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Surface Tension of a Charged and Polarized System

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Introduction

An understanding of the interfacial tension of the electrochemical interface and how it varies with the compositions of the phases adjoining the interface and with the potential drop across the interface is central to modern theories of electrochemistry.

In the polarizable interface, with which we are concerned here, a change in \( \delta U \), the electrostatic potential drop across the interface, produces a new equilibrium state (no current flows), with the potential drop across the interface, and this work cannot be written in terms of the work done by the surroundings.

Surface tension calculations for phases containing charged and polarizable particles may be based on density-functional theories or involve molecular distribution functions and intermolecular forces explicitly; of course, the surface tension of the interface between two phases is not simply the sum of single-phase surface tensions. Although thermodynamic approaches have been fruitful in electrochemistry (indeed, the Gibbs–Lippmann equation is normally derived thermodynamically), a statistical mechanical formula for the surface tension is needed to relate thermodynamic properties to molecular properties. Because the interface between two phases containing charged and polarizable particles is a region within which there exist large electric fields, local electric charge densities, and rapidly varying species densities, the usual derivation of the expression for the interfacial tension in terms of molecular distribution functions is not valid. A correctly defined formula for surface tension is needed for a true molecular theory of the interface. We give a new derivation of such a formula here, and isolate the electrostatic or long-range contribution. For several physical models, we will show that our surface tension formula again leads to the Lippmann equation.

Commonly, the surface tension formula for a charged and polarized interface is obtained starting from a formula such as

\[
\gamma = \int_{-\infty}^{\infty} dz \left[ p - p_c(z) \right]
\] (1)

for a plane interface, perpendicular to the \( z \) axis, in which only short-range forces exist. Here, \( p \) is the pressure in either homogeneous phase and \( p_c \), sometimes called the tangential pressure, involves particle densities and interparticle forces in a direction parallel to the interface. For a system containing Coulombic long-range forces, it can be argued that a term proportional to the square of the electric field should be added to \( p_c \), so that one writes instead of (1)

\[
\gamma = \int_{-\infty}^{\infty} dz \left[ p - p_c(z) - E^2(z)/8\pi \right]
\] (2)

A term in \( E^2 \) also appears in the surface tension formula in terms of correlation functions for a multicomponent charged fluid. If each partial direct correlation function is written as

\[
c_{\alpha\beta}(r) = \zeta_{\alpha\beta}(r) - \frac{Z_\alpha Z_\beta e^2}{|r - r'| kT}
\] (3)

the surface tension becomes \(-4\pi^{-1} \int dz E^2(z)\) plus a term in the \( \zeta_{\alpha\beta}(r) \).

The argument for the term \(-E^2/8\pi\) given by Sanfeld is as follows: In the absence of electric fields, the condition of mechanical equilibrium for a spherically symmetric system is

\[
(p_n/p_r) = -2r^2(p_n - p_r)
\] (4)

where \( r \) is distance from the center, and \( p_n \) and \( p_r \) are the pressures normal (radial) and tangential to the interface. If an electric field is present, a force \( \rho E + P (\partial E/\partial r) \) should be added to the force \(-p_n/p_r\). Here \( \rho \) is the charge density, \( P \) the electric polarization, and \( E \) the field; \( P \) and \( E \) are in the radial direction, and \( \nabla (E + 4\pi P) = 4\pi \rho \).

Then

\[
\frac{\partial p_n}{\partial r} \text{ becomes } \frac{\partial p_n}{\partial r} - \frac{\partial (E^2/8\pi)}{\partial r} - \frac{\partial (\rho E + P \partial E/\partial r)}{\partial r}
\] (5)

Setting the electrical force on a small volume element equal to the integral over the bounding surface of an electrical pressure \( p^e \) leads to

\[
2rE \left( \frac{E}{4\pi} + P \right) + r^2 \frac{\partial}{\partial r} \left( \frac{E^2}{4\pi} + PE \right) = 2r(p_n - p_n^e) + r^2 \left( \rho E + P \frac{\partial E}{\partial r} \right)
\]

This simplifies to

\[
\left( \frac{E}{4\pi} + P \right) = p_n^e - p_n
\]
which, combined with (4), suggests that one should replace \( p_n \) and \( p_t \) by

\[
p_n' = p_n + \frac{E^2}{8\pi} \quad p_t' = p_t - \frac{E^2}{8\pi} - \frac{EP}{2}
\]

