

## Mesoscopic Treatment of a Fluid/Liquid Interface. 1. Theory

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A thermodynamic model of a fluid/liquid interface based on the redistribution of “elastic” energy as a consequence of the contact between formerly isolated phases is proposed. The interface consists of two sub-phases adjacent to their respective bulks. Each sub-phase is capable of storing elastic potential energy. The adsorption isotherms are reproduced in the usual way, equalizing the chemical potential of the adsorbent between the bulk phases and the interface. In this formalism, the interfacial energy results from a sum of two terms each belonging to a subphase and can be expressed in terms of the activity of one component of the system in one bulk phase and at the interface.

### Introduction

Still today most undergraduate textbooks of physical chemistry avoid thermodynamic consideration of interfaces when treating the subject of phase equilibrium. The interfacial energy is introduced as an additional free energy contribution: the work that has to be done on the system at constant temperature and pressure to increase its interface. Such additional contribution is usually negligible in most systems because the free energy is an extensive thermodynamic quantity, and the size of the interface is generally small in comparison to the size of the bulk phases. Hence, the conventional approach to the problem avoids the complex definition of an interfacial chemical potential for each substance, and simplifies the analytical procedure for finding the value of their chemical potential at equilibrium ( $\mu_{\text{eq}}$ ).

It is clear however that whenever the adsorption process is important a suitable definition of interfacial chemical potentials is necessary. This is the case of long-lasting emulsions for instance, where the stability of the dispersion is intimately related to the total interfacial area and the surfactant surface excess. It is also especially important for fluid/liquid systems in general since, up to this date, it is not possible to measure the interfacial composition simultaneously and independently from the bulk composition. Furthermore, the analytical form of an interfacial chemical potential is also interesting from a more fundamental point of view. If equilibrium is reached by equalization of the chemical potentials and the interfacial potential is substantially different from the bulk, the properties of the system at equilibrium could be sensibly affected by the characteristics of the interface.

Other considerations regarding the appropriate definition of interfacial chemical potentials concern the nature of the state of the equilibrium itself. Starting from the Gibbs adsorption model,<sup>1–2</sup> almost all theoretical descriptions of surfactant adsorption to gas/liquid and liquid/liquid interfaces commence

with the equalization of the chemical potentials between the bulk phase(s) and the interface. Such equilibrium condition is achieved between bulk phases counterbalancing energetic differences with configurational entropy contributions dependent on the local composition of the different constituents. The presence of an interface introduces an anisotropy in the system and generates inhomogeneities in the spatial distribution of components. This brings an additional complication to the equilibrium problem: interfaces are usually highly ordered, and such an ordered state is opposed to the necessary increase of entropy required for equilibrium.

An insightful discussion along with a review of the most relevant aspects to be considered in the formulation of an interfacial chemical potential can be found in ref 3. Butler was probably the first to define such potential for the description of the adsorption process and the energy excess occurring in the interface.<sup>4</sup> Among other contributions, Lucassen-Reynders<sup>3,5</sup> introduced the concept of partial molar areas in order to ascribe the interfacial free energy  $\gamma A$  to each contributing molecule. On the other hand, Cahn and Hilliard developed a completely different model in which the interfacial free energy is expressed as a function of the density gradient between the phases in contact.<sup>6,7</sup> The interface is described in this model as a diffuse and continuous zone. Starting from the calculation of the Helmholtz free energy arising from the referred model, and the momentum balance condition, Carey and Scriven proposed a formal development of the interface gradient density model,<sup>8</sup> which was subsequently extended to the description of binary systems.<sup>9</sup> The validity of this model depends on the reliability of the equations of state used, and there is no direct connection in it between activities and chemical potentials.

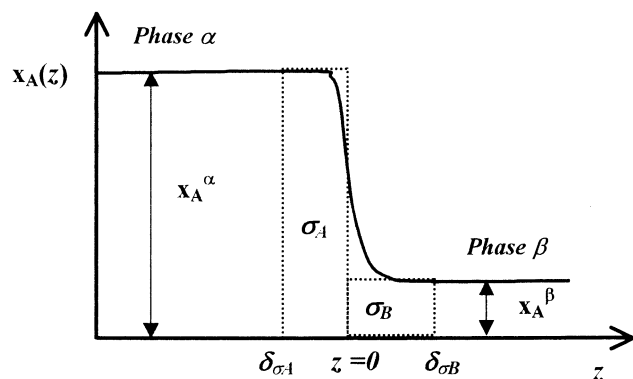
On the basis of the definition of interfacial chemical potential given by Butler, Sugimoto<sup>10,11</sup> recently proposed an alternative formalism for understanding the interfacial tension in terms of molecular activities. In this case, not only is the interfacial chemical potential different from bulk but it is additionally supposed that such initial difference cannot be overcome preventing equalization of the chemical potentials. In that model, Sugimoto goes back to a description of the interface as a

