\sigma} \right) = \int_{r_i}^{r_e} (p_e - p_T - \frac{1}{2} \epsilon_0 E^2) r^2 dr \quad (42)$$

If we neglect (a) the contribution of the region  $r_i < r_\Sigma$ , (b) the contribution to the pressure other than the kinetic pressure, and (c) the chemical force potential  $W_i$ , we have

$$p_e - p_T = kT \sum_i n_{ie} (1 - \exp[q_i(\psi + U)/kT])$$

where  $n_{ie}$  is the concentration of species  $i$  at  $r_e$ . In the expansion of the exponential, the leading term cancels out the "1" and the next term vanishes because  $\sum_i q_i n_{ie} = \rho(r_e) = 0$ . The following term in the expansion gives a negative contribution to  $p_e - p_T$ . Since  $-\frac{1}{2} \epsilon_0 E^2$  is necessarily negative, (42) predicts  $\sigma$  to be *negative*. This is because we have

ignored the contribution of the metal phase and of the short-range repulsion in  $W_i$ . In our model, both of these are assumed independent of potential, so that they give a positive but constant contribution to  $\sigma$  as a function of potential. At the potential of zero charge the electric field and the concentration gradients vanish. At other potentials, these give a negative contribution to  $\sigma$ , as shown above. That  $\sigma$  goes through a maximum at the point of zero charge is well known.

The example above emphasizes one of the important points that emerge from calculations of the kind carried out in this article. In the computation of the change of  $\sigma$ , we observe cancellation between contributions arising from electric field terms and contributions arising from pressure terms. This is simply because the pressure depends on the concentration and the concentrations of charged and polar species are partly determined by electrical forces. This sort of compensation is necessary in a demonstration of the Lippmann equation from a molecular point of view. One can show this more explicitly by deducing the Lippmann equation from the well-known Guoy-Chapman model. A discussion of the Lippmann equation in this context has recently been given;<sup>17</sup> some previous work on the subject was early done by Herzfeld and by Frumkin.<sup>18</sup>

### Appendix

Although the volume force  $\mathbf{E}\rho$  cannot in general be shown equivalent to a surface force (it is not the gradient of a tensor), the symmetry of the present problem permits a simplification of this kind. Consider the basic infinitesimal volume element, formed by the surfaces

$$r = r_0, \quad r = r_0 + dr, \quad \theta = \theta_0, \quad \theta = \theta_0 + d\theta, \\ \phi = \phi_0, \quad \phi = \phi_0 + d\phi$$

Here  $\theta$  is the azimuthal angle and  $\phi$  the polar angle. The bounding surfaces may be taken as plane in the present discussion. The electric force on this volume is

$$\mathbf{F} = \mathbf{K} dV \epsilon_0 E_r r_0^{-2} d(r_0^2 E_r)/dr \quad (\text{A1})$$

where  $\mathbf{K}$  is a unit vector in the radial direction and the volume of the element is

$$dV = r_0^2 \sin \theta_0 dr d\theta d\phi$$

Poisson's equation has been used in (A1). It will be shown that  $\mathbf{F}$  may be written as an integral over the bounding surface of  $d\mathbf{S} \cdot \mathbf{p}'$  where  $\mathbf{p}'$  is a fictitious pressure tensor with components  $p_N'$  and  $p_T'$  in the radial and tangential directions and  $d\mathbf{S}$  is the normal element of surface.

It is clear that the integral of  $d\mathbf{S} \cdot \mathbf{p}'$  will be in the  $\mathbf{K}$  direction so that we need calculate only the component in this direction to show equivalence to  $\mathbf{F}$ . The integral of  $d\mathbf{S} \cdot \mathbf{p}'$  over the face defined by  $r = r_0 + dr$  is

$$-p_N'(r_0 + dr)(r_0 + dr)^2 \sin \theta_0 d\theta d\phi$$

and the corresponding quantity for the face  $r = r_0$  is

$$p_N'(r_0)(r_0)^2 \sin \theta_0 d\theta d\phi$$

Expanding  $p_N'(r_0 + dr)$  in a power series in  $dr$  and keeping the term first order in  $dr$ , we have a net contribution to  $\mathbf{K} \cdot \mathbf{p} \cdot d\mathbf{S}$  of

$$-(2r_0 p_N' + r_0^2 dp_N'/dr) dr d\theta d\phi \sin \theta_0$$

The total force on the faces  $\phi = \phi_0$  or  $\phi = \phi_0 + d\phi$  is  $p_T'(r_0)r_0 dr d\theta$ ; to obtain the component of the force in the  $\mathbf{K}$  direction, we must multiply by a direction cosine. In Fig-