(5)

the added terms being \( p_n' \) and \( p_t' \). Now integrating eq 3 from the interior to the exterior of the interface gives

\[
-2\int r^{(p_n' - p_t') \, dr} = p_n - p_t
\]

Since, for a spherical interface, the surface tension \( \gamma \) is defined by the Young–Laplace equation\(^9\) as \( \gamma = (p_n - p_t) \), where \( r \), is the surface of tension:

\[
\gamma = \frac{r}{\gamma} \int r^{(p_n' - p_t') \, dr}
\]

For an interface of large radius, approaching planarity, this becomes \( f(p_n' - p_t') \, d\gamma \), and mechanical equilibrium requires that \( p_n' \) be constant through the interface and equal to the pressure of either homogeneous phase bounding the interface. Therefore,

\[
\gamma = \frac{f(p_n' - p_t') \, d\gamma} \]

There are several problems with this derivation. Most important is the lack of a precise explicit definition of \( p_n \) and \( p_t \) in the presence of electric fields. If \( EP/8\pi \) is the contribution to the tangential pressure of the long-range forces, the remainder of \( p_t \) should include the kinetic pressure \( kT\Sigma n_i \) and the contribution of the short-range forces. But there should also be a short-range contribution to the pressure involving the electrostatic interaction and short-range correlations, as identified in a previous treatment\(^1\) of the Lippmann equation for the ideally polarizable electrode. Furthermore, Hurwitz and D’Alkaine\(^10\) derive, starting from the same electrostatic force as Sanfeld, \( p_\epsilon + P(\partial\epsilon/\partial r) \)

\[
p_n' = p_n - \frac{D^2}{8\pi} = \frac{E^2}{8\pi} - EP - 2\pi P^2
\]

which differs from Sanfeld’s result\(^6\) by the term \(-2\pi P^2\). In fact, Sanfeld concludes from his thermodynamic discussion of surface tension in a charged and polarized system that the definition of \( p_n \) or \( p_t \) is a matter of convention. If \( p_n \) and \( p_t \) are not well defined, one cannot say a formula for \( \gamma \) has been derived. Only a statistical mechanical treatment can resolve the ambiguity.

Another problem is that the replacements of (5) are not correct in general. Both Sanfeld\(^6\) and Hurwitz and D’Alkaine\(^10\) use the formulas for the stresses in a charged and polarized system to derive their formulas. The stress tensor \( \sigma_{ij} \) was derived by Landau and Lifshitz\(^11\) by considering the work done in displacing unit area of surface within a charged and polarized medium. They found

\[
4\pi\sigma_{ij} = \delta_{ij} \left[ -4\pi P^2 - \iint_0^E D\,d\gamma + \iint_0^E \left( \frac{\partial D}{\partial n} \right) \,d\gamma \right] + E_D\delta_{ij}
\]

for a polarized one-component system of density \( n \), where \( P^2 \) is the local pressure that would exist in the absence of the field, but with the same matter (presumably including the same distributions and interparticle correlations) present. If the polarization \( P \) is proportional to \( n \), then

\[
-\iint_0^E D\,d\gamma + n\iint_0^E \left( \frac{\partial D}{\partial n} \right) \,d\gamma =
\]

\[
-\iint_0^E D\,d\gamma + n\iint_0^E \frac{P}{n} \,d\gamma = -\iint_0^E P \,d\gamma
\]

and

\[
4\pi\sigma_{ij} = \delta_{ij} \left[ -4\pi P^2 - \left( \frac{E^2}{8\pi} \right) \right] + E_D\delta_{ij}
\]

Since \( p_n = -\sigma_{nn} \) and \( p_t = -\sigma_{tt} \), one may recover eq 5. Thus (5) is not valid in general but requires \( P \) to be proportional to \( n \).

Looking further, one sees that for a system involving long-range forces the usual derivation\(^12\) of a basic surface tension formula such as (1) is not possible. Such a derivation defines the surface tension as the work required to change the surface area of a system by unity. Let the system be defined by \( 0 \leq x \leq a, 0 \leq y \leq b, 0 \leq z \leq c \), where the interface is near \( z = c/2 \). Then one can increase \( c \) by the infinitesimal amount \( \delta c \) and decrease the system at constant temperature in which each \( r_{ij} \) changes by the same fractional amount, i.e., \( R_i - R_i + \delta R_i - R_i \), with \( \delta R_i = (R_i/2)\delta R_i \), and \( r_{ij} \) with \( \delta r_{ij} \) with \( \delta r_{ij} = (r_{ij}/2)\delta R_i \).