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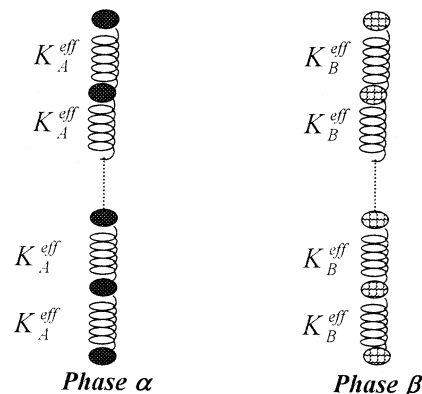
**Figure 1.** According to the model of T. Sugimoto refs 10–11, the interface can be divided into two subregions  $\sigma_A$  and  $\sigma_B$  which extend from  $z = 0$  to  $\delta_A$  and  $\delta_B$  respectively. These denote the small regions in each bulk phase up to which the perturbation of the interface extends. For completeness, the molar fraction of matrix component A ( $x_A$ ) in phases  $\alpha$  and  $\beta$  is also shown.

discontinuous zone, assuming a liquid lattice of homogeneous density in the whole bulk until the interfacial region is reached, departing in this way from the continuous models for the interface.

In the present work, we adopt the description of the interface proposed by Sugimoto<sup>10,11</sup> consisting of two subphases (Figure 1), such that a sharp change in density occurs at the intermediate plane ( $z = 0$ ) between them. Yet, in our case, we additionally allow smooth modifications of density inside each of these subphases. As will be shown below, this consideration allows the description of equilibrium without having to recourse to a different thermodynamic development from the one usually followed in the description of two-phase equilibrium, i.e., maintaining the general condition of equal chemical potentials for each component in different phases (regions). In our view, the present approach enriches the understanding of the interfacial tension in terms of the molecular activity.

### The Elastic Field

It is well-known that in the presence of an interface surface-active molecules diffuse and adsorb very quickly.<sup>12</sup> That response is similar to the way in which elementary charges move in a dielectric media in the presence of an electric field. When an electric field  $E$  is applied, charges move in the dielectric creating a capacitor, inside which, the final value of the electric field is equal to  $E' = KE$ , where  $K$  is a constant dependent on the dielectric material. Thus, the external field produces a charge movement at a microscopic level which translates into a macroscopic response to the perturbation: a new field of magnitude  $KE$ . In a liquid system, the surface-active molecules move to the interface as soon as it is created. It is clear that the forces that cause diffusion of surfactant molecules are chemical in nature. This behavior is the consequence of the chemical affinity of these molecules for the interface: Surfactants have both a hydrophobic and a hydrophilic molecular region sufficiently separated along the backbone of the molecule. Those structures have marked affinities for nonpolar and polar environments, respectively, and can be suitably accommodated in the two distinct regions of the interface. Thus, those molecules feel that the field is “on” as long as the interface exists. The final result is an equilibrium situation in which the free energy per surfactant molecule is equal in the bulk phases and the interface, even though the surfactant concentration is considerably higher at the interfacial layers. It is clear however that the



**Figure 2.** Molecular interactions within “bulk” phases according to an elastic model of an interface.

interfacial environment has been completely modified as a response to this “chemical” field. The question is, Could the interfacial tension be obtained as a function of the molecular response of the system to the creation of an interface? The present paper addresses this question using the fact that the interfacial tension can be both understood as the free energy per unit area or as the force per unit length required to increase the interfacial area. For this purpose, we will consider fluid phases as elastic media similar to that of a network of springs, capable of storing energy through effective interactions, in the same way that springs do. It is important to notice at this point that usual models for macromolecular solutions start from a reticule of points: molecular segments and solvent molecules are distributed in such network, keeping fixed the geometrical distribution of points.<sup>13–16</sup> In the present work, we take into account the network distortion to accommodate the excess energy that accumulates at the interface.

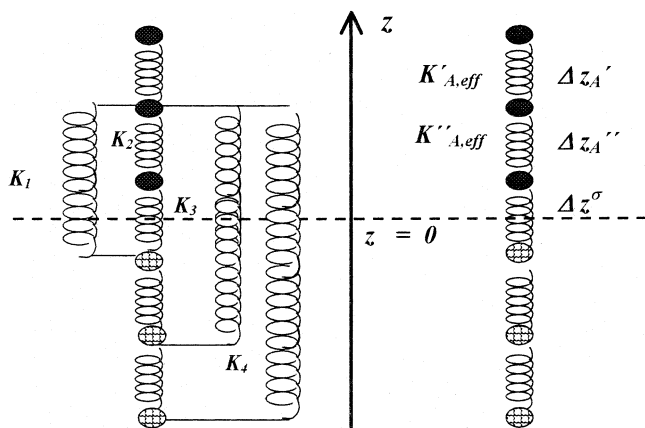
To introduce the concept of an elastic field, let us first consider each phase as a network of interconnected beads and springs. Each bead can represent a molecule or a group of molecules (macroscopic differential) that interacts with other beads through effective intermolecular springs (Figure 2). The elastic constants of these springs result from direct molecule–molecule interactions as well as long-range many-body forces. Within bulk phase  $\alpha$ , “molecules” A interact with an effective constant  $K_A^{\text{eff}}$  because of the local homogeneity of the surroundings. Similarly, the molecules B of phase  $\beta$  interact internally with an effective constant  $K_B^{\text{eff}}$  as shown in Figure 2 for one-dimensional case.

