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Surface Tension of a Charged and Polarized System

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Usually, the formula for the surface tension of a planar charged and polarized interface is obtained from that for a system involving only short-range forces, $\gamma = \int_{-\infty}^{\infty} dz [p - p_x(z)]$, by replacing the tangential pressure p_x by $p_x + E^2/8\pi$. Problems with this include (a) p_x is no longer explicitly defined, (b) the electrostatic stress term $E^2/8\pi$ is not correct in general but only if polarization is proportional to density of polarizable species, (c) the derivation of the formula in terms of p and p_x involves calculating the work to expand a volume containing the interface, and this work cannot be written in terms of the pressure of the surroundings when there are long-range forces. To derive a formula free from these objections, we consider the spherical system contained between $r = R_1$ and $r = R_2$ and containing charged and dipolar particles, the orientation of the latter giving rise to the electrical polarization. There is no electric field, electric polarization, or local charge density for $r < R_1$ or for $r > R_2$. If this system is expanded keeping the ratios of all radii fixed, the work done by the surroundings is $4\pi(p_1 R_1^2 \delta R_1 - p_2 R_2^2 \delta R_2)$, which is set equal to the change in free energy, calculated from the canonical partition function. The surface tension is defined as $(R_0/2)(p_1 - p_2)$, where R_0 is the surface of tension. When R_1 becomes infinite (plane interface), the value of R_0 becomes irrelevant. Both long-range and short-range terms in the surface tension are shown to behave properly for $R_1 \rightarrow \infty$, the long-range terms being proportional to $\int dr [-\rho(r) V(r) + 3P(r) E(r)]$ (P = polarization). If only charged particles are present (no polarization), correlations and short-range forces are neglected, and the distribution of each charged species n_i follows the Boltzmann law with energy $q_i V$, it is shown that $kT \sum_i n_i - E^2/8\pi$ is independent of z . Using this fact with our surface tension formula, we prove the Lippmann equation. If dipolar particles are present as well as charged particles, the former must be included in $\sum_i n_i$. Then the quantity $kT \sum_i n_i - E^2/8\pi - EP$ is shown independent of z , and our surface tension formula again leads to the Lippmann equation.

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.¹⁻⁴ In the polarizable interface, with which we are concerned here, a change in U , the electrostatic potential drop across the interface, produces a new equilibrium state (no current flows), with the change in interfacial tension γ given by the Gibbs–Lippmann equation, $(\partial\gamma/\partial U)_{T,\text{comp}} = -Q$, where Q is the surface charge density on one side of the interface. 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;⁵ 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^{1,4}), 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 derived 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 verifies the Gibbs–Lippmann equation.

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

$$\gamma = \int_{-\infty}^{\infty} dz [p - p_x(z)] \quad (1)$$

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_x , 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 argued⁶ that a term proportional to

the square of the electric field should be added to p_x , so that one writes instead of (1)

$$\gamma = \int_{-\infty}^{\infty} dz (p - p_x(z) - E^2(z)/8\pi) \quad (2)$$

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

$$c_{\alpha\beta}(\mathbf{r}, \mathbf{r}') = \tilde{c}_{\alpha\beta}(\mathbf{r}, \mathbf{r}') - \frac{Z_\alpha Z_\beta e^2}{|\mathbf{r} - \mathbf{r}'|kT}$$

the surface tension becomes $-(4\pi)^{-1} \int dz E^2(z)$ plus a term in the $\tilde{c}_{\alpha\beta}$.⁷

The argument for the term $-E^2/8\pi$ given by Sanfeld⁶ is as follows: In the absence of electric fields, the condition of mechanical equilibrium for a spherically symmetric system is

$$(\partial p_n / \partial r) = -2r^{-1}(p_n - p_t) \quad (3)$$

where r is distance from the center, and p_n and p_t 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 $-(\partial p_n / \partial r)$. Here ρ is the charge density, P the electric polarization, and E the field; P and E are in the radial direction, and $\nabla \cdot (\mathbf{E} + 4\pi \mathbf{P}) = 4\pi \rho$. Then

$$\frac{\partial p_n}{\partial r} \text{ becomes } \frac{\partial p_n}{\partial r} - \frac{\partial(E^2/8\pi)}{\partial r} - \frac{\partial(EP)}{\partial r} \quad (4)$$

Setting the electrical force on a small volume element equal to the integral over the bounding surface of an electrical pressure p^e leads to⁸

$$2rE\left(\frac{E}{4\pi} + P\right) + r^2 \frac{\partial}{\partial r} \left(\frac{E^2}{4\pi} + PE\right) = 2r(p^e_t - p^e_n) + r^2 \left(\rho E + P \frac{\partial E}{\partial r}\right)$$

This simplifies to

$$E\left(\frac{E}{4\pi} + P\right) = p^e_t - p^e_n$$

which, combined with (4), suggests that one should replace p_i and p_n by

$$p_i' = p_i + \frac{E^2}{8\pi} \quad p_n' = p_n - \frac{E^2}{8\pi} - EP \quad (5)$$

the added terms being p_i^e and p_n^e . Now integrating eq 3 from the interior to the exterior of the interface gives

$$-2 \int_i^e r^{-1} (p_n' - p_i') dr = p_e - p_i$$

Since, for a spherical interface, the surface tension γ is defined by the Young-Laplace equation⁹ as $1/2r_\gamma(p_i - p_e)$, where r_γ is the surface of tension:

$$\gamma = r_\gamma \int_i^e r^{-1} (p_n' - p_i') dr$$

For an interface of large radius, approaching planarity, this becomes $\int (p_n' - p_i') dz$, 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, $\gamma = \int (p - p_i') dz$, which is eq 2 (with $p_i = p_x$).