The change in the free energy of the system is the work done on the system by the surroundings, i.e.
The surface tension of a charged and polarized system depends on the orientation of particles and the volume of the system. The interaction between particles depends on their species and, if dipolar species are involved, on particle orientations as well as particle positions. The differentiation of the partition function, \( \delta A \), where the partition function defining the orientation, so that \( S_d Q_i(s) \), orientation of particle \( i \), is given by

\[
Q_N = \prod_i N_i^{-1} \int \prod_i \left( \int dr_i^{(0)} \left( 4\pi C \right)^{-1} d\Omega_i^{(0)} \right) e^{-\beta U} \tag{6}
\]

Here \( N_i \) is the number of particles of species \( i \), and \( \Phi \) is the interparticle interaction energy:

\[
\Phi = \lambda \sum_{i,j \neq i} \delta_i(r_i, r_j, \Omega_i^{(0)}, \Omega_j^{(0)})
\]

The interaction between particles depends on their species (\( \phi_i \)), if dipolar species are involved, particle orientations as well as particle positions enter \( \phi_i \). The integral over \( r_i^{(0)} \) extends over the volume of the system, and \( \Omega_i^{(0)} \), which gives the orientation of particle \( s \) of species \( i \), extends over the angles defining the orientation, so that \( \int d\Omega_i^{(0)} = 4\pi C \), where \( C = 1 \) for a cylindrically symmetric particle and \( 2\pi \) for others (because of the third Euler angle). We have

\[
\frac{\partial A}{\partial R_2} = \left( \frac{4\pi}{R_2^3} \right) (p_1 R_1^3 - p_2 R_2^3) = -kT \frac{\partial Q_N}{\partial R_2} \tag{7}
\]

The differentiation of \( Q_N \) is carried out using scaled coordinates. Let \( r_i^{(0)} = s_i^{(0)} R_2 \), so that \( s_i^{(0)} \) is held constant while \( R_2 \) changes. Using spherical coordinates for \( r_i^{(0)} \):

\[
Q_N = \prod_i N_i^{-1} \int \prod_i \left( \int R_i^{(0)} R_i^{(0)} d\Omega_i^{(0)} \right) \times \int \sin \theta_i^{(0)} d\theta_i^{(0)} \int d\phi_i^{(0)} \left( 4\pi C \right)^{-1} \left( \int d\Omega_i^{(0)} \right) e^{-\beta U} \tag{8}
\]

so that

\[
\left( \frac{\partial Q_N}{\partial R_2} \right) = \left( \frac{3}{4\pi} \sum_i R_i^{(0)} \right) \frac{1}{R_2} \sum_i \left( \frac{\partial Q_i^{(0)}}{\partial R_2} \right) \times \int d\Omega_i^{(0)} e^{-\beta U} \tag{9}
\]

where \( \Phi^* \) and \( \phi_i^* \) are \( \Phi \) and \( \phi_i \) expressed in terms of \( R_2 \) and \( s_i^{(0)} \). Inserting the result of differentiation into (7), we obtain

\[
\frac{4\pi}{R_2} (p_1 R_1^3 - p_2 R_2^3) = -3kT \frac{1}{R_2} + \frac{1}{2Q_N R_2} \prod_i \left( \int (4\pi C)^{-1} \int d\Omega_i^{(0)} e^{-\beta U} \right) \times e^{-\beta U} \sum_i \left( \frac{\partial Q_i^{(0)}}{\partial R_2} \right) \tag{10}
\]

We now introduce the usual one- and two-particle distribution functions \( n_i \) and \( n_{ij} \), where

\[
n_{eq}(r, \Omega, r', \Omega') = \frac{1}{N_i N_j (4\pi C)^{-1} \int d\Omega_i^{(0)} \left( 4\pi C \right)^{-2} \int d\Omega_i^{(0)} d\Omega_i^{(0)} d\Omega_i^{(0)} d\Omega_i^{(0)} e^{-\beta U}} \tag{11}
\]

If species \( k \) and \( l \) are identical, \( N_k N_l \) is replaced by \( \frac{1}{2} N_k (N_k - 1) \). Replacing the remaining integration variables in (8) by \( r_i, \Omega_i, r_j, \Omega_j \), we have

\[
4\pi(p_1 R_1^3 - p_2 R_2^3) = -3kT \int_{R_1} \left( 4\pi C \right)^{-1} dr_i d\Omega_i \sum_{r_i} n_i(r_i, \Omega_i) + \frac{1}{2} \sum_{r_i} \left( \frac{\partial U_{eq}}{\partial r_i} \right) + \frac{1}{2} \sum_{r_i} \left( \frac{\partial U_{eq}}{\partial \Omega_i} \right) \tag{12}
\]