When phases  $\alpha$  and  $\beta$  are brought into contact, each original network will be distorted as a consequence of the redistribution of energy near the interface. The local environment of some molecules in the vicinity of the interface will change depending on the  $z$  position of each interfacial plane (coordinate  $z$  perpendicular to the interface). Even in the cases in which the local environment is similar, the short range and long-range perturbations produce effective spring constants, a function of the relative position of their interfacial plane (Figure 3).

Figure 3 illustrate the adhesion (contact) process between two originally separate phases at constant temperature and pressure. If the energy were purely elastic, the value  $\Delta z^\sigma$  will change until mechanical equilibrium. The distribution of force along the  $z$  axis will be such that

$$K_{AB} \Delta z^\sigma = K_{A,\text{eff}}'' \Delta z_A'' = K_{B,\text{eff}}'' \Delta z_B'' \quad (1)$$

$K_{AB}$  is an average force constant for the new A–B interaction. Thus, in the vicinity of  $z = 0$ , the values of  $\Delta z_A''$  and  $\Delta z_B''$  will



**Figure 3.** Force constant variation as a function of their relative distance to the interface. Effective constants result from many-body interactions. Their value depend from their distance to the interface.

change until

$$\Delta z_B'' = \frac{K_{A,\text{eff}}''}{K_{B,\text{eff}}''} \Delta z_A'' \quad (2)$$

Thus, the molecules will move from their initial positions in such a manner that the perturbations will be adsorbed by the two phases  $\alpha$  and  $\beta$ . From mechanical equilibrium (eq 1), we have

$$E_\beta = \frac{1}{2} \frac{(K_{A,\text{eff}}'' \Delta z_A'')^2}{K_{B,\text{eff}}''} = \frac{K_{A,\text{eff}}''}{K_{B,\text{eff}}''} E_\alpha \quad (3)$$

Consequently,  $E_\alpha \neq E_\beta$  if  $K_{A,\text{eff}}'' \neq K_{B,\text{eff}}''$ , as it occurs for distinct phases. Therefore, the perturbation due to the creation of the interface will extend from the interface to different depths within each bulk phase, until the effect of the perturbation is negligible and the spring constants are the same as in an isolated bulk phase.

Because the intermolecular potential deviates appreciably from this oversimplified harmonic oscillator model, let us introduce the concept of the field of elastic energy, by considering the functions  $g_\alpha(z)$  and  $g_\beta(z)$  whose analytical form depend on the composition of the system and the average molecular distance. These functions are a measure of the cohesive energy of an isolated-bulk system ( $\alpha$  or  $\beta$ ). Function  $g(z)$  has therefore a chemical nature and includes the effects of dipole–dipole interactions, quadrupole–quadrupole interactions, etc., between molecules. Although the analogy between these potential fields and its mechanical harmonic interpretation can be carried out much further (see Appendix A), let us simplify the present mesoscopic description of the real system by saying that field  $g(z)$  acts on the three-dimensional system along the  $z$  axis, producing isotropic distributions of force in the  $xy$  directions perpendicular to  $z$ . Such a field acts similarly to an electric field in the dielectric media, where the field is initially homogeneous, but charge rearrangement can occur. In such cases, the total energy per unit volume stored in a dielectric material can be expressed as in ref 17

$$E_\xi = \frac{1}{2} \epsilon_0 (1 + \chi_e) \xi^2 \quad (4)$$

In this expression,  $\epsilon_0$  is the permittivity of vacuum,  $\chi_e$  is the electric susceptibility of the dielectric material, and  $\xi$  is the value of the external electric field that acts upon the system. As

Thomson formally demonstrated, density of energy  $E_\xi$  is a free energy (ref 17).

In the case of a magnetic field  $\Pi$ , the energy per unit volume is given by the expression

$$E_\Pi = \frac{1}{2} \mu_0' (1 + \chi_M) \Pi^2 \quad (5)$$

Here  $\mu_0'$  is the magnetic permeability in a vacuum, and  $\chi_M$  is the magnetic susceptibility of the material. Following this analogy, we introduce the energy per unit volume due to an elastic field over a liquid network, which can be expressed as

$$E_g = \frac{1}{2} \kappa_0 (1 + \chi_g) g_\alpha^2 \quad (6)$$

In this expression,  $\kappa_0$  is the elastic permittivity of one pure fluid (a measurement of the rigidity of the liquid network) and  $\chi_g$  is the elastic susceptibility, the sensibility of the system to changes in the field  $g(z)$ .