There are several problems with this derivation. Most important is the lack of a precise explicit definition of p_n and p_i in the presence of electric fields. If $E^2/8\pi$ is the contribution to the tangential pressure of the long-range forces, the remainder of p_i' should include the kinetic pressure $kT \sum n_i$ 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 treatment⁸ of the Lippmann equation for the ideally polarizable electrode. Furthermore, Hurwitz and d'Alkaine¹⁰ derive, starting from the same electrostatic force as Sanfeld, $\rho E + P(\partial E/\partial r)$

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

which differs from Sanfeld's result⁶ 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_i is a matter of convention. If p_n and p_i are not well defined, one cannot say a formula for γ 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 Sanfeld⁶ and Hurwitz and D'Alkaine¹⁰ use the formulas for the stresses in a charged and polarized system to derive their formulas. The stress tensor σ was derived by Landau and Lifschitz¹¹ by considering the work done in displacing unit area of surface within a charged and polarized medium. They found

$$4\pi\sigma_{ik} = \delta_{ik} \left[-4\pi p^0 - \int_0^E \mathbf{D} \cdot d\mathbf{E} + n \int_0^E \left(\frac{\partial \mathbf{D}}{\partial n} \right) d\mathbf{E} \right] + E_i D_k$$

for a polarized one-component system of density n , where p^0 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 $\mathbf{P}$ is proportional to n , then

$$-\int_0^E \mathbf{D} \cdot d\mathbf{E} + n \int_0^E \left(\frac{\partial \mathbf{D}}{\partial n} \right) d\mathbf{E} = -\int_0^E \mathbf{D} \cdot d\mathbf{E} + n \int_0^E 4\pi \frac{\mathbf{P}}{n} \cdot d\mathbf{E} = -\int_0^E \mathbf{E} \cdot d\mathbf{E}$$

and $4\pi\sigma_{ik} = \delta_{ik} [-4\pi p^0 - 1/2 E^2] + E_i D_k$. Since $p_i = -\sigma_{xx}$ and $p_n = -\sigma_{zz}$, one may recover eq 5. Thus (5) is not valid in general but requires $\mathbf{P}$ to be proportional to n .

Looking further, one sees that for a system involving long-range forces the usual derivation^{12,13} 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 a by the infinitesimal amount δa and b by δb and decrease

Figure 1. Geometry of the region $R_1 < r < R_2$, which is imagined to be expanded in the derivation of the surface tension formula. In the regions $r < R_1$, at pressure p_1 , and $R > R_2$, at pressure p_2 , are homogeneous and isotropic phases, containing no (average) electric fields, polarizations, or charge densities. The surface $r = R_0$ is the surface of tension.

c by $(c/a)\delta a + (c/b)\delta b$, so that the volume is constant to first order and the interfacial area increases by $a\delta b + b\delta a$. Calculating the change in free energy leads to a formula such as eq 1 if there are only short-range forces, because the work involved can be written in terms of pressures in the surroundings. One need not consider the surroundings in detail since the importance of interactions in regions far from the boundaries of the system can be made as small as desired by increasing the size of the system. This is not so if there are electric fields for some value of z for all x and y . In this case, one must specify what deformation is carried out on the surroundings during the deformation of the system. The surroundings must, like the system, be charged and polarized, so that interaction of the system with faroff parts of the surroundings may not be neglected.

In the present article we give a new derivation of a formula for the surface tension of a system with long-range forces, free from the above objections. To avoid considering the surroundings explicitly, we consider a spherically symmetric system, with unpolarized surroundings, which is eventually allowed to approach planarity. Long-range terms in the surface tension formula are isolated, and an explicit unambiguous expression for the "pressure" or short-range terms is obtained.

Basic Formula

Consider a spherically symmetric system, extending from $r = R_1$ to $r = R_2$ (where r is the distance from the center), as shown in Figure 1. The regions $r < R_1$ and $r > R_2$ contain homogeneous and isotropic phases 1 and 2, so that the electric field, charge density, and polarization density vanish in these regions. Since the forces exerted by the surroundings are short-range only and can be expressed as pressure with the conventional definitions, we can conveniently consider the work done during a deformation of the system to derive our formula. We will eventually allow the radii R_1 and R_2 to become large compared to their difference, which corresponds to a planar interface.

