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## Statistical Mechanical Derivation of the Lippmann Equation. The Dielectric Constant

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We consider the polarizable electrochemical interface with spherical symmetry, and show that the common assumption of an invariant dielectric constant violates the mechanical equilibrium condition, unless its value is that of vacuum. The polarizable particles must be taken into account explicitly, which we do by deriving distribution functions for interacting charged and polarizable particles, neglecting short-range forces and short-range correlations. Calculating the change in surface tension when the distributions change so as to keep constant the temperature and the pressure inside and outside the interface, we obtain the Lippmann equation.

### Introduction

The Lippmann equation, which relates the surface tension and surface charge density of the ideally polarizable interface to the potential drop across the interface, is of fundamental importance to our understanding<sup>1</sup> of the electrochemical double layer. The proof by thermodynamics was given 100 years ago<sup>2</sup> but a general statistical mechanical proof, in terms of the molecular species which make up the interface, is not available. Since only such a proof can give the interpretation on the molecular level of such quantities as surface charge density, we have attempted, in several recent publications,<sup>3,4</sup> to construct such a proof. Starting from the balance of forces for interacting ions, the Lippmann equation was obtained<sup>3</sup> when only the changes in long-range (electrostatic) forces were considered. To take into consideration polarizable molecules, we assumed a Boltzmann distribution for their density. As shown in the next paragraph, the common assumption that these molecules may be taken into account by insertion of a dielectric constant into the force laws is in contradiction to the mechanical equilibrium condition. It is the purpose of the present paper to show how the Lippmann equation follows from the general statistical mechanical equilibrium conditions for interacting charged and polarizable species.

The explicit consideration of the polarizable (solvent) species is necessary for a consistent proof of the Lippmann equation. Their behavior cannot be subsumed under a dielectric constant  $\epsilon$  of fixed value. If the solvent molecules are not allowed to readjust to changes in electrical conditions, mechanical equilibrium is violated, as we now show.<sup>5</sup> The mechanical equilibrium condition in the presence of an electric field is<sup>6</sup>

$$\frac{dp}{dx} = \frac{d}{dx} [(\epsilon - \frac{1}{2}\epsilon_0)E^2] \quad (1)$$

where the system is supposed to be homogeneous in the  $y$  and  $z$  directions, so that the electric field  $E$  is necessarily in the  $x$  direction. If the derivative of the pressure  $p$  involves only the derivative of the densities  $n_i$  of charged species (ions) and these obey a Boltzmann distribution, (1) becomes

$$kT \frac{d}{dx} \sum_i n_{i0} e^{-e_i \psi(x)/kT} = (\epsilon - \frac{1}{2}\epsilon_0) \frac{d}{dx} E^2 \quad (2)$$

Here,  $n_{i0}$  is the density of ionic species  $i$  for  $x = \infty$ , where the electrical potential  $\psi$  is zero. These assumptions are the con-

ventional ones, used in the Gouy–Chapman, Debye–Hückel, and other theories, and can be used to generate a proof of the Lippmann equation.<sup>5,7</sup> However, the left side of eq 2 may be written:

$$kT \sum_i n_i \frac{d}{dx} (-e_i \psi/kT) = - \sum_i n_i e_i \frac{d\psi}{dx} = E\rho = E \frac{d(\epsilon E)}{dx}$$

using the Poisson equation appropriate to a region of dielectric constant  $\epsilon$ . Equation 2 now becomes

$$\epsilon E dE/dx = (2\epsilon - \epsilon_0)E dE/dx$$

This can hold only for  $\epsilon = \epsilon_0$  (no dielectric present).

For  $\epsilon \neq \epsilon_0$  there is a contradiction between the assumptions and the mechanical equilibrium condition (1), although both should follow from thermal equilibrium. A proof of the Lippmann equation<sup>5,7</sup> from the density distributions of the Gouy–Chapman theory, which require  $\epsilon = \text{constant}$ , is unsatisfactory for this reason. A more consistent proof can be given<sup>5</sup> using the assumptions of the theory, which are not themselves inconsistent for low enough ion densities.

