

# Thermodynamics of Surface Tension: Application to Electrolyte Solutions

Yan Levin<sup>1</sup>

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In this contribution to the special issue of the *Journal of Statistical Physics* dedicated to Michael Fisher on his 70th birthday, I shall review two thermodynamically distinct routes for obtaining the interfacial tension of liquid-vapor interfaces in mixtures. A specific application to the calculation of excess surface tension of aqueous electrolyte solutions will be presented.

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**KEY WORDS:** Surface tension; electrolyte; interface; adsorption isotherm.

## 1. INTRODUCTION

It is a pleasure to dedicate this review to Michael Fisher on the occasion of his 70th birthday. The paper deals with two subjects which are dear to Michael's heart, the Thermodynamics and the Coulomb Systems. Here I will review two thermodynamically distinct routes to surface tension of aqueous electrolyte solutions. The first, grand canonical route, goes all the way to the pioneering work of Gibbs on the foundations of thermodynamics and statistical mechanics<sup>(1)</sup> and is the usual method used by physical chemists. Application of the Gibbs adsorption isotherm to the calculation of surface tension of electrolyte solutions started with the works of Wagner<sup>(2)</sup> and Onsager and Samaras<sup>(3)</sup> early in the 20th century. The second, canonical method, has been introduced recently and was found to work very well for symmetric 1:1 electrolytes.<sup>(4,5)</sup>

## 2. GRAND-CANONICAL ROUTE

Many elementary thermodynamics and statistical mechanics texts neglect to deal with all the subtleties leading to the Gibbs adsorption

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<sup>1</sup> Instituto de Física, Universidade Federal do Rio Grande do Sul, Caixa Postal 15051, CEP 91501-970, Porto Alegre, RS, Brazil; e-mail: levin@if.ufrgs.br

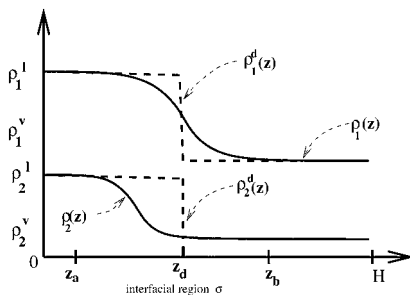


Fig. 1. Schematic density profiles inside a solution:  $\rho_1(z)$  is the characteristic density variation of water across the liquid-vapor interface,  $\rho_2(z)$  is the concentration profile of solute. The hypothetical dividing surface separating the liquid from the vapor is located at  $z = z_d$ . The discontinuous "bulk" profiles for solvent and solute are  $\rho_1^d(z)$  and  $\rho_2^d(z)$ , respectively. Note that differently from non-ionic solutes for which  $\rho_2(z)$  extends all the way into the vapor phase, because of a favorable gain in solvation free energy aqueous electrolytes are completely confined to the liquid phase.

isotherm. While these do not seriously affect the results for surface tension of surfactant solutions, the increase of interfacial tension of water due to salts is proportionately much smaller. Thus, a particular care must be taken with the thermodynamics in order to account for all the relevant contributions. We start, therefore, by reviewing the thermodynamics leading to the Gibbs adsorption isotherm.<sup>(1,6)</sup>

Consider an aqueous solution in equilibrium with vapor, Fig. 1. The bulk density of liquid is  $\rho_1^l$  and the bulk density of vapor is  $\rho_1^v$ . The variation of density is confined to the interfacial region  $\sigma$  located between  $z_a$  and  $z_b$ , where  $z$  is the axis perpendicular to the interface. The thermodynamic equilibrium requires the constancy of chemical potentials of solute and solvent and of the pressure throughout the system. The differential internal energy of the interfacial region  $\sigma$  is

$$dE^\sigma = T dS^\sigma - P dV^\sigma + \gamma dA^\sigma + \sum \mu_i dN_i^\sigma, \quad (1)$$

where  $T$ ,  $P$ ,  $S$ ,  $V$ ,  $A$ ,  $\gamma$ ,  $\mu_i$ ,  $N_i$  are the temperature, pressure, entropy, volume, area, surface tension, chemical potential, and the number of particles of type  $i$ . The superscript  $\sigma$  stands for the interfacial properties. The sum runs over all the species, solute and solvent. Since the internal energy  $E$  is an extensive function of  $\{S, V, A, N_i\}$ , application of Euler theorem for first order homogeneous functions allows the integration of Eq. (1) yielding,

$$E^\sigma = TS^\sigma - PV^\sigma + \gamma A^\sigma + \sum \mu_i N_i^\sigma. \quad (2)$$