The system is at equilibrium at temperature T . Let p_1 and p_2 be the pressures of the homogeneous phases 1 and 2. Within the system, $\mathbf{r}_i^{(s)}$ is the position of particle number s of species i , so $r_i^{(s)}$ is the distance of this particle from the origin. Each particle of species i carries a charge q_i and a permanent dipole moment μ_i . The electric polarization arises from the orientation of these moments; electronic polarization is not included in the model.

We calculate the free energy change for a deformation of the system at constant temperature in which each $r_i^{(s)}$ changes by the same fractional amount, i.e., $R_2 \rightarrow R_2 + \delta R_2$, $R_1 \rightarrow R_1 + \delta R_1$ with $\delta R_1 = (R_1/R_2)\delta R_2$, and $r_i^{(s)} \rightarrow r_i^{(s)} + \delta r_i^{(s)}$ with $\delta r_i^{(s)} = (r_i^{(s)}/R_2)\delta R_2$. The change in the free energy of the system is the work done on the system by the surroundings, i.e.

$$\delta A = p_1(4\pi R_1^2 \delta R_1) - p_2(4\pi R_2^2 \delta R_2) = (4\pi/R_2)(p_1 R_1^3 - p_2 R_2^3) \delta R_2$$

In terms of the partition function, $\delta A = -kT(\partial \ln Q_N / \partial R_2) \delta R_2$, where the partition function Q_N is given by

$$Q_N = [\prod_i N_i!]^{-1} \left\{ \prod_i \left(\int d\mathbf{r}_i^{(s)} (4\pi C)^{-1} d\Omega_i^{(s)} \right) e^{-\Phi/kT} \right\} \quad (6)$$

Here N_i is the number of particles of species i , and Φ is the interparticle interaction energy:

$$\Phi = \frac{1}{2} \sum_{i,j} \sum_{s,t} \phi_{ij}(\mathbf{r}_i^{(s)}, \mathbf{r}_j^{(t)}, \Omega_i^{(s)}, \Omega_j^{(t)})$$

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

$$\left(\frac{\partial A}{\partial R_2} \right)_{T, N_i, p_1, p_2} = \left(\frac{4\pi}{R_2} \right) (p_1 R_1^3 - p_2 R_2^3) = \frac{-kT \left(\frac{\partial Q_N}{\partial R_2} \right)}{Q_N} \quad (7)$$

The differentiation of Q_N is carried out using scaled coordinates.

Let $\mathbf{r}_i^{(s)} = s_i^{(s)} R_2$, so that $s_i^{(s)}$ is held constant while R_2 changes. Using spherical coordinates for $\mathbf{r}_i^{(s)}$

$$Q_N = \prod_i (N_i!)^{-1} \prod_s \left\{ \int_{R_1/R_2}^1 R_2^3 (s_i^{(s)})^2 ds_i^{(s)} \times \int_0^\pi \sin \theta_i^{(s)} d\theta_i^{(s)} \int_0^{2\pi} d\phi_i^{(s)} (4\pi C)^{-1} \int d\Omega_i^{(s)} \right\} e^{-\Phi^*/kT}$$

so that

$$(\partial Q_N / \partial R_2) = (3 \sum_i N_i) R_2^{-1} Q_N + \prod_i (N_i!)^{-1} \prod_s \left\{ (4\pi C)^{-1} \times \int d\mathbf{r}_i^{(s)} d\Omega_i^{(s)} \right\} e^{-\Phi^*/kT} (-2kT)^{-1} \sum_{kl} \sum_u \sum_v (\partial \phi_{kl}^* / \partial R_2)$$

where Φ^* and ϕ_{kl}^* are Φ and ϕ_{kl} expressed in terms of R_2 and $s_i^{(s)}$. Inserting the result of differentiation into (7), we obtain

$$\frac{4\pi}{R_2} (p_1 R_1^3 - p_2 R_2^3) = -3kT \frac{\sum_i N_i}{R_2} + \frac{1}{2Q_N R_2} \prod_i \left\{ (4\pi C)^{-1} \int d\mathbf{r}_i^{(s)} d\Omega_i^{(s)} \right\} \times e^{-\Phi^*/kT} \sum_{kl} \sum_u \sum_v \left[r_k^{(u)} \left(\frac{\partial \phi_{kl}}{\partial r_k^{(u)}} \right) + r_l^{(v)} \left(\frac{\partial \phi_{kl}}{\partial r_l^{(v)}} \right) \right] \quad (8)$$

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

$$n_{kl}(\mathbf{r}_k^{(u)}, \Omega_k^{(u)}, \mathbf{r}_l^{(v)}, \Omega_l^{(v)}) = \frac{1}{N_k N_l Q_N} \prod_i \left\{ (4\pi C)^{-1} \times \int d\mathbf{r}_i^{(s)} d\Omega_i^{(s)} \right\} \left\{ (4\pi C)^{-2} \int d\mathbf{r}_k^{(u)} d\Omega_k^{(u)} \int d\mathbf{r}_l^{(v)} d\Omega_l^{(v)} \right\}^{-1} e^{-\Phi^*/kT} \quad (9)$$