### Basic Equations

We turn now to a proof from general statistical mechanical relations. For simplicity, we consider only the solution side of the metal–solution interface, so that the metal side serves only as a source of fields which act on the particles of the solution. The potential drop across the metal surface is supposed to be unchanged when the surface charge density changes. (It is possible<sup>4</sup> to treat the entire interface, including both metal and solution sides, but the present treatment conforms to the usual models discussed for the metal–solution interface.) For a spherical interface with surface tension  $\rho$  and surface of tension at radius  $r_\sigma$ , we showed<sup>3</sup>

$$\Delta\rho r_\sigma^2 = - \int_{r_i}^{r_\sigma} r^2 dr (\Delta p_T + \frac{1}{2}\epsilon_0 \Delta E^2) \quad (3)$$

where “ $\Delta$ ” means “change in” and  $p_T$  is the pressure in the tangential direction, except for the contribution of long-range forces, which have been separated out in the last term. The electric field  $E$  is in the radial direction, and vanishes at  $r = r_e$  (far outside the interfacial region). The metal surface is at  $r = r_i$ . Included in  $p_T$  are forces due to short-range interactions and correlations as well as the “kinetic” contribution. Only the latter will be considered here, so that

$$p_T = \sum_{i=0}^n n_i kT \quad (4)$$

assuming thermal equilibrium where  $n_i$  is the number density of species  $i$ . There are  $n$  chemical species, with  $n_0$  referring to the solvent, whose molecules are uncharged and polarizable; the other species have charged but nonpolarizable molecules.

The balance of forces between the molecules is treated, as previously,<sup>3</sup> using a formalism given by Mazur.<sup>8</sup> Under conditions of equilibrium and constant temperature

$$\nabla(\rho_k kT) = \langle m_k \ddot{\mathbf{R}}_k \delta(\mathbf{R}_k - \mathbf{R}) f \rangle \quad (5)$$

where  $f$  is the distribution function in phase space,  $\rho_k$  is the number density of particle  $k$  at point  $\mathbf{R}$ , and fences indicate integration over phase space.  $\mathbf{R}_k$  gives the position of the center of mass of  $k$ . The charged particles which make up particle  $k$  are labeled  $ki$  and have charges  $e_{ki}$ , while those making up particle  $l$  have charges  $e_{lj}$ , so that

$$m_k \ddot{\mathbf{R}}_k = -(4\pi\epsilon_0)^{-1} \sum_i \nabla_{ki} \left( \sum_{j \neq k} e_{ki} e_{lj} |\mathbf{R}_{ki} - \mathbf{R}_{lj}|^{-1} \right) \quad (6)$$

The position of particle  $ki$  is given by

$$\mathbf{R}_{ki} = \mathbf{R}_k + \mathbf{r}_{ki} \quad (7)$$

with  $\mathbf{r}_{ki}$  supposed to be small. This allows us to write, after carrying out the differentiation in (6) and expanding  $|\mathbf{R}_{ki} - \mathbf{R}_{lj}|^{-3}$  in a power series

$$\begin{aligned} -4\pi\epsilon_0 m_k \ddot{\mathbf{R}}_k = & \sum_i e_{ki} \sum_{j \neq k} e_{lj} [\mathbf{R}_i + \mathbf{r}_{ij} \\ & - (\mathbf{R}_k + \mathbf{r}_{ki})] [|\mathbf{R}_k - \mathbf{R}_j|^{-3} + \mathbf{r}_{ki} \cdot \nabla_{R_k} |\mathbf{R}_k - \mathbf{R}_j|^{-3} \\ & + \mathbf{r}_{lj} \cdot \nabla_{R_l} |\mathbf{R}_k - \mathbf{R}_j|^{-3} + \mathbf{r}_{ki} \mathbf{r}_{lj} \cdot \nabla_{R_k} \nabla_{R_l} |\mathbf{R}_k - \mathbf{R}_j|^{-3}] \quad (8) \end{aligned}$$

Terms like  $\mathbf{r}_{ki} \mathbf{r}_{kh}$  have been dropped; they correspond to moments higher than first order.