As usual the Gibbs free energy for the interface is defined through the Legendre transform

$$G^\sigma = E^\sigma - TS^\sigma + PV^\sigma - \gamma A^\sigma, \quad (3)$$

which after substitution of internal energy, Eq. (2), reduces to

$$G^\sigma = \sum \mu_i N_i^\sigma. \quad (4)$$

The Gibbs free energy is a natural function of  $\{T, P, \gamma, N_i^\sigma\}$  and its differential is

$$dG^\sigma = -S^\sigma dT + V^\sigma dP - A^\sigma d\gamma + \sum \mu_i dN_i^\sigma. \quad (5)$$

On the other hand differentiating Eq. (4), we find

$$dG^\sigma = \sum \mu_i dN_i^\sigma + \sum N_i^\sigma d\mu_i. \quad (6)$$

Comparing Eq. (5) with Eq. (6) we are led to a Gibbs–Duhem-like equation for the interface,

$$S^\sigma dT - V^\sigma dP + A^\sigma d\gamma + \sum N_i^\sigma d\mu_i = 0. \quad (7)$$

Now let's consider in more detail a two component system. In this case Eq. (7) simplifies to

$$S^\sigma dT - V^\sigma dP + A^\sigma d\gamma + N_1^\sigma d\mu_1 + N_2^\sigma d\mu_2 = 0. \quad (8)$$

The chemical potentials are uniform throughout the system and their variations can be obtained by considering the bulk liquid phase. Remembering that a change in concentration of solute affects the chemical potentials of both solute and solvent, we have

$$d\mu_1 = -s_1 dT + v_1 dP + \left(\frac{\partial \mu_1}{\partial c_b}\right)_{T,P} dc_b, \quad (9)$$

and

$$d\mu_2 = -s_2 dT + v_2 dP + \left(\frac{\partial \mu_2}{\partial c_b}\right)_{T,P} dc_b, \quad (10)$$

where the  $s_1$  and  $v_1$  are the partial entropy and volume per particle of solvent,  $s_2$  and  $v_2$  are the partial entropy and volume per particle of solute, and  $c_b$  is the concentration of solute, all the values taken inside the bulk liquid phase. Substituting Eqs. (9) and (10) into Eq. (8), the Gibbs–Duhem equation for the interface becomes,

$$(S^\sigma - N_1^\sigma s_1 - N_2^\sigma s_2) dT - (V^\sigma - N_1^\sigma v_1 - N_2^\sigma v_2) dP + A^\sigma d\gamma + \left[ N_1^\sigma \left( \frac{\partial \mu_1}{\partial c_b} \right)_{T,P} + N_2^\sigma \left( \frac{\partial \mu_2}{\partial c_b} \right)_{T,P} \right] dc_b = 0. \quad (11)$$

For a truly two component system pressure cannot be held constant if  $T$  or  $c_b$  is varied. However, presence of an inert gas does not significantly affect aqueous surface tension, so that in practice  $P$  can be kept fixed.<sup>(6)</sup> With the help of the Gibbs–Duhem equation for the bulk liquid,

$$N_1 \left( \frac{\partial \mu_1}{\partial c_b} \right)_{T,P} + N_2 \left( \frac{\partial \mu_2}{\partial c_b} \right)_{T,P} = 0, \quad (12)$$

where  $N_1$  and  $N_2$  are the bulk numbers of solvent and solute molecules, Eq. (11) reduces to two equations,

$$\left( \frac{\partial \gamma}{\partial T} \right)_{c_b,P} = - \left[ \frac{S^\sigma}{A^\sigma} - \Gamma_1^\sigma s_1 - \Gamma_2^\sigma s_2 \right], \quad (13)$$