If species k and l are identical, $N_k N_l$ is replaced by $1/2 N_k (N_k - 1)$. Replacing the remaining integration variables in (8) by $\mathbf{r}_1$, Ω_1 , $\mathbf{r}_2$, and Ω_2 , we have

$$4\pi(p_1 R_1^3 - p_2 R_2^3) = -3kT \int_{R_1}^{R_2} (4\pi C)^{-1} d\mathbf{r}_1 d\Omega_1 \sum_i n_i(\mathbf{r}_1, \Omega_1) + \frac{1}{2} \sum_{kl} (4\pi C)^{-2} \times \int d\mathbf{r}_1 d\mathbf{r}_2 d\Omega_1 d\Omega_2 n_{kl}(\mathbf{r}_1, \Omega_1, \mathbf{r}_2, \Omega_2) \left\{ r_1 \left(\frac{\partial \phi_{kl}}{\partial r_1} \right) + r_2 \left(\frac{\partial \phi_{kl}}{\partial r_2} \right) \right\} \quad (10)$$

Let R_0 be between R_1 and R_2 ; although its precise value is later shown to be unimportant, it should correspond to the region in which electric field and polarization are nonzero. Equation 10 may be rewritten as

$$(4\pi/3)(p_1 R^3 - p_2 R^3) = - \int_{R_1}^{R_2} (4\pi C)^{-1} d\mathbf{r}_1 d\Omega_1 \left(kT \sum_i n_i(\mathbf{r}_1, \Omega_1) - \frac{1}{6} \int_{R_1}^{R_2} (4\pi C)^{-1} d\mathbf{r}_2 d\Omega_2 \sum_{ij} n_{ij}(\mathbf{r}_1, \Omega_1, \mathbf{r}_2, \Omega_2) \left[r_1 \left(\frac{\partial \phi_{ij}}{\partial r_1} \right) + r_2 \left(\frac{\partial \phi_{ij}}{\partial r_2} \right) \right] - p_1 \Theta(R_0 - r_1) - p_2 \Theta(r_1 - R_0) \right) - p_1 (4\pi/3)(R_0^3 - R_1^3) - p_2 (4\pi/3)(R_2^3 - R_0^3) \quad (11)$$

where $\Theta(x)$ is the step function: $\Theta(x) = 1$, $x < 0$ and $\Theta(x) = 0$, $x \geq 0$. In the right member of (11), the integrand vanishes when r_1 is near R_1 or R_2 , since the electrostatic terms vanish after angular averaging and ϕ_{kl} depends only on r_{12} so that $r_1(\partial \phi_{kl}/\partial r_1) + r_2(\partial \phi_{kl}/\partial r_2) = r_{12}(d\phi_{kl}/dr_{12})$. The pressure in a homogeneous phase is given by

$$pV = kT \sum_i N_i - \frac{1}{6} \sum_{kl} (4\pi C)^{-2} \int d\mathbf{r}_1 d\mathbf{r}_2 d\Omega_1 d\Omega_2 n_{kl}(\mathbf{r}_1, \Omega_1, \mathbf{r}_2, \Omega_2) r_{12} d\phi_{kl}/dr_{12} \quad (12)$$

so that the pressure term cancels off the others in the integrand of (11) when r_1 is near R_1 or R_2 .

We may now introduce the surface tension according to Laplace's equation:⁹

$$2\gamma/R_0 = p_1 - p_2 \quad (13)$$

Here, R_0 must be taken as the surface of tension,^{6,13} its value being defined in terms of the moments of the tangential forces. On 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

$$4\pi(2\gamma)R_0^2 = -3kT \int_{R_1}^{R_2} (4\pi C)^{-1} d\mathbf{r}_1 d\Omega_1 \sum_i n_i(\mathbf{r}_1, \Omega_1) + \frac{1}{2} \int_{R_1}^{R_2} (4\pi C)^{-1} d\mathbf{r}_1 d\Omega_1 \int_{R_1}^{R_2} (4\pi C)^{-1} d\mathbf{r}_2 d\Omega_2 \times \sum_{ij} n_{ij}(\mathbf{r}_1, \Omega_1, \mathbf{r}_2, \Omega_2) \left(r_1 \frac{\partial \phi_{ij}}{\partial r_1} + r_2 \frac{\partial \phi_{ij}}{\partial r_2} \right) + 3 \int_{R_1}^{R_2} (4\pi C)^{-1} d\mathbf{r}_1 d\Omega_1 (p_1 \Theta(R_0 - r_1) + p_2 \Theta(r_1 - R_0)) \quad (14)$$

The one-particle distribution $n_i(\mathbf{r}_1, \Omega_1)$ may be integrated over Ω_1 to give $n_i(\mathbf{r}_1)$.