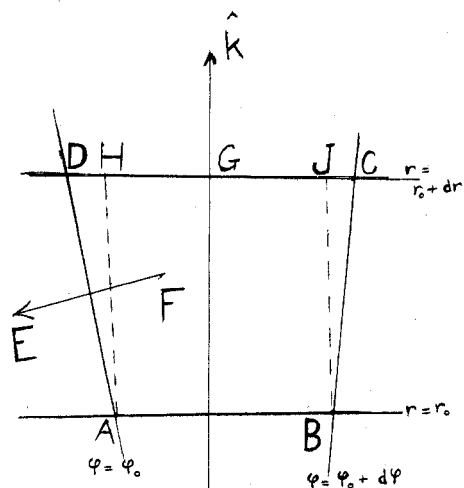


Figure 1. Face of the infinitesimal volume element corresponding to  $\theta = \text{constant}$ . The faces corresponding to  $r = \text{constant}$  and to  $\phi = \text{constant}$  are viewed end-on.  $\mathbf{EF}$  is normal to the face  $AD$  and  $\mathbf{k}$  represents the radial direction, so  $\phi$  is normal to the faces  $CD$  and  $AB$ .

ure 1, we show the faces  $\phi = \phi_0$  and  $\phi = \phi_0 + d\phi$ , viewed in a direction perpendicular to a surface  $ABCD$  on which  $\theta$  is constant. The direction cosine is  $\cos(\langle \mathbf{EFG} \rangle)$ ; since  $\mathbf{EF}$  is normal to  $AD$ ,  $\cos(\langle \mathbf{EFG} \rangle) = \sin(\langle \mathbf{DAH} \rangle)$ . Now  $\overline{AB} = r_0 \sin \theta_0 d\phi = \overline{HJ}$  and  $\overline{DC} = (r_0 + dr) \sin \theta_0 d\phi$ , so that  $\sin(\langle \mathbf{DAH} \rangle) = (\frac{1}{2} dr \sin \theta_0 d\phi) / (\overline{AD})$ . Since  $\overline{AD} = dr$  (to the order of our calculations),  $\cos(\langle \mathbf{EFG} \rangle) = \frac{1}{2} \sin \theta_0 d\phi$  and the net contribution of the faces considered is, in the  $\mathbf{K}$  direction

$$2(p_T'(r_0)r_0 dr d\theta)(\frac{1}{2} \sin \theta_0 d\phi)$$

In a similar manner, we show that the net contribution of the faces  $\theta = \theta_0$  and  $\theta = \theta_0 + d\theta$  is

$$r_0 p_T'(r_0) \sin \theta_0 dr d\theta d\phi$$

Thus the total force calculated in terms of  $\mathbf{p}'$  on the six faces is

$$\mathbf{F}' = \mathbf{K} \left[ 2p_T' r_0 \sin \theta_0 dr d\theta d\phi - \frac{d}{dr} (r_0^2 p_N') \sin \theta_0 dr d\theta d\phi \right] \quad (\text{A2})$$

Setting this quantity equal to  $\mathbf{F}$  we obtain

$$\epsilon_0 E_r \frac{d}{dr} (r_0^2 E_r)_0 = 2p_T' r_0 - \frac{d}{dr} (r^2 p_N')_0 \quad (\text{A3})$$

as a condition on  $p_T'$  and  $p_N'$ . Equation A3 is satisfied if we take

$$p_T' = \frac{1}{2} \epsilon_0 E_r^2 \quad p_N' = -\frac{1}{2} \epsilon_0 E_r^2 \quad (\text{A4})$$

Then the volume force due to the electric field is equal to the integral of the normal component of  $\mathbf{p}'$  over the surface. Since this holds for the basic infinitesimal volume element, it holds for an arbitrary volume which may be built from the infinitesimal elements; the contribution of the volume force is additive over the elements while, for the contribution of the surface force, only that of the exterior surface remains. Stated another way, the force on an arbitrary volume may be calculated by ignoring the electric field but replacing the ordinary pressure tensor  $\mathbf{p}$  by  $\mathbf{p} + \mathbf{p}'$ .

Now we consider the volume defined by

$$r_0 < r < r_0 + dr; \quad 0 < \theta < \alpha; \quad 0 < \phi < 2\pi$$

Applying our rule and demanding that the total force vanish, we have

$$2(p_T + p_T')r_0 = d(r^2 p_N' + r^2 p_N)/dr$$

or

$$(2p_T + \epsilon_0 E_r^2)r_0 = d[r^2(p_N - \frac{1}{2}\epsilon_0 E_r^2)] \quad (A5)$$

This condition for mechanical equilibrium has been derived by Sanfeld and others.<sup>14</sup>

The force  $\mathbf{F}^*$  of section III is, like the electric field, also in the radial direction at each point. It is not the gradient of a pressure-like term ( $\nabla \times \mathbf{F}^* \neq 0$ ), but its effect can also be taken into account by a fictitious pressure. Since  $\mathbf{F}^*$  is a short-range force by virtue of  $h_{kl}$ , we may suppose it to be included in  $\mathbf{p}$ .