Although eqs 4–6 look very similar, there are certain differences between the electric/magnetic and elastic fields described above. First, the former fields are external, whereas the elastic field arises from the asymmetry produced by the phases in contact, and the intermolecular interactions. Second, in the case of the electric field, there exist discrete charges which move under the action of the initial field until the final state is achieved. In the case of an elastic field, the properties of each “spring” depend on the intrinsic properties of the molecules (polarizability, dipole moment, etc) and the properties of the surrounding neighbors. The field acts on the molecular distribution that, upon particle rearrangements, modify the initial value of the field.

A close look at eq 6 shows that if the rigidity of our liquid network increases the magnitude of the energy per unit volume stored is higher. The susceptibility measures the effect of all components on the system: for instance, the presence of a surfactant changes the network significantly increasing its flexibility, and as a consequence, the energy per unit volume stored would be less than in the pure matrix component. In this case, the susceptibility will vary between 0 and  $-1$ , and the storage of the elastic potential energy will include deeper layers within the bulk. Thus, it is clear that the interface will increase in size with the adsorption of surfactant molecules. Furthermore, it is clear that if sufficient surfactant is introduced in the system the variation of the elastic field will be so high that the system will be equivalent to a different system formerly made out of different “springs”.

### Fugacity of a Molecule in the Elastic Field of the Interface

The energy stored in a macroscopic infinitesimal plane  $\pi$  can be calculated multiplying the total free energy per volume by the volume of the plane:

$$E_\pi = \frac{1}{2} \kappa_0 (1 + \chi_g) g_\alpha^2 \delta_\pi A_\pi \quad (7)$$

Here  $\delta_\pi$  and  $A_\pi$  are the width and the area of the macroscopic plane  $\pi$ . The “coefficient” multiplying the square of the elastic field

$$H = \frac{1}{2} \kappa_0 (1 + \chi_g) \delta_\pi A_\pi \quad (8)$$

is an extensive quantity, and thus can be expressed as the sum

of the partial molar contribution of the components of the system:

$$H = \sum_i n_i \left( \frac{\partial H}{\partial n_i} \right)_{P,T,n_j \neq n_i} = \sum_i h_i n_i \quad (9)$$

In this expression  $h_i$ , depends on the concentrations of all constituents of plane  $\pi(z)$ . In this way,  $h_i(z)$  can be understood as an intrinsic property of each molecule in that plane, which, when appropriately multiplied by the field squared, gives as a result the contribution of species “ $i$ ” to the total potential energy that can be stored within that plane. The exact form of  $h_i(z)$  depends on the molecular theory employed for the description of the partial molar free energy of component “ $i$ ” in plane  $\pi(z)$ . In the most general case,<sup>18</sup>  $h_i(z)$  can be approximated by a series in the number of moles of  $i$  ( $n_i$ ) per unit area of plane  $\pi(z)$ ,  $\Gamma_i$  ( $z$ ):

$$h_i = Q_0 + Q_1 \Gamma_i + Q_2 \Gamma_i^2 + \dots + Q_n \Gamma_i^n \quad (10)$$

Here  $h_i$  ( $\Gamma_i(z)$ ) depends on the concentration of all species that constitute the plane, and such dependence is included in the coefficients  $Q_i$ . Accordingly, the energy stored in plane  $\pi(z)$  can be written as

$$E^\pi = g_\alpha^2(z) \sum_i h_i n_i = \sum_i g_\alpha^2(z) h_i n_i \quad (11)$$

The local concentration of molecule  $i$  in phase  $\alpha$  comes from its affinity with the global field  $g_\alpha$  that diminishes toward the bulk of that phase. Continuing the analogy with the electric and magnetic fields, the absolute mobility of that molecule will equilibrate its diffusion at a given  $z$  coordinate

$$\frac{D_i}{kT} = u_{i,\text{abs}} \quad (12)$$

Here,  $D_i$  is the coefficient of diffusion of component  $i$ ,  $k$  is the Boltzmann constant, and  $u_{i,\text{abs}}$  is the absolute mobility defined by  $u_{i,\text{abs}} = V_{di}/F_i$ . In this expression  $V_{di}$  is the velocity of molecule  $i$  subject to a force  $F_i$ , generated by the global field  $g_\alpha$ .