Passing to the limit of infinite R_1 , R_2 , and R_0 , one has a planar interface, with the variable of integration r_1 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

$$\int_{R_1}^{R_2} d\mathbf{r}_1 d\Omega_1 f(r_1, \Omega_1) \approx 4\pi R_0^2 \int_{R_1}^{R_2} dz_1 d\Omega_1 f(r_1, \Omega_1)$$

when f is a function which is nonzero only for r_1 between R_1 and R_2 . Similarly

$$\int_{R_1}^{R_2} d\mathbf{r}_1 d\Omega_1 \int_{R_1}^{R_2} d\mathbf{r}_2 d\Omega_2 g(\mathbf{r}_1, \Omega_1, \mathbf{r}_2, \Omega_2) \approx 4\pi R_0^2 \int_{R_1}^{R_2} dz_1 d\Omega_1 G(r_1, \Omega_1)$$

if g vanishes except when r_1 is between R_1 and R_2 and r_{12} is small. This follows because $\int d\mathbf{r}_2 d\Omega_2 g(\mathbf{r}_1, \Omega_1, \mathbf{r}_2, \Omega_2)$ 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 Ω_1 .

Returning to (14), we write ϕ_{kl} as $\phi_{kl}^e + \phi_{kl}^s$ (e = electrostatic, s = short-range) and¹³

$$n_k(r_1\Omega_1r_2\Omega_2) = n_k(r_1\Omega_1) n_l(r_2\Omega_2) [1 + h_{kl}(r_1\Omega_1r_2\Omega_2)] \quad (15)$$

where the correlation function h_{kl} approaches 0 for large r_{12} . The integrand in the second term of (14) is a sum of a short-range term from ϕ_{kl}^s and a term involving the long-range electrostatic potential which includes the true long-range terms

$$\sum_{ij} n_i(r_1\Omega_1) n_j(r_2\Omega_2) \left[r_1 \left(\frac{\partial \phi_{ij}^e}{\partial r_1} \right) + r_2 \left(\frac{\partial \phi_{ij}^e}{\partial r_2} \right) \right]$$

and short-range terms from h_{ij} , which are nonzero only over a limited range of r_2 around r_1 . Thus the terms involving ϕ_{ij}^s 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_0^2 . Their contribution to γ is then independent of R_0 as $R_0 \rightarrow \infty$.

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 h_{ij} . If the short-range terms are to be called pressures, like p_n and p_i in (1)–(5), one should remember that the electrostatic forces contribute to the pressures.^{8,14}

If the interaction potential ϕ_{ij} is wholly short range and isotropic, we can pass to the limit of a planar interface and show that (14) is equivalent to a familiar surface tension expression. When R_1 , R_2 , and R_0 become infinite, p_1 and p_2 become equal to p_0 , the pressure in the homogeneous phases, and (14) becomes

$$4\pi(2\gamma)R_0^2 = -3kT(4\pi R_0^2) \int_{-\infty}^{\infty} dz_1 \sum_i n_i(z_1) + \frac{4\pi R_0^2}{2} \int_{-\infty}^{\infty} dz_1 \int dr_{12} \sum_{ij} n_{ij}(z_1, r_{12}) r_{12} \phi'(r_{12}) + 3 \int_{-\infty}^{\infty} dz_1 p_0$$

The normal pressure, which is equal to p_0 , is constant through the interface:

$$3p_0 = 3kT \sum_i n_i(z_1) - \frac{3}{2} \int dr_{12} \frac{z_{12}^2}{r_{12}} \phi'(r_{12}) \int_0^1 d\alpha \sum_{ij} n_{ij}(r_{12}, z_1 - \alpha r_{12}, z_1 + (1-\alpha)r_{12})$$

where¹⁵ the arguments of n_{ij} are now the interparticle distance and the z coordinates of the two particles. Substituting for p_0 in the surface tension expression, we have

$$4\gamma = \int_{-\infty}^{\infty} dz_1 \int dr_{12} [\phi'(r_{12})/r_{12}] \left[r_{12}^2 \sum_{ij} n_{ij}(r_{12}, z_1, z_1 + z_{12}) - 3z_{12}^2 \int_0^1 d\alpha \sum_{ij} n_{ij}(r_{12}, z_1 - \alpha z_{12}, z_1 + (1-\alpha)z_{12}) \right]$$

Since¹³

$$\int_{-\infty}^{\infty} dz_1 \int_0^1 d\alpha \sum_{ij} n_{ij}(r_{12}, z_1 - \alpha z_{12}, z_1 + (1-\alpha)z_{12}) = \int_{-\infty}^{\infty} dz_1 n_{ij}(r_{12}, z_1, z_2)$$

this leads to

$$\gamma = \frac{1}{4} \int_{-\infty}^{\infty} dz_1 \int dr_{12} \phi'(r_{12}) [r_{12} - (3z_{12}^2/r_{12})] \sum_{ij} n_{ij}(r_{12}, z_1, z_1 + z_{12}) \quad (16)$$

a well-known expression¹³ for the surface tension.