and,

$$\left( \frac{\partial \gamma}{\partial \mu_2} \right)_{T,P} = - \left[ \Gamma_2 - \frac{N_2}{N_1} \Gamma_1 \right], \quad (14)$$

where  $\Gamma_1 = N_1^\sigma / A^\sigma$  and  $\Gamma_2 = N_2^\sigma / A^\sigma$ . Equation (13) states that the variation of surface tension with respect to temperature is minus the excess entropy, compared to the entropy content of the same amount of material inside the liquid phase. Equation (14), called the Gibbs adsorption isotherm, shows that the change of surface tension with respect to chemical potential of solute is minus the excess of solute inside  $\sigma$ , over the amount which would be present for the same quantity of solvent in a bulk liquid phase. Note that the term “excess” is used both when the interfacial region has higher (positive excess) or lower (negative excess) concentration of solute, as compared to the bulk liquid phase. Since the thermodynamic stability requires  $\partial \mu_2 / \partial c_b > 0$  at fixed temperature, Eq. (14) shows that a positive surface excess of solute leads to a lower interfacial tension, while a negative surface excess of solute results in a higher surface tension. Finally, we note

that Eq. (14) is invariant with respect to the specific location of the dividing surfaces  $z_a$  and  $z_b$ , as long as they completely enclose the region of strong density variation.

The surface tension can be obtained by integrating Eqs. (13) and (14). Of course, this requires a specific microscopic model which would allow us to calculate the excess entropy and the excess amount of solute inside  $\sigma$ . Such model can, in principle, be provided by statistical mechanics.<sup>(3,7)</sup>

In the language of statistical mechanics the calculations based on Eqs. (13) and (14) are intrinsically grand-canonical. The number of particles inside  $\sigma$  fluctuates and is determined by the condition of equilibrium between the interfacial region and the bulk phases. Unfortunately to actually solve a statistical mechanical model, one is invariably forced to make approximations. It might be, therefore, worthwhile to explore different routes to surface tension, each one requiring different approximations. Of course, in an exact calculation all the thermodynamic routes will lead to the same result. With approximate theories this, however, is no longer the case and some routes can be significantly better than others. With this in sight, we have explored the canonical route to surface tension.<sup>(4,5)</sup>

### 3. CANONICAL ROUTE

Suppose that the system depicted in Fig. 1 which contains

$$N_1 = A \int_0^H \rho_1(z) dz \quad (15)$$

particles of solvent and

$$N_2 = A \int_0^H \rho_2(z) dz \quad (16)$$

particles of solute is confined to a cylindrical box of height  $H$  and cross-sectional area  $A$ . We shall define the "bulk" density of solvent and solute inside the liquid phase as  $\rho_1^l = \rho_1(0)$  and  $\rho_2^l = \rho_2(0)$ , respectively; and the "bulk" density of solvent and solute inside the vapor phase as  $\rho_1^v = \rho_1(H)$  and  $\rho_2^v = \rho_2(H)$ . The internal energy of the whole system is

$$E = TS - PV + \gamma A + \mu_1 N_1 + \mu_2 N_2, \quad (17)$$

Now we would like to ask which part of this energy is due to the interface? That is, if instead of a continuous density profiles  $\rho_1(z)$  and  $\rho_2(z)$ , we would have two discontinuous "bulk" profiles  $\rho_1^d(z)$  and  $\rho_2^d(z)$ , depicted

in Fig. 1, what would be the change in internal energy of the system? Although easy to pose, this question carries some subtlety. Specifically where should we put the dividing surface? Also, what is the meaning of a discontinuous profile? This latter question is fairly easy to answer. To obtain a discontinuous profile we divide the total volume into two sub-cylinders of heights  $z_d$  and  $H - z_d$ . In the first sub-cylinder of height  $z_d$  and volume  $V^l = Az_d$ , there will be  $N_1^l(z_d) = \rho_1^l V^l$  molecules of solvent and  $N_2^l(z_d) = \rho_2^l V^l$  molecules of solute. In the second sub-cylinder of height  $H - z_d$  and volume  $V^v = A(H - z_d)$ , there will be  $N_1^v(z_d) = \rho_1^v V^v$  molecules of solvent and  $N_2^v(z_d) = \rho_2^v V^v$  molecules of solute. To keep the uniform density distribution characteristic of the bulk phases, we impose periodic boundary conditions in the  $z$  direction on each sub-cylinder. The internal energy of the first sub-cylinder, corresponding to the bulk liquid, is then