As implied above, the composition of each plane formerly composed of only one matrix element, will change so that it can equilibrate the net force that acts upon it. The response of each plane component will depend on the local chemical environment of that plane. For every plane  $\pi$  in the *interfacial subphase of bulk*  $\alpha$ , we can write the chemical potential as

$$\mu_A^\pi = \mu_A^{0\pi} + RT \ln a_A^\pi \quad (13)$$

where

$$\mu_A^{0\pi} = \mu_A^0(\text{bulk}) + g_\alpha^2(z) h_A \quad (14)$$

This expression is similar to that obtained by Hill for the case of a ideal dilute gas in an electric field:<sup>19</sup>  $\mu = \mu(0) - (\xi^2/2)(\alpha + \mu_0^2/3kT)$ , where  $\mu(0)$  is the chemical potential in the absence of electric field  $\xi$ ,  $\alpha$  is the polarizability of the gas molecule, and  $\mu_0$  is its dipole moment.

Following eqs 13 and 14

$$RT \ln \left( \frac{\lambda_A^{0\pi}}{\lambda_A^0} \right) = g_\alpha^2(z) h_A \quad (15)$$

The quantity  $\lambda_A^{0\pi}$  is the standard fugacity of the matrix

component A in the plane  $\pi$ , and  $\lambda_A^0$  is the fugacity of the component A in the bulk of phase  $\alpha$ . Here we take into account that, because of the distortions of the network, the molecule of a given plane  $\pi(z \sim 0)$  close to the interface will have an intermolecular distance different from the bulk, and thus, their standard fugacity will be different.

The chemical potential of substance A in the bulk  $\alpha$  is

$$\mu_A^\alpha = \mu_A^0(\text{bulk}) + RT \ln a_A^\alpha \quad (16)$$

Now, when the absolute mobility (given by the response of the field  $g_\alpha(z)$ ) is equal to the potential of diffusion at that plane, the chemical potentials of the bulk and the interface are equal

$$\mu_A^\alpha = \mu_A^\pi \quad (17)$$

Thus

$$\mu_A^0(\text{bulk}) + RT \ln a_A^\alpha = \mu_A^0(\text{bulk}) + g_\alpha^2(z) h_A + RT \ln a_A^\pi \quad (18)$$

From which we get

$$RT \ln \frac{a_A^\pi}{a_A^\alpha} = -g_\alpha^2(z) h_A \quad (19)$$

So it is clear that, whenever  $g_\alpha(z) \neq 0$ , the activity in plane  $\pi$  will be different from the correspondent activity in the bulk of the liquid phase  $\alpha$ .

Another way to derive eq 19 from the condition of equilibrium (eq 17) is to equalize the fugacities instead of the chemical potentials

$$RT \ln \lambda_A^\alpha = RT \ln \lambda_A^\pi \quad (20)$$

Here  $\lambda_A^\alpha$  and  $\lambda_A^\pi$  are the fugacities of component A in the bulk  $\alpha$  and in the plane  $\pi$ . Following Lewis–Randal definition<sup>20</sup>

$$RT \ln (a_A^\alpha \lambda_A^0) = RT \ln (a_A^\pi \lambda_A^{0\pi}) \quad (21)$$

Or equivalently

$$RT \ln \left( \frac{a_A^\pi}{a_A^\alpha} \right) = -RT \ln \left( \frac{\lambda_A^{0\pi}}{\lambda_A^0} \right) \quad (22)$$

We thus recover eq 19 from eqs 22 and 15.

### Relationship between the Interfacial Tension and the Fugacity Coefficient

The following treatment is similar to that of Sugimoto<sup>10,11</sup> except for the fact that eq 14 would be used as the correct expression for the standard chemical potential at the interface.

In the usual thermodynamic treatment, the interfacial tension is introduced in the equation of the total energy as an additional term  $\gamma A^\pi$ : The total energy of an interfacial plane  $\pi$  is then equal to

$$U^\pi = TS^\pi - PV^\pi + \gamma^\pi A^\pi + \sum_i \mu_i^{\pi*} n_i^\pi \quad (23)$$

where  $\mu_i^{\pi*} = \mu^0(\text{bulk}) + RT \ln a_i^\pi$  is usually defined as the surface chemical potential and sometimes assumed to be the true chemical potential.<sup>9</sup> Here,  $\gamma^\pi$  is the contribution of plane  $\pi$  to the total interfacial tension  $\gamma^\sigma$ , therefore:



$$A^\sigma \Delta\gamma^\sigma = \sum_k A^{\pi_k} \Delta\gamma^{\pi_k} \quad (24)$$

where  $\Delta\gamma^\sigma = \gamma^\sigma - \gamma_0^\sigma$ . Here,  $\gamma_0^\sigma$  is the interfacial tension of the “clean” fluid/liquid system in the absence of adsorbed substances (see Appendix B). For phases  $\alpha$  and  $\beta$ , it corresponds to initial fields  $g_\alpha^0(z)$  and  $g_\beta^0(z)$ . Term  $\Delta\gamma_k^\pi = \gamma_k^\pi - \gamma_{0k}^\pi$  measures the change in the elastic energy accumulated in plane  $\pi_k$  due to adsorption.