Long-Range Terms

To show that the long-range terms in (14) can in fact be written as $4\pi R_0^2$ multiplied by an integral independent of R_0 , we rewrite them in terms of the electric field and electrostatic potential. We thus consider

$$L = (4\pi C)^{-2} \int_{R_1}^{R_2} dr_1 d\Omega_1 \int_{R_1}^{R_2} dr_2 d\Omega_2 \times \sum_{ij} n_i(r_1\Omega_1) n_j(r_2\Omega_2) \left(r_1 \frac{\partial \phi_{ij}}{\partial r_1} + r_2 \frac{\partial \phi_{ij}}{\partial r_2} \right)$$

with

$$\phi_{ij} = \frac{q_i q_j}{r_{12}} - \frac{q_i \mu_j r_{12}}{r_{12}^3} - \frac{q_j \mu_i r_{12}}{r_{12}^3} + \frac{r_{12}^2 \mu_i \mu_j - 3(\mu_i r_{12})(\mu_j r_{12})}{r_{12}^5} \quad (17)$$

Now $n_i(r_1) = (4\pi C)^{-1} \int d\Omega_1 n_i(r_1\Omega_1)$ is the total density of particles of species i at r_1 and $\sum_i n_i(r) q_i$ is the charge density $\rho(r)$. Similarly, the average dipole moment of molecules of species i located at r_1 is

$$\mathbf{m}_i = \int d\Omega_1 n_i(r_1\Omega_1) \mu_i / \int d\Omega_1 n_i(r_1\Omega_1) \quad (18)$$

and $\sum_i n_i(r) \mathbf{m}_i$ is the dipole density or electric polarization $\mathbf{P}(r)$, which is in the radial direction. Then, after carrying out the differentiations with respect to r_1 and r_2 , the long-range terms become

$$L = \int \int dr_1 dr_2 \left\{ -\rho(r_1) \rho(r_2) r_{12}^{-1} - \rho(r_1) P(r_2) \frac{r_1^2 - r_2^2 - r_{12}^2}{r_2 r_{12}^3} - P(r_1) \rho(r_2) \frac{r_2^2 - r_1^2 - r_{12}^2}{r_1 r_{12}^3} + P(r_1) P(r_2) \frac{-3r_{12}^4 - 6r_{12}^2(r_1^2 + r_2^2) + 9(r_1^2 - r_2^2)^2}{4r_{12}^5 r_1 r_2} \right\} \quad (19)$$

We now introduce the electric potential and electrostatic field, calculated in terms of the charge density and dipole density of polarization.

The relation between the "microscopic fields" resulting from molecular charge densities and the "macroscopic fields" of the Maxwell equations have been discussed by many authors, including the classic treatments of Van Vleck¹⁶ and Böttcher.¹⁷ It is shown that one must average the microscopic fields, which result only from true charges, over small volumes which contain large numbers of molecules to get the macroscopic fields. This allows the use of a multipole expansion in $\mathbf{r}/\mathbf{R}$, where $\mathbf{r}$ is a displacement vector from an origin at the center of gravity of the molecular charge distribution to an element of the charge density (nuclei and electrons) assigned to the molecule, and $\mathbf{R}$ is the vector from the center of gravity to the position of the observer, so that $\mathbf{r}/\mathbf{R}$ is small. Then a molecule is characterized by its total charge and dipole moment, the latter being an integral over the molecule of charge density multiplied by $\mathbf{r}$. In calculating the field, one has thus to exclude contributions of a small volume about the observation point. This is responsible for the ambiguity in the definition of the field discussed by Sanfeld⁶ and by Hurwitz.¹⁰ It is shown by Böttcher¹⁷ that the electric field, calculated as the force on a unit charge, will obey the Maxwell equation $\nabla \cdot \mathbf{D} = 4\pi\rho$ if one calculates the force due to all matter outside a cylinder of infinite length and infinitesimally small radius oriented in the field direction. De Groot and Suttrop¹⁴ show that $\mathbf{E}$ satisfies the Maxwell equation when written as

$$\mathbf{E}(r_1) = -\mathcal{P} \int dr_2 \{ \rho(r_2) + \mathbf{P}(r_2) \cdot \nabla_2 \} |\mathbf{r}_1 - \mathbf{r}_2|^{-1} - \int ds_2 \mathbf{n}_2 \cdot \mathbf{P}(r_2) \nabla_1 |\mathbf{r}_1 - \mathbf{r}_2|^{-1}$$

where the second integral is over the surface of a small volume around r_1 , equivalent to Böttcher's cylinder. They also show that one may write

$$\mathbf{E}(r_1) = -\nabla_1 \int \{ \rho(r_2) + \mathbf{P}(r_2) \cdot \nabla_2 \} |\mathbf{r}_1 - \mathbf{r}_2|^{-1} \quad (20)$$

with convergent integrals.