After multiplying out the terms we introduce the total charges of the molecules

$$e_k = \sum_i e_{ki}, \quad e_l = \sum_j e_{lj}$$

and the molecular dipole moments

$$\mu_k = \sum_i e_{ki} \mathbf{r}_{ki}, \quad \mu_l = \sum_j e_{lj} \mathbf{r}_{lj}$$

Then we multiply (8) by  $\delta(\mathbf{R}_k - \mathbf{R}) f$  and integrate over phase space. The leading term on the right side is

$$\begin{aligned} & \sum_{i \neq k} \int d\mathbf{R}' \langle e_{ki} e_{lj} \delta(\mathbf{R}_k - \mathbf{R}) \delta(\mathbf{R}_l - \mathbf{R}') f(\mathbf{R}_i \\ & \quad - \mathbf{R}_k) |\mathbf{R}_k - \mathbf{R}_l|^{-3} \rangle \\ & = \sum_{i \neq k} \int d\mathbf{R}' \rho_{ki}(\mathbf{R}, \mathbf{R}') e_{ki} e_{lj} |\mathbf{R}' - \mathbf{R}| |\mathbf{R} - \mathbf{R}'|^{-3} \quad (9) \end{aligned}$$

where  $\rho_{kl}$  is a two-particle distribution function. Ignoring short-range correlations,  $\rho_{kl}(\mathbf{R}, \mathbf{R}')$  becomes  $\rho_k(\mathbf{R}) \rho_l(\mathbf{R}')$ . Correlation terms are also being dropped from  $p_T$ , but we have so far been unable to demonstrate explicit cancellation of all the correlation terms in the Lippmann equation. We ignore the short-range correlations for all terms when averaging (8) over phase space. Now grouping together the particles by species, we find for species  $h$  (note  $n_h = \sum_k^{(h)} \rho_k$ )

$$\begin{aligned} & -4\pi\epsilon_0 \sum_k^{(h)} m_h \langle \ddot{\mathbf{R}}_k \delta(\mathbf{R}_k - \mathbf{R}) f \rangle \\ & = \int d\mathbf{R}' [e_h n_h(\mathbf{R}) \rho(\mathbf{R}') (\mathbf{R}' - \mathbf{R}) |\mathbf{R} - \mathbf{R}'|^{-3} \\ & \quad + (e_h n_h(\mathbf{R}) P(\mathbf{R}') - \bar{\mu}_h(\mathbf{R}) n_h(\mathbf{R}) \rho(\mathbf{R}')) |\mathbf{R} - \mathbf{R}'|^{-3} \\ & \quad + (\mathbf{R}' - \mathbf{R}) (\bar{\mu}_h(\mathbf{R}) n_h(\mathbf{R}) \rho(\mathbf{R}') - e_h n_h(\mathbf{R}) P(\mathbf{R}')) \\ & \quad \cdot \nabla_{R'} |\mathbf{R} - \mathbf{R}'|^{-3} + (P(\mathbf{R}') n_h(\mathbf{R}) \bar{\mu}_h(\mathbf{R}) \\ & \quad + n_h(\mathbf{R}) \bar{\mu}_h(\mathbf{R}) P(\mathbf{R}')) \cdot \nabla_{R'} |\mathbf{R} - \mathbf{R}'|^{-3} \\ & \quad + (\mathbf{R} - \mathbf{R}') n_h(\mathbf{R}) \bar{\mu}_h(\mathbf{R}) P(\mathbf{R}') \cdot \nabla_{R'} \nabla_{R'} |\mathbf{R} - \mathbf{R}'|^{-3}] \quad (10) \end{aligned}$$