Now, if we consider the interface as a normal thermodynamic system described by its volume, entropy, and number of moles,<sup>2</sup> we can also express the energy associated to plane  $\pi$  as

$$U^\pi = TS^\pi - PV^\pi + \sum_i \mu_i^\pi n_i^\pi \quad (25)$$

Substitution of the expression of the chemical potential previously deduced (eqs 13 and 14) into eq 25, gives

$$U^\pi = TS^\pi - PV^\pi + \sum_i g_\alpha^2 h_i n_i^\pi + \sum_i (\mu^0(\text{bulk}) + RT \ln a_i^\pi) n_i^\pi \quad (26)$$

Therefore, from eqs 23 and 26, we obtain

$$\gamma^\pi A^\pi = \sum g_\alpha^2(z) h_i n_i^\pi \quad (27a)$$

or equivalently<sup>10</sup>

$$\gamma^\pi A^\pi = \sum (\mu_i^\pi - \mu_i^{\pi*}) n_i^\pi \quad (27b)$$

According to eqs 27a and 27b, the interfacial tension arises as a consequence of the perturbation of the elastic field because of the adsorption of molecules of the other phase to plane  $\pi(z)$ .

On the other hand, the free energy of the plane  $\pi$  can be written as it is formulated for a conventional bulk phase

$$G^\pi = \sum_i \mu_i^\pi n_i^\pi \quad (28)$$

If the differential of eq 27 is compared to the classical expression

$$dG^\pi = V^\pi dP - S^\pi dT + A^\pi d\gamma^\pi + \sum_i \mu_i^{\pi*} dn_i^\pi \quad (29)$$

we observe that at constant temperature and pressure, there is consistency between eqs 28 and 29, only if

$$A^\pi d\gamma^\pi = \sum_i g_\alpha^2(z) h_i dn_i^\pi \quad (30)$$

This result relates the tensoactive effect of a given component to its particular response to the elastic field  $g_\alpha(z)$ , acting over the plane  $\pi(z)$ . Notice that it is not necessary that the chemical potentials of the interface ( $\mu_i^\pi$ ) and the bulk-phase ( $\mu_i^\alpha$ ) be different to obtain a non-zero value for the interfacial tension. This was required by Sugimoto's model<sup>10</sup> in order to get a nonzero value on the right-hand side of equation

$$A^\pi d\gamma^\pi = \sum_i (\mu_i^\alpha - \mu_i^\pi) dn_i^\pi \quad (31)$$

Notice also the difference between the right-hand side of eq 27 and that of eq 31 (from Sugimoto). Furthermore, eqs 19 and 30 connect the interfacial tension contribution of one plane with difference between activities of that interfacial plane and the bulk-phase, in such a way that equalization of the chemical

potentials between the bulk phases and the interface can be maintained in our model, although the activities may differ.

### Interfacial Tension

Here, an expression of the interfacial tension is obtained starting from a description of the interface similar to that previously suggested by Sugimoto<sup>11</sup> (see Figure 1).

Let us define the following variables:

$$N_i = \frac{1}{V_i(z)}$$

and

$$y_i = \frac{A_i^\pi}{A_z} \quad (32)$$

Here  $N_i$  is the maximum molar density of component  $i$  in a plane  $\pi(z)$  located at  $z$ , with its normal perpendicular to the interface, and  $y_i$  is the fraction of the total area occupied by component “ $i$ ” in that plane.  $V_i$  and  $A_i$  are respectively the partial molar volume of  $i$  and its partial molar area under the conditions  $dP = 0$  and  $dT = 0$ , and  $A_z$  is the total area of the plane  $\pi(z)$ .

For a plane of width  $\delta\pi$  we have

$$\frac{\sum n_i}{A} = \sum_i \delta_\pi N_i y_i = \sum_i \Gamma_i = \text{constant} \quad (33)$$

Following the arguments given in the previous sections, the density of each plane has to be constant, and therefore, there has to be a dynamic equilibrium between a molecule  $i$  in the bulk  $\alpha$  and such a plane. Thus, the amount of molecules that go into the plane must be equal to the amount of molecules that come out of the plane. Taking the component  $A$  as the matrix element of phase  $\alpha$ , equilibrium can be formulated between the bulk concentration of any molecule and the composition of the plane

$$(y_A^\pi N_A^\pi) A(\pi) + (y_i^\pi N_i^\pi) i(\alpha) \leftrightarrow (y_i^\pi N_i^\pi) i(\pi) + (y_A^\pi N_A^\pi) A(\alpha) \quad (34)$$

where:  $N_i^\pi = N_i \sigma_\pi$ . Using the mass action law

$$(y_A^\pi N_A^\pi) \mu_A^{\pi*} + (y_i^\pi N_i^\pi) \mu_i^\alpha = (y_i^\pi N_i^\pi) \mu_i^{\pi*} + (y_A^\pi N_A^\pi) \mu_A^\alpha \quad (35)$$