The one-particle distribution \( n_i(r_i, \Omega_i) \) may be integrated over \( \Omega_i \), to give \( n_i(r_i) \). The pressure term also has to be considered. The pressure term cancels off the others in the integrand of (11) when \( r_i \) is near \( R_1 \), or \( R_2 \). We may now introduce the surface tension according to Laplace's equation:

\[
2\gamma / R_0 = p_1 - p_2 \tag{13}
\]

Here, \( R_0 \) must be taken as the surface tension of a macroscopic level, the surface tension is meaningful only when \( R_0 \) is large compared to the thickness of the interface, which is also the situation which permits the measurement of \( R_0 \). Combining eqs 11 and 13, we have

\[
4\pi(2\gamma R_0) = -3kT \int_{R_1} \left( 4\pi C \right)^{-1} dr_1 d\Omega_1 \sum_{r_1} n_1(r_1, \Omega_1) + \frac{1}{2} \sum_{r_1} \left( \frac{\partial U_{eq}}{\partial r_1} \right) + \frac{1}{2} \sum_{r_1} \left( \frac{\partial U_{eq}}{\partial \Omega_1} \right) + 3 \int_{R_1} \left( 4\pi C \right)^{-1} dr_1 d\Omega_1 (p_1 \theta(R_0 - r_1) + p_2 \theta(r_1 - R_0)) \tag{14}
\]

The one-particle distribution \( n_i(r_i, \Omega_i) \) may be integrated over \( \Omega_i \) to give \( n_i(r_i) \). Passing to the limit of infinite \( R_1, R_2, R_0 \), on has a planar interface, with the variable of integration \( r_i \) in the integral becoming the coordinate perpendicular to the plane of the interface. If \( R_1 \) and \( R_2 \) are large compared to their difference, \( R_1 \) and \( R_2 \) become essentially equal to \( R_0 \) and

\[
\int_{R_1} dr_1 d\Omega_1 f(r_1, \Omega_1) = 4\pi R_0^2 \int_{R_1} d\Omega_1 f(r_1, \Omega_1) \tag{15}
\]

when \( f \) is a function which is zero only for \( r_i \) between \( R_1 \) and \( R_2 \). Similarly

\[
\int_{R_1} dr_1 d\Omega_1 \int_{R_1} dr_2 d\Omega_2 g(r_1, \Omega_1, r_2, \Omega_2) = 4\pi R_0^2 \int_{R_1} d\Omega_1 G(r_1, \Omega_1) \tag{16}
\]

if \( g \) vanishes except when \( r_i \) is between \( R_1 \) and \( R_2 \) and \( r_i \) is small. This follows since \( \int d\Omega_1 G(r_1, \Omega_1, r_2, \Omega_2) \) approaches a finite limit, \( G(r_1, \Omega_1) \), independent of \( R_0 \) (the effective volume of integration does not change as \( R_1, R_2, \) and \( R_0 \) increase). The value of this
limit, by the symmetry of our system, depends only on \( r_1 \) and \( \Omega_i \). Returning to (14), we write \( \phi_{ij} \) as \( \phi_{ij}^s + \phi_{ij}^p \) (\( s = \) short-range) and \( \phi_{ij}^p \) is wholly short range and isotropic, so one may write

\[
\phi_{ij}^p = \frac{q a_{ij}^2}{r_1} \frac{q a_{ij}^2}{r_2} \frac{q a_{ij}^2}{r_2^{1/2}}
\]

The true long-range terms will be considered separately in the next section. We emphasize here that the long-range (electrostatic) potentials make a contribution to the short-range terms involving \( \phi_{ij}^p \). If the short-range terms are to be called pressures, like \( p_1 \) and \( p_2 \) in (1)-(5), one should remember that the electrostatic forces contribute to the pressures.

The correlation function \( h_{ij} \) approaches 0 for large \( r_{ij} \). Thus the terms involving \( h_{ij} \) in (14), as well as the terms involving \( h_{ij} \) and the terms depending only on \( r_1 \) (terms from the \( n_i \)), make a contribution to the curly bracket of (14) which is proportional to \( R_0^3 \). Their contribution to \( \gamma \) is then independent of \( R_0 \) as \( R_0 \to \infty \).