Here  $\rho(\mathbf{R})$  is the electric charge density at  $\mathbf{R}$

$$\rho(\mathbf{R}) = \sum_k e_k n_k(\mathbf{R}) \quad (11)$$

and  $P(\mathbf{R})$  the polarization at  $\mathbf{R}$

$$P(\mathbf{R}) = \sum_k \bar{\mu}_k(\mathbf{R}) n_k(\mathbf{R}) \quad (12)$$

In (10) and (12),  $\bar{\mu}_h$  is the average electric dipole moment of a molecule of species  $h$  at point  $\mathbf{R}$ . Unlike the molecular charge  $e_h$ , it depends on position in space. We will assume below, consistent with our neglect of short-range forces, that  $\bar{\mu}_h(\mathbf{R})$  depends only on the electric field at  $\mathbf{R}$ .

Equation 10 may be simplified using the definition of the electric field,

$$\begin{aligned} E = & -(4\pi\epsilon_0)^{-1} \int d\mathbf{R}' \rho(\mathbf{R}') (\mathbf{R}' - \mathbf{R}) |\mathbf{R}' - \mathbf{R}|^{-3} \\ & - (4\pi\epsilon_0)^{-1} \int d\mathbf{R}' P(\mathbf{R}') \cdot \nabla_{R'} \nabla_{R'} |\mathbf{R} - \mathbf{R}'|^{-1} \quad (13) \end{aligned}$$

Then, combining with eq 5, we find, for the case of spherical symmetry

$$kT dn_k/dr = e_k n_k(r) E(r) + \bar{\mu}_k(r) n_k(r) dE/dr$$

For a charged particle ( $\bar{\mu}_k = 0$ ) this leads to

$$d(\ln n_k)/dr = (e_k/kT)(-d\psi/dr)$$

or

$$n_k(r) = n_k(r_e) e^{-e_k(\psi - \psi_e)}$$

where  $\psi_e = \psi(r_e)$ . In our previous treatment<sup>3</sup> we introduced an additional term in the exponential, corresponding to short-range ("chemical") forces due to the metal, so that

$$n_k(r) = n_k(r_e) e^{-(e_k\psi - e_k\psi_e + W_k(r))/kT} \quad (14)$$

For the uncharged but polarizable solvent molecules

$$d(\ln n_0)/dr = (kT)^{-1} \bar{\mu}_0(r) dE/dr$$

or

$$n_0(r) = n_0(r_e) \exp \left[ (kT)^{-1} \int_{r_e}^r dr \bar{\mu}_0(r) (dE/dr) \right]$$

Introducing an additional force due to the metal and assuming that  $\bar{\mu}_0$  depends only on  $E$ , we have

$$n_0(r) = n_0(r_e) \exp \left[ \left( \int_0^E \bar{\mu}_0(E) dE - W_0(r) \right) / kT \right] \quad (15)$$

The distributions (14) and (15), except for the  $W_i$  short-range terms, have now been shown to follow directly from the condition of mechanical equilibrium (5) and the electrostatic force law.

The electric field (13) leads to the Maxwell equation  $\nabla \cdot \mathbf{D} = \rho$ . (Mazur<sup>8</sup> has derived this fact from the definition of  $\mathbf{E}$  in terms of the component charges  $e_{ki}$  and  $e_{lj}$ .) To see this, we calculate  $\nabla \cdot \mathbf{E}$  as follows:

$$\begin{aligned} \nabla_R \cdot \mathbf{E} &= -(4\pi\epsilon_0)^{-1} \int d\mathbf{R}' \rho(\mathbf{R}') \nabla_R \cdot \nabla_R |\mathbf{R} - \mathbf{R}'|^{-1} \\ &\quad + (4\pi\epsilon_0)^{-1} \int d\mathbf{R}' P(\mathbf{R}') \cdot \nabla_R \nabla_R \cdot \nabla_R |\mathbf{R} - \mathbf{R}'|^{-1} \\ &= \epsilon_0^{-1} \int d\mathbf{R}' \rho(\mathbf{R}') \delta(\mathbf{R} - \mathbf{R}') - \epsilon_0^{-1} \int d\mathbf{R}' P(\mathbf{R}') \\ &\quad \cdot \nabla_R \delta(\mathbf{R} - \mathbf{R}') \end{aligned}$$