It follows

$$y_A^\pi N_A^\pi (\mu_A^{\pi*} - \mu_A^\alpha) = y_i^\pi N_i^\pi (\mu_i^{\pi*} - \mu_i^\alpha) \quad (36)$$

Thus, using the definition of the chemical potential given by eqs 13 and 14, we obtain

$$RT \ln \frac{(a_A^\alpha)^{\nu_i} a_i^\pi}{(a_A^\pi)^{\nu_i} a_i^\alpha} = - \{ \nu_i g_\alpha^2(z) h_A - g_\alpha^2(z) h_i \} \quad (37)$$

Being  $\nu_i = (N_A y_A / N_i y_i) = \Gamma_A / \Gamma_i$ , the constant of adsorption of molecule  $i$  in plane  $\pi$ ,  $K_i^\alpha$  is equal to

$$K_i^\alpha = \exp \left\{ - \frac{g_\alpha^2(z) (\nu_i h_A - h_i)}{RT} \right\} \quad (38)$$

and also

$$K_i^\alpha = \frac{(a_A^\alpha)^{v_i} a_i^\pi}{(a_A^\pi)^{v_i} a_i^\alpha} \quad (39)$$

To obtain the interfacial tension, the partial contribution of each plane (eq 30) has to be added up. Thus, eq 30 has to be integrated from  $\alpha$  ( $z = -\infty$ ) to  $\beta$  ( $z = +\infty$ ) passing through plane  $\pi$  ( $z = 0$ ), taking into account that  $dn_i = A_z N_i y_i dz$ . If  $\sigma = \sigma_A + \sigma_B$  (Figure 1), then

$$\Delta\gamma^\sigma = \frac{\int_{-\infty}^0 \sum_i g_\alpha^2(z) h_i A_z N_i y_i dz}{A^\sigma} + \frac{\int_0^{+\infty} \sum_i g_\beta^2(z) h_i A_z N_i y_i dz}{A^\sigma} \quad (40)$$

The relevant variations of the integrand occur in a limited region close to the interfacial plane. A macroscopic infinitesimal  $\epsilon$  can be used to carry out the integration around  $z = 0$ , excluding intervals the  $[+\epsilon, 0]$  and  $[0, -\epsilon]$ . Hence

$$\Delta\gamma^{\sigma_A} = \frac{\int_{-\infty}^{-\epsilon} \sum_i g_\alpha^2(z) h_i A_z N_i y_i dz}{A^{\sigma_A}} \quad (41)$$

$$\Delta\gamma^{\sigma_B} = \frac{\int_{+\epsilon}^{+\infty} \sum_i g_\beta^2(z) h_i A_z N_i y_i dz}{A^{\sigma_B}} \quad (42)$$

and in this way it is possible to separate the variation of the interfacial tension in two contributions coming from both sides of the interfacial plane

$$\Delta\gamma^\sigma = \Delta\gamma^{\sigma_A} + \Delta\gamma^{\sigma_B} \quad (43)$$

### Equidistribution of Force within Subphase $\sigma_A$

The force that acts over a plane should be distributed uniformly between all bidimensional points that define the plane. The net force that acts along coordinate  $z$  over a matrix molecule  $A$  is equal to the net force that acts over any molecule  $i$  in the referred bidimensional network. Whenever the molecules have different sizes or surface densities,  $N_A^\pi \neq N_i^\pi \Rightarrow \delta_\pi N_A \neq \delta_\pi N_i$ , and therefore, the balance of forces yields

$$\frac{d(g_\alpha^2(z) h_A)}{dz} = \frac{\delta_\pi N_i}{\delta_\pi N_A} \frac{d(g_\alpha^2(z) h_i)}{dz} \quad (44)$$

The preceding equation can be integrated for a given plane at  $z$ , taking  $z = -\infty$  as the lower limit, where the elastic field caused by the perturbation of the interfacial boundary is zero:  $g_\alpha(z = -\infty) = 0$ , so

$$\int_{z=-\infty}^z \frac{d(g_\alpha^2(z) h_A)}{dz} dz = \frac{\delta_\pi N_i}{\delta_\pi N_A} \int_{z=-\infty}^z \frac{d(g_\alpha^2(z) h_i)}{dz} dz \quad (45)$$

Therefore

$$N_A [g_\alpha^2(z) h_A] = N_i [g_\alpha^2(z) h_i] \quad (46)$$

This result allows reducing the number of variables required describing the system.