$$E^l(z_d) = TS^l(z_d) - PV^l + \mu_1 N_1^l(z_d) + \mu_2 N_2^l(z_d), \quad (18)$$

and the internal energy of the second sub-cylinder, corresponding to the bulk vapor, is

$$E^v(z_d) = TS^v(z_d) - PV^v + \mu_1 N_1^v(z_d) + \mu_2 N_2^v(z_d). \quad (19)$$

Because of the arbitrariness in the location of the dividing surface, in general,  $N_1 \neq N_1^l(z_d) + N_1^v(z_d)$  and  $N_2 \neq N_2^l(z_d) + N_2^v(z_d)$ . Therefore the surface internal energy,  $E^s(z_d) = E - E^l(z_d) - E^v(z_d)$ , is

$$E^s(z_d) = TS^s(z_d) + \gamma A + \mu_1 N_1^s(z_d) + \mu_2 N_2^s(z_d), \quad (20)$$

where  $S^s(z_d) = S - S^l(z_d) - S^v(z_d)$ ,  $N_1^s = N_1 - N_1^l(z_d) - N_1^v(z_d)$ , and  $N_2^s = N_2 - N_2^l(z_d) - N_2^v(z_d)$ . Since the Helmholtz free energy is given in terms of the Legendre transform of the internal energy,  $F^s = E^s - TS^s$ , Eq. (20) can be rewritten as,

$$F^s(z_d) - \mu_1 N_1^s(z_d) - \mu_2 N_2^s(z_d) = \gamma A. \quad (21)$$

The statistical mechanics allows us, in principle, to calculate the excess surface Helmholtz free energy as well as the chemical potentials and the surface excess of solvent and solute. The thermodynamics relates these to surface tension through Eq. (21). Note that while the three terms on the left hand side of Eq. (21) are dependent on the location of the dividing surface, the right hand side does not. Thus, we can fix the position of  $z_d$  so that the surface excess of solvent is zero,  $N_1^s(z_d^G) = 0$ . This specific choice corresponds

to the, so called, Gibbs dividing surface. With the location of  $z_d^G$  specified, the surface tension becomes

$$\gamma = \frac{F^s(z_d^G) - \mu_2 N_2^s(z_d^G)}{A}, \quad (22)$$

Now, let's define the *liquid* surface excess of solute as

$$\Delta^l = A \int_0^{z_d^G} [\rho_2(z) - \rho_2^l] dz, \quad (23)$$

and the *vapor* surface excess of solute as

$$\Delta^v = A \int_{z_d^G}^H [\rho_2(z) - \rho_2^v] dz. \quad (24)$$

Noting that  $N_2^s = \Delta^l + \Delta^v$  and

$$\mu_2 = \left. \frac{\partial F_{\text{bulk}}^l}{\partial N_2^l} \right|_{T, V^l} = \left. \frac{\partial F_{\text{bulk}}^v}{\partial N_2^v} \right|_{T, V^v}, \quad (25)$$

Eq. (22) can be rewritten as

$$\gamma = \frac{1}{A} \left[ F(N_1, N_2) - F_{\text{bulk}}^l(N_1^l, N_2^l) - F_{\text{bulk}}^v(N_1^v, N_2^v) - \frac{\partial F_{\text{bulk}}^l}{\partial N_2^l} \Delta^l - \frac{\partial F_{\text{bulk}}^v}{\partial N_2^v} \Delta^v \right], \quad (26)$$

where  $F(N_1, N_2)$  is the total Helmholtz free of the system with interface.