The electrostatic potential at point r_1 due to distributions of charges and dipoles is

$$V(\mathbf{r}_1) = \int d\mathbf{r}_2 \rho(\mathbf{r}_2) |\mathbf{r}_1 - \mathbf{r}_2|^{-1} + \int d\mathbf{r}_2 \mathbf{P}(\mathbf{r}_2) \cdot \nabla_2 |\mathbf{r}_1 - \mathbf{r}_2|^{-1} = \int d\mathbf{r}_2 \left(\rho(\mathbf{r}_2) r_{12}^{-1} + P(\mathbf{r}_2) \frac{r_1^2 - r_2^2 - r_{12}^2}{2r_2 r_{12}^3} \right) \quad (21)$$

Then, using (20) and the fact that the polarization and the electric field at each point are in the radial direction

$$\mathbf{E}(\mathbf{r}_1) = -\frac{\partial}{\partial r_1} \int d\mathbf{r}_2 \left\{ \rho(\mathbf{r}_2) + P(\mathbf{r}_2) \frac{\partial}{\partial r_2} \right\} \frac{1}{r_{12}} = -\frac{\partial}{\partial r_1} \int d\mathbf{r}_2 \left\{ \frac{\rho(\mathbf{r}_2)}{r_{12}} + P(\mathbf{r}_2) \frac{r_2^2 - r_1^2 + r_{12}^2}{-2r_{12}^3 r_2} \right\} = \int d\mathbf{r}_2 \left\{ \rho(\mathbf{r}_2) \frac{r_1^2 - r_2^2 + r_{12}^2}{r_1 r_{12}^3} + P(\mathbf{r}_2) \frac{-r_{12}^4 - 2r_{12}^2(r_1^2 + r_2^2) + 3(r_1^2 - r_1^2)^2}{4r_1 r_2 r_{12}^5} \right\} \quad (22)$$

Introducing the definitions of V and $\mathbf{E}$, the long-range terms are

$$L = \int d\mathbf{r}_1 [-\rho(r_1) V(r_1) + 3P(r_1) E(r_1)] \quad (23)$$

Since $\nabla \cdot \mathbf{V} = -\mathbf{E}$ and $\nabla \cdot \mathbf{D} = 4\pi\rho$ with $\mathbf{D} = \mathbf{E} + 4\pi\mathbf{P}$

$$-\int d\mathbf{r}_1 \rho(r_1) V(r_1) = -(4\pi)^{-1} \int d\mathbf{r}_1 [\nabla \cdot (\mathbf{V}\mathbf{D}) - \mathbf{D} \cdot \nabla V] = -(4\pi)^{-1} \int d\mathbf{r}_1 \mathbf{D} \cdot \mathbf{E}$$

where the volume integral of $\nabla \cdot (\mathbf{V}\mathbf{D})$ is converted into a surface integral which vanishes because $\mathbf{D} = 0$ on the boundaries of the system. Finally

$$L = \int d\mathbf{r}_1 [-(4\pi)^{-1} E(r_1)^2 + 2\mathbf{P}(r_1) \cdot \mathbf{E}(r_1)] \quad (24)$$

In the passage to the planar interface, one simply replaces r_1 by z_1 and the integral over r_1 to $4\pi R_0^2$ times the integral over z_1 .

The surface tension formula now becomes

$$2\gamma = \int_{-\infty}^{\infty} dz_1 (4\pi C)^{-1} d\Omega_1 \left\{ -3kT \sum_i n_i(r_1 \Omega_1) + \frac{1}{2} \int (4\pi C)^{-1} d\mathbf{r}_2 d\Omega_2 \sum_{ij} n_{ij}(z_1 \Omega_1 r_2 \Omega_2) \left(z_1 \frac{\partial}{\partial z_1} + z_2 \frac{\partial}{\partial z_2} \right) \phi_{ij}^s + \frac{1}{2} \int (4\pi C)^{-1} d\mathbf{r}_2 d\Omega_2 \sum_{ij} n_i(z_1 \Omega_1) n_j(z_2 \Omega_2) h_{ij}(z_1 \Omega_1 r_2 \Omega_2) \times \left(z_1 \frac{\partial}{\partial z_1} + z_2 \frac{\partial}{\partial z_2} \right) \phi_{ij}^e - \frac{E(z_1)^2}{8\pi} - E(z_1) P(z_1) + 3p \right\} \quad (25)$$

where p is the pressure in either homogeneous phase. The integrand of (25) is nonzero only in the region of inhomogeneity, so integrals over z may be extended to the range $-\infty$ to ∞ . To compare (25) with other formulas for the surface tension of a charged and polarized system, one requires a quantity, like p_n' of (5), which is conserved through the interface (independent of z) and hence becomes equal to p in the homogeneous phases.

Lippmann Equation

The Lippmann equation, normally derived thermodynamically,^{1,4,18} is $(\partial\gamma/\partial U)_{p,T,\text{comp}} = -Q$ where pressure, temperature, and composition of the homogeneous phases bounding the interface are kept constant. Here, U is the potential drop across the interface, $V(\infty) - V(-\infty)$, and Q the surface charge density on the + side of the interface. The total surface charge density of the interface, which is electrically neutral, is zero. To define Q , each charged species is assigned to one side or the other of the interface, i.e., to the homogeneous phase at $z \rightarrow +\infty$ or that at $z \rightarrow -\infty$. Then, denoting by $\sum_i^{(+)}$ and $\sum_i^{(-)}$ sums over species belonging to the + and - sides ($\sum_i = \sum_i^{(+)} + \sum_i^{(-)}$), the surface charge densities for each side of the interface are

$$Q_+ = \int_{-\infty}^{\infty} dz \sum_i^{(+)} q_i n_i(z) \quad (26)$$

$$Q_- = \int_{-\infty}^{\infty} dz \sum_i^{(-)} q_i n_i(z) = -Q_+$$

with $Q_- = -Q_+$ because of overall electrical neutrality.