In the presence of electric polarization, the volume force (see eq 31) may again be replaced by a surface force. In this case, the force on the basic infinitesimal volume element includes a term due to electric polarization  $P_r$ . Equation A1 is replaced by

$$\mathbf{F} = K dV \left( E_r r_0^2 \frac{d(r^2 \epsilon E_r)_0}{dr} + P_r \frac{dE_r}{dr} \right) \quad (A6)$$

where  $P_r = (\epsilon - \epsilon_0)E_r$ . In this case we have, similarly to (A3)

$$E_r \frac{d}{dr} (r^2 \epsilon E_r)_0 + \frac{1}{2}(\epsilon - \epsilon_0)r_0^2 \frac{d(E_r^2)}{dr} = 2p_T' r_0 - \frac{d}{dr} (r^2 p_N')$$

This is satisfied if we take

$$p_T' = \frac{1}{2}\epsilon_0 E_r^2 \quad p_N' = \frac{1}{2}(\epsilon_0 - 2\epsilon)E_r^2 \quad (A7)$$

Thus, in the case of spherical symmetry, one can use the force laws valid in the absence of electric field, provided that the tangential pressure is replaced by  $p_T + \frac{1}{2}\epsilon_0 E_r^2$  and the radial pressure is replaced by  $p_N + \frac{1}{2}(\epsilon_0 - 2\epsilon)E_r^2$ . Of course, the previous rule, in the absence of polarization, is a special case of this one.

## References and Notes

- (1) A. Frumkin, O. Petry, and B. Damaskin, *J. Electroanal. Chem.*, **27**, 81 (1970).
- (2) B. B. Damaskin, *Elektrokhimiya*, **5**, 771 (1969) [English translation: *Sov. Electrochem.*, **5**, 717 (1969)]. G. Morand and J. Hladik, "Electrochimie des Sels Fondus," Masson, Paris, 1969; J. O'M. Bockris and D. M. Dražić, "Electrochemical Science," Taylor and Francis, London, 1972.
- (3) (a) J. O'M. Bockris and A. K. N. Reddy, "Modern Electrochemistry," Plenum Press, New York, N.Y., 1970, Chapter 7; (b) A. Sanfeld, "An Introduction to the Thermodynamics of Charged and Polarized Layers," Wiley-Interscience, London, 1968, Chapter 14; (c) M. J. Spaarnay, "The Electrical Double Layer," Pergamon Press, Oxford, 1972, Chapter 2 ["International Encyclopedia of Physical Chemistry and Chemical Physics," Vol. 14-4].
- (4) W. Lorenz, *Z. Phys. Chem. (Leipzig)*, **219**, 421 (1962); **224**, 145 (1963); **232**, 176 (1966).
- (5) B. B. Damaskin, *Elektrokhimiya*, **5**, 771 (1969) [English translation: *Sov. Electrochem.*, **5**, 717 (1969)].
- (6) P. Delahay, "Double Layer and Electrode Kinetics," Wiley-Interscience, New York, N.Y., 1965, Chapter 2.
- (7) M. A. Proskurnin and A. N. Frumkin, *Trans. Faraday Soc.*, **31**, 110 (1935).
- (8) D. Schuhmann, C. Cachet, I. Epelboin, and L. Viet, *J. Chim. Phys.*, **62**, 1214 (1965); C. Cachet, I. Epelboin, J. C. Lestrade, and P. Ravel, *C. R. Acad. Sci.*, **264**, 1524 (1967); C. Cachet, I. Epelboin, J. C. Lestrade, and K. C. Narasimhan, *Bull. Soc. Chim. Fr.*, **5**, 1452 (1969); C. Cachet, Thesis, University of Paris, 1971.
- (9) (a) F. H. Stillinger and J. G. Kirkwood, *J. Chem. Phys.*, **33**, 1282 (1960); (b) J. Frenkel, "Kinetic Theory of Liquids," Dover Publications, New York, N.Y., 1946, p 361; (c) S. Levine, G. M. Bell, and D. Calvert, *Can. J. Chem.*, **40**, 518 (1962); (d) F. H. Stillinger, *J. Chem. Phys.*, **35**, 1584 (1961); (e) F. P. Buff and F. H. Stillinger, *J. Chem. Phys.*, **39**, 1911 (1963); (f) V. S. Krylov, *Electrochim. Acta*, **9**, 1247 (1964); (g) F. P. Buff, *J. Chem. Phys.*, **23**, 419 (1955).
- (10) S. Ono and S. Kondo, "Molecular Theory of Surface Tension in Liquids: Handbuch der Physik X," 1960, p 134.
- (11) (a) S. Levine, J. Mingins, and G. M. Bell, *J. Electroanal. Chem.* **13**, 280 (1967); (b) Reference 6, Chapter 5.
- (12) Reference 6, Section 4-5.
- (13) P. Mazur, *Advan. Chem. Phys.*, **1**, 309 (1958).
- (14) A. Sanfeld, "Introduction to the Thermodynamics of Charged and Polarized Layers," Wiley-Interscience, London, 1968, Chapter 17.
- (15) Reference 9b, Chapters 6 and 7.
- (16) L. Landau and E. Lifschitz, "Physique Statistique," Mir, Moscow, 1967, Section 11.
- (17) J. Goodisman, *J. Chim. Phys.*, accepted for publication.
- (18) K. Herzfeld, *Phys. Zeit.*, **21**, 28, 61 (1920); A. Frumkin, *Acta Physico-chim. URSS*, **18**, 473 (1943).