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The densities for each side of the interface are

\[ \rho (r_1) V(r_1) \]

interface, which is electrically neutral, is zero. To define \( Q \), each charged and polarized system, one requires a quantity, like \( \Gamma \), to the homogeneous phase at each point are in the radial direction.

Since \( V(r_1) \) is the Lippmann equation. Note that it was necessary to differentiate the volume integral of \( V(r_1) \) which involves only long-range terms, is

\[ \sum dE/dz = \sum \frac{n_i(z)}{kT} \frac{dV}{dz} = \sum \frac{n_i(z)}{kT} \frac{dV}{dz} \]

Introducing the surface charge densities \( Q_+ \) and \( Q_- \)

\[ Q_+ = \int_{-\infty}^{\infty} \frac{dE}{dz} \sum \frac{n_i(z)}{kT} = \int_{-\infty}^{\infty} \frac{dE}{dz} \sum \frac{n_i(z)}{kT} \]

with \( Q_+ = -Q_- \) because of overall electrical neutrality.

The most commonly used model for the electrochemical interface is the Gouy–Chapman model, although it is usually applied to only one side of the interface since other being taken as surroundings. In this model interparticle correlations and short-range forces are neglected, and each charged species obeys a Boltzmann relation:

\[ n_i(z) = n_i(\pm \infty) \exp\left[ -q_i(V(z) - V(\pm \infty))/kT \right] \]

Each species is referred to the homogeneous phase at \( +\infty \) or the phase at \( -\infty \).

To verify the Lippmann equation for this model, we first differentiate \( \sum n_i(z) \) with respect to \( z \):

\[ \sum \frac{dn_i}{dz} = \int_{-\infty}^{\infty} \frac{dE}{dz} \sum \frac{n_i(z)}{kT} = \sum \frac{n_i(z)}{kT} \frac{dV}{dz} \]

Since \( \sum n_i(z) = \rho \) (4πr2/4πr2), this shows that \( kT \sum n_i(z) - E(z)/8\pi \) is independent of \( z \) and hence equal to \( \rho \) at \( z = \pm \infty \). Then, (25), which involves only long-range terms, is

\[ 2\gamma = \int_{-\infty}^{\infty} -\frac{1}{8\pi} E(z)^2 - \frac{1}{2} P(z) E(z) + 3kT \sum n_i(z) - E(z) \]

Since no polarizable species are present

\[ \gamma = \int_{-\infty}^{\infty} -\frac{E(z)^2}{4\pi} = \int_{-\infty}^{\infty} [p - kT \sum n_i(z) - E(z)/8\pi] \]

Now for a change at constant \( p \) and \( T \)

\[ \Delta\gamma = \int_{-\infty}^{\infty} -\sum q_i n_i \Delta V(\pm \infty) - \sum \Delta q_i n_i \Delta V(=0) - \rho \Delta V \]

Introducing the surface charge densities \( \Gamma_+ \) and \( \Gamma_- \), we have

\[ \Delta\gamma = -\rho \Delta V(\pm \infty) - \rho \Delta V \]

which is the Lippmann equation. Note that it was necessary to take a dielectric constant of unity here and assume no polarizable species were present, even though it is usual in the Gouy–Chapman model to represent the polarizable species (solvent) by introducing a dielectric constant different from unity.

In the presence of polarizable species, \( kT \sum n_i(z) - E^2/8\pi \) is not independent of \( z \), because the density of the polarizable species should be included in \( \sum n_i(z) \) and \( P \neq 0 \). It has been suggested (see eq 5) that in this case \( kT \sum n_i(z) - E^2/8\pi \) is not independent of \( z \), with \( E = D = E + 4\pi P \). To verify this, we write \( \sum = \sum^{(+)} + \sum^{(-)} \), where \( P = \sum^{(0)} n_{\mu i} \) (sum over polarizable species) and the dipole moment \( \mu_i \) may depend on \( E \). Then we write a Boltzmann expression for each polarizable species:

\[ n_i(z) = n_i(\pm \infty) e^{-z(\pm \infty)} \]