The most commonly used model for the electrochemical interface^{1,4,18} is the Gouy-Chapman model, although it is usually applied to only one side of the interface, the other being taken as surroundings. In this model interparticle correlations and short-range forces are neglected, and each charged species obeys a Boltzmann relation:

$$n_i(z) = n_i(\pm\infty) \exp\{-q_i[V(z) - V(\pm\infty)]/kT\} \quad (27)$$

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 $\sum_i n_i(z)$ with respect to z :

$$\sum_i dn_i/dz = -\sum_i \frac{n_i}{kT} q_i \frac{dV}{dz} = \sum_i n_i q_i \frac{E(z)}{kT}$$

Since $\sum_i n_i q_i = \rho = (4\pi)^{-1} (dE/dz)$, this shows that $kT \sum_i n_i(z) - E(z)^2/8\pi$ is independent of z and hence equal to p at $z \rightarrow \pm\infty$. Then (25), which involves only long-range terms, is

$$2\gamma = \int_{-\infty}^{\infty} dz \left\{ -3kT \sum_i n_i(z) - \frac{1}{8\pi} E(z)^2 - \frac{1}{2} P(z) E(z) + 3kT \sum_i n_i(z) - 3 \frac{E(z)^2}{8\pi} \right\}$$

Since no polarizable species are present

$$\gamma = \int_{-\infty}^{\infty} dz [-E(z)^2/4\pi] = \int_{-\infty}^{\infty} dz [p - kT \sum_i n_i(z) - E(z)^2/8\pi] \quad (28)$$

Now for a change at constant p and T

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

Introducing the surface charge densities Q_+ and Q_- , we have

$$\Delta\gamma = -Q_+ \Delta[V(+\infty) - V(-\infty)] \quad (29)$$

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

$$n_i(z) = n_i(\pm\infty) e^{-f_i(E)/kT} \quad (30)$$

Now, using (27) for the charged species

$$\frac{d}{dz} \left\{ kT \sum_i n_i - \frac{E^2}{8\pi} - EP \right\} = -\rho \frac{dV}{dz} - \sum_i^{(0)} n_i \frac{df_i}{dE} \frac{dE}{dz} - \frac{E}{4\pi} \left(\frac{dE}{dz} + 4\pi \frac{dP}{dz} \right) - P \frac{dE}{dz} = - \left(\sum_i^{(0)} n_i \frac{df_i}{dE} + \sum_i^{(0)} n_i \mu_i \right) \frac{dE}{dz} \quad (31)$$

since $E + 4\pi P = D$ and $dE/dz = 4\pi\rho$. For (31) to vanish, f_i must

equal $-\int_0^E dE' \mu_i(E')$. In previous work,^{8,19} f_i , which is the work required to introduce a dipolar particle into an electric field, was written in this way by analogy to (27), in which $q_i(V - V(\pm\infty))$ appears as the work required to introduce a charged particle.

According to (31), $kT\sum_i n_i - E^2/8\pi - EP$ is independent of z , so that it may replace p in the surface tension formula (25). Then we get

$$\gamma = \int_{-\infty}^{\infty} dz \left\{ -\frac{E^2}{8\pi} + p - kT\sum_i n_i \right\}$$

which is identical to (28). Now, however

$$\Delta\gamma = \int_{-\infty}^{\infty} dz \left\{ -\frac{E\Delta E}{4\pi} + \rho\Delta V - \sum_i^{(+)} q_i n_i \Delta V(+\infty) - \sum_i^{(-)} q_i n_i \Delta V(-\infty) - kT\sum_i^{(0)} n_i \left(\frac{-1}{kT} \frac{df_i}{dE} \right) \Delta E \right\}$$

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

$$\Delta\gamma = \int_{-\infty}^{\infty} dz \{ P\Delta E + \sum_i^{(0)} n_i (-\mu_i) \Delta E \} - Q_+ \Delta V(+\infty) - Q_- \Delta V(-\infty) = -Q_+ \Delta[V(+\infty) - V(-\infty)] \quad (32)$$

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 parts²⁰ of the double layer, with very different dielectric constants, and some workers²¹ have introduced a dielectric constant which varies as a function of distance d from the electrode, approaching the bulk dielectric constant as $d \rightarrow \infty$. 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, R_0 . 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 R_0 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 interparticle correlations, and the distribution of each charged species is Boltzmann-like. We show that the pressure in the direction normal to the interface is $kT\sum_i n_i(z) - E(z)^2/8\pi$, 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 $kT\sum_i n_i(z) - E(z)^2/8\pi$ is then no longer conserved through the interface. This inconsistency with mechanical equilibrium can be remedied if polarizable species are included in $\sum_i n_i$ and

$$n_j(z) = n_j(\pm\infty) \exp\left[\int_0^E dE' \mu_j(E')\right]$$

for each polarizable species. Then $kT\sum_i n_i - (E^2/8\pi) - EP$ 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,^{5,22} 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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