Carrying out the second integral by parts and rearranging, we find

$$\nabla \cdot (\epsilon_0 \mathbf{E}) + \nabla \cdot P = \rho \quad (16)$$

Defining  $\mathbf{D}$  as  $\epsilon_0 \mathbf{E} + P$  or as  $\epsilon \mathbf{E}$ , we have the desired equation. In our model for the ionic solution, the polarization  $P(\mathbf{R})$  is just  $n_0(\mathbf{R}) \bar{\mu}_0(\mathbf{R})$ .

### Lippmann Equation

We now use (14), (15), and (16) to derive the Lippmann equation. Using (14) and (15) in (4), the change in the tangential pressure is

$$\begin{aligned} \Delta p_T &= \sum_{i=0}^n \Delta n_i kT = n_0 \Delta \left[ \int_0^E \bar{\mu}_0(E) dE - W_0(r) \right] \\ &\quad + \sum_{i=1}^n n_i \Delta [-e_i \psi(r) + e_i \psi_e - W_i(r)] \end{aligned}$$

Assuming  $W_0$  and  $W_i$  are invariant to the change in electrical conditions, we have

$$\Delta p_T = n_0 \bar{\mu}_0(E) \Delta E - \rho (\Delta \psi - \Delta \psi_e)$$

to be substituted into (3). This gives

$$\Delta \sigma r_\sigma^2 = - \int_{r_i}^{r_e} r^2 dr (P \Delta E - \rho \Delta \psi + \rho \Delta \psi_e + \epsilon_0 E \Delta E) \quad (17)$$

Using (16) and integrating by parts

$$\begin{aligned} \int_{r_i}^{r_e} r^2 dr \rho \Delta \psi &= \int_{r_i}^{r_e} r^2 dr \left[ \frac{1}{r^2} \frac{d}{dr} r^2 (\epsilon_0 E + P) \right] \Delta \psi \\ &= [r^2 (\epsilon_0 E + P) \Delta \psi]_{r_i}^{r_e} - \int_{r_i}^{r_e} r^2 dr (\epsilon_0 E + P) \frac{d \Delta \psi}{dr} \end{aligned}$$

Now  $E$  and  $P$  vanish for  $r = r_e$ , while  $\epsilon_0 E + P$  at  $r = r_i$  is equal to the electric displacement  $D$  within the metal, which vanishes, plus  $Q$ , the charge per unit area on the metal. Thus we have (note that  $d \Delta \psi / dr = -\Delta E$ )

$$\int_{r_i}^{r_e} r^2 dr \rho \Delta \psi = -r_i^2 Q \Delta \psi_i + \int_{r_i}^{r_e} r^2 dr (\epsilon_0 E + P) \Delta E$$

On substituting this into (17), we find, after cancellation of terms

$$\Delta \sigma r_\sigma^2 = -(\Delta \psi_e) \int_{r_i}^{r_e} r^2 dr \rho - r_i^2 Q \Delta \psi_i \quad (18)$$

The overall electroneutrality of the interface means that the total charge on the solution side must equal  $-Q r_i^2$ . Furthermore, the change in  $U$ , the potential drop across the interface, is equal to  $\Delta(\psi_i - \psi_e)$ . Therefore (18) gives us the Lippmann equation

$$\Delta \sigma r_\sigma^2 = -Q r_i^2 \Delta U$$

Since the thickness of the interface is small compared to the radius of the metal drop,  $r_\sigma$  is essentially equal to  $r_i$ .

### References and Notes

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