In the thermodynamic limit  $\Delta^l/N_2^l \ll 1$  and  $\Delta^v/N_2^v \ll 1$ , and Eq. (26) simplifies to

$$\gamma = \frac{1}{A} [F(N_1, N_2) - F_{\text{bulk}}^l(N_1^l, N_2^l + \Delta^l) - F_{\text{bulk}}^v(N_1^v, N_2^v + \Delta^v)]. \quad (27)$$

This is the principal thermodynamic result of this paper, which will serve as the starting point for our analysis of the interfacial tension of electrolyte solutions. The fact that  $N_1 = N_1^l + N_1^v$  and  $N_2 = N_2^l + N_2^v + \Delta^l + \Delta^v$  signifies that the calculations based on Eq. (27) must be performed with a *fixed* number of solvent and solute molecules. This accounts for the adjective “canonical” in the name of this thermodynamic route to surface tension.

For strong electrolytes, we have an additional simplification. Because of the high dielectric constant of water, ions inside the liquid have a significantly lower electrostatic free energy compared to ions inside the vapor.

The probability of finding an ion inside bulk liquid  $p_l$ , compared to its probability of being inside bulk vapor  $p_v$  is

$$\frac{p_l}{p_v} = e^{-\beta W}, \quad (28)$$

where  $\beta = 1/k_B T$  and  $W$  is the solvation energy, which can be estimated from the Born equation,

$$W = \frac{q^2}{d} \left( \frac{1}{\epsilon_l} - \frac{1}{\epsilon_v} \right). \quad (29)$$

In this formula  $q$  is the ionic charge,  $d$  is the ionic diameter,  $\epsilon_l$  is the dielectric constant of liquid, and  $\epsilon_v$  is the dielectric constant of vapor. For water  $\epsilon_l/\epsilon_v \approx 80$ , so that  $\beta W$  can be well approximated by  $-\lambda_B \epsilon_l/d\epsilon_v$ , where  $\lambda_B = \beta q^2/\epsilon_l$  is the Bjerrum length. For water at room temperature and monovalent ions  $\lambda_B = 7.2 \text{ \AA}$ , while the characteristic diameter of a hydrated ion is approximately  $d \approx 4 \text{ \AA}$ . Therefore, the concentration of ions in vapor can be estimated to be  $\rho_2^v = \rho_2^l \exp(-140)$ , which is immeasurably low. Furthermore, a rapid decrease of the dielectric constant for  $z > z_d^G$  should strongly inhibit presence of ions in the interfacial region, confining them to  $z < z_d^G$ , so that  $N_2^v = 0$  and  $\Delta^v = 0$ .

#### 4. A SIMPLE MODEL OF AN ELECTROLYTE

Let us now consider a simple model of an aqueous electrolyte<sup>(5)</sup> confined to a cylinder of cross-sectional area  $A$  and height  $H$ . The  $N$  ions will be idealized as hard spheres of diameters  $d$ , carrying charge  $+q$  or  $-q$  at their center. Suppose that the Gibbs dividing surface is located at the top of the cylinder. To simplify the model, we shall further assume that on crossing the Gibbs dividing surface from below the dielectric constant drops discontinuously from  $\epsilon = 80$ , characteristic of bulk water, to  $\epsilon = 1$ , characteristic of vacuum. From the previous discussion, the increase in surface tension of water due to electrolyte is

$$\gamma^{ex} = \lim_{A, H, N \rightarrow \infty} \frac{1}{A} (F^{ex} - F_{\text{bulk}}^{ex}), \quad (30)$$

where the thermodynamic limit is taken in such a way as to preserve the bulk concentration,  $c_b = N/2AH$ . In Eq. (30),  $F^{ex}$  is the excess Helmholtz free energy due to electrolyte in the presence of liquid-vapor interface, while  $F_{\text{bulk}}^{ex}$  is the excess free energy of the *same amount* of electrolyte but



dissolved within the bulk liquid phase of the same volume. The  $F_{\text{bulk}}^{\text{ex}}$  can be calculated using the periodic boundary conditions at the top and the bottom of the cylinder.