Now, using (27) for the charged species

\[ \frac{d}{dz} \left( kT \sum n_i(z) - E^2/8\pi - EP \right) = -\rho \frac{dV}{dz} - \sum q_i n_i \frac{dE}{dz} - \frac{E \frac{dE}{dz} + 4\pi P \frac{dE}{dz}}{4\pi} \]

since \( E + 4\pi P = D \) and \( dE/dz = 4\pi P \). For (31) to vanish, \( f_i \) must
equal - \int_0^\infty dE' \mu_0(E'). In previous work,^19 f_n is the work required to introduce a dipolar particle into an electric field, was written in this way by analogy to (27), in which \( q(V - V(\pm \infty)) \) appears as the work required to introduce a charged particle. According to (31), \( kT \sum n(z) - E^2/8\pi \) is independent of \( z \), so that it may replace \( p \) in the surface tension formula (25). Then we get

\[ \gamma = \int_{-\infty}^{\infty} dz \left\{ -\frac{E_0 dE}{8\pi} + p - kT \sum n_i \right\} \]

which is identical to (28). Now, however

\[ \Delta \gamma = \int_{-\infty}^{\infty} dz \left\{ \frac{\Delta E}{4\pi} + \rho \Delta V - \Sigma q_i n_i \Delta V(\pm \infty) - \right\}

\[ \sum i q_i n_i \Delta V(\pm \infty) - kT \sum n_i \left( \frac{-1}{kT} \frac{d\phi_j}{dE} \right) \Delta E \]

The term in \( \rho \Delta V \) integrated by parts, gives \((4\pi)^{-1} (E + 4\pi p) \Delta E \), so

\[ \Delta \gamma = \int_{-\infty}^{\infty} dz \left[ P \Delta E + \sum n_i (-d \phi) \Delta E \right] - Q_0 \Delta V(\pm \infty) - \]

\[ Q_0 \Delta V(\pm \infty) = -Q_0 \Delta V(\pm \infty) - \]

\[ (32) \]

and the Lippmann equation is satisfied for this model. According to (30), there is an inconsistency in the Gouy-Chapman model when the polarizable species are considered only as providing a dielectric constant; the density of polarizable species must vary in space because of the variation in electric field (electrostriction). This implies a spatial variation of dielectric constant. Many models for the electrolyte part of the electrochemical double layer posit a position-dependent dielectric constant. Almost always, one distinguishes between the compact and diffuse parts^20 of the double layer, with very different dielectric constants, and some workers have introduced a dielectric constant which varies as a function of distance \( d \) from the electrode, approaching the bulk dielectric constant as \( d \to \infty \). The present work suggests that the spatial variation of dielectric constant should depend on the state of charge of the electrode. (Note that the dielectric constant is generally mostly due to orientation of permanent dipoles; the electronic polarizability of solvent molecules has not been considered here.)

Conclusions

We have derived a formula for the surface tension of an interfacial system containing charged and polarizable species in terms of the interparticle potentials and the one- and two-particle distribution functions, eq 14. This formula is for a spherical interface and involves the surface of tension, \( \gamma \). The long-range terms, involving integrals of products of the electrostatic interaction potentials and one-particle distributions, are extracted and rewritten in terms of the electrostatic potential, electric charge density, and electric polarization, eq 23. Then, on passing to the limit of a planar interface, the value of \( \gamma \) becomes irrelevant, as short-range terms approach proper limits, leading to an explicit formula for the surface tension of a planar interface, eq 25.

Several simple models for an electrochemical interface are then considered in light of the derived formula. The commonly used Gouy-Chapman model neglects short-range forces and inter-particle correlations, and the distribution of each charged species is Boltzmann-like. We show that the pressure in the direction normal to the interface is \( kT \sum n(z) - E^2/8\pi \), which is independent of \( z \), if there are no polarizable species present. Then we show that the Lippmann equation, eq 29, is verified. Commonly, the Gouy-Chapman model is used for ions in a solution of dielectric constant different from unity, but \( kT \sum n(z) - E^2/8\pi \) is then no longer conserved through the interface. This inconsistency with mechanical equilibrium can be remedied if polarizable species are included in \( \sum n_i \) and

\[ n_i(z = \pm \infty) \exp \left[ \int_0^{\infty} dE' \mu_0(E') \right] \]

for each polarizable species. Then \( kT \sum n(z) - (E^2/8\pi) \) is independent of \( z \), and the Lippmann equation is satisfied. The variation of the density of polarizable species with position means that the dielectric constant is not a constant but a function of position.

It will be of interest to investigate other models in the same way as we have investigated the Gouy-Chapman model, to see what is required for conservation of normal pressure and to test whether the Lippmann equation is satisfied. Similarly, our surface tension formula should be analyzed to see under what conditions the surface tension can be written as a sum of the contributions of the two phases (e.g., metal and electrolyte), and when one is justified in considering one phase only and treating the other as an impenetrable barrier and a source of electric field. Other commonly used approximations should also be investigated, now that we have a completely explicit formula for the surface tension.

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