As was already mentioned, the decrease in free energy due to solvation inhibits entrance of ions into the interfacial region, producing an ion-free layer adjacent to the Gibbs dividing surface. The different hydration characteristics of anions and cations can make their exclusion layers to have different width. Let us call the width of a cation exclusion layer  $\delta_+$  and the width of an anion exclusion layer  $\delta_-$ . Furthermore, let us for the moment neglect all the electrostatic and hardcore interactions, beyond their contribution to the formation of ion-free layers. In this case the total free energy of an electrolyte solution inside the cylinder takes a particularly simple entropic form,

$$F^{\text{ex}} = k_B T N_+ [\ln(c_+ A^3) - 1] + k_B T N_- [\ln(c_- A^3) - 1], \quad (31)$$

where  $N_+ = N_- = N/2$ ,  $c_+ = N_+/A(H - \delta_+)$ ,  $c_- = N_-/A(H - \delta_-)$ , and  $A$  is the thermal de Broglie wavelength. On the other hand the bulk free energy,  $F_{\text{bulk}}^{\text{ex}}$ , is given by exactly the same expression, but with  $c_+ = c_- = c_b \equiv N/2AH$ , since the periodic boundary condition destroys the ion free layers. Substituting into Eq. (30) we find a simple result,

$$\gamma^{\text{ex}} = k_B T c_b (\delta_+ + \delta_-). \quad (32)$$

Neglect of direct electrostatic interactions results in excess surface tension scaling linearly with the concentration of electrolyte.<sup>(6,7)</sup> Equation (32) is quite different from the Onsager–Samaras (OS) limiting law,<sup>(3)</sup>

$$\gamma_{LL}^{\text{ex}} = \gamma_0 [-\ln(\kappa \lambda_B / 2) - 2\gamma_E + 3/2]. \quad (33)$$

where  $\gamma_E = 0.577215665\dots$  is the Euler's constant,  $\gamma_0 = q^2 c_b / 2\epsilon$ , and  $\kappa = \sqrt{8\pi q^2 c_b / \epsilon k_B T}$  is the inverse Debye length. The OS limiting law is believed to be universally valid for all electrolytes at infinite dilution. In this respect, it is supposed to be analogous to the Debye limiting laws for bulk electrolytes. Comparing Eq. (33) with Eq. (32) we see, however, that only the first term inside the square brackets is universal, while the existence of ion free layers leads to corrections which scale linearly with the electrolyte concentration. Although, Onsager and Samaras tried to extend their theory to finite densities, they have overlooked existence of ion free layers and thus missed an important contribution to the surface tension.

The experimental measurements show a purely linear dependence of excess surface tension on concentration,<sup>(8)</sup> with the validity of OS limiting law restricted to very low electrolyte densities. Neglect of electrostatic

interaction is clearly a strong oversimplification. The advantage of the canonical formalism, besides its thermodynamic simplicity, is that the electrostatics can be easily taken into account. Thus, the Debye-Hückel theory<sup>(9-11)</sup> for bulk electrolytes can be extended to take into account the liquid-vapor interface.<sup>(4, 5)</sup> This calculation, which is in excellent agreement with experiments, shows that for NaCl, existence of an ion free layer of width  $\delta_+ = \delta_- = 2.125 \text{ \AA}$ , characteristic of ionic hydration radius, accounts for about 30% of the total contribution to  $\gamma^{ex}$ , for 0.5 M to 1 M solutions. Electrostatics becomes even more important at lower concentrations. For solutions with  $c_b < 0.3 \text{ M}$  the electrostatics is over 80% dominant, but the OS limiting law fails to be a reasonable approximation until  $c_b < 0.1 \text{ M}$ . Furthermore, even an extended grand-canonical calculation<sup>(3)</sup> which goes beyond the limiting laws, significantly underestimates the role of electrostatics.<sup>(4, 5)</sup> This suggests that the canonical route to surface tension of aqueous electrolytes is more reliable.

It would be interesting to see if the electrostatic calculations for symmetric electrolytes can be extended to the asymmetric systems with distinct  $\delta_+$  and  $\delta_-$ , perhaps along the same lines as used recently by Michael Fisher and collaborators for the asymmetric bulk electrolytes.<sup>(12)</sup>

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