Applying the mean value theorem, the width of subphase  $\sigma_A$  can be calculated

$$\delta_{\sigma_A} = \frac{\int_{-\infty}^{-\epsilon} \sum_i g_\alpha^2(z) h_i N_i y_i dz}{\sum_i g_\alpha^2(-\epsilon) h_i N_i y_i} \quad (47)$$

Here it has been assumed that the perturbation that exist in this subphase is located at  $z = -\epsilon$ , which should carry the most representative value (median) of each variable. If eq 46 is substituted in the expression of the interfacial tension (eq 41) for subphase  $\sigma_A$  and  $A_z = A^{\sigma_A}$

$$\Delta\gamma^{\sigma_A} = \sum_i g_\alpha^2(-\epsilon) h_i(-\epsilon) N_i y_i \delta_{\sigma_A} \quad (48)$$

If the matrix component is separated from other components in the sum  $\sum'$ , we have  $y_A + \sum' y_i = 1$ . Then, eq 48 can be written as

$$\Delta\gamma^{\sigma_A} = (N_A g_\alpha^2(-\epsilon) h_A (y_A + \sum' y_i)) \delta_{\sigma_A} \quad (49)$$

Because the density in each plane is constant,  $N_A y_A + \sum' N_i y_i$  is also constant, which implies that  $\gamma^{\sigma_A}$  is a linear function of the energy that acts upon only one component, as is shown by eq 49. Going back to our initial definition of the chemical potential given by eq 13, we obtain from eq 19 a useful thermodynamic relation that we can use for practical purposes

$$\Delta\gamma^{\sigma_A} = \left( -N_A^\alpha RT \ln \frac{a_A^{\sigma_A}}{a_A^\alpha} \right) \delta_{\sigma_A} \quad (50)$$

Similarly

$$\Delta\gamma^{\sigma_B} = \left( -N_B^\beta RT \ln \frac{a_B^{\sigma_B}}{a_B^\beta} \right) \delta_{\sigma_B} \quad (51)$$

Hence, the perturbation of the global interfacial tension can be written in terms of an initial condition  $\gamma_0^\sigma$

$$\gamma^\sigma = -N_A^{\sigma_A} RT \ln \frac{a_A^{\sigma_A}}{a_A^\alpha} - N_B^{\sigma_B} RT \ln \frac{a_B^{\sigma_B}}{a_B^\beta} + \gamma_0^\sigma \quad (52)$$

in which

$$-(N_A^\alpha) \delta_{\sigma_A} = -N_A^{\sigma_A} \quad \text{and} \quad -(N_B^\beta) \delta_{\sigma_B} = -N_B^{\sigma_B} \quad (53)$$

### Adsorption Isotherms

Except for the meaning of the elastic field variables, eq 41 is identical to that obtained by Sugimoto.<sup>10-11</sup> Thus, the adjustment of the present theory to the adsorption isotherms can be carried out following the procedure detailed in ref 11.

For infinite dilution

$$\gamma^\sigma = \sum_i' \Gamma_i^{\sigma_A} RT + \sum_i' \Gamma_i^{\sigma_B} RT + \gamma_0^\sigma \quad (54)$$

$$\gamma^\sigma - \gamma_0^\sigma = (\sum_i' \Gamma_i^{\sigma_A} + \sum_i' \Gamma_i^{\sigma_B}) RT \quad (55)$$

Here  $\Gamma_i^{\sigma_A}$  and  $\Gamma_i^{\sigma_B}$  are the surface concentrations of the two subphases. Equation 55 can be recognized as the ideal gas equations for molecules adsorbed at the interface.

Using the equilibrium condition in a multicomponent system, and assuming low adsorption levels in sub-phase  $\sigma_A$  in phase  $\alpha$ , and  $\sigma_B$  in phase  $\beta$

$$\gamma^\sigma = -N_A^{\sigma A} RT \ln \left( 1 - \frac{\sum_i K_i^{\alpha} x_i^{\alpha}}{1 + \sum_i \nu_i K_i^{\alpha} x_i^{\alpha}} \right) - N_B^{\sigma B} RT \ln \left( 1 - \frac{\sum_i K_i^{\beta} x_i^{\beta}}{1 + \sum_i \nu_i K_i^{\beta} x_i^{\beta}} \right) + \gamma_0^\sigma \quad (56)$$

Here we have

$$\nu_i = \frac{N_A^{\sigma A} y_A^{\sigma A}}{N_i^{\sigma A} y_i^{\sigma A}} = \frac{\Gamma_A^{\sigma A}}{\Gamma_i^{\sigma A}} \nu_i = \frac{N_B^{\sigma B} y_B^{\sigma B}}{N_i^{\sigma B} y_i^{\sigma B}} = \frac{\Gamma_B^{\sigma B}}{\Gamma_i^{\sigma B}} \quad (57)$$

Furthermore,  $K_i^\beta$  has the same physical meaning as given by eqs 38 and 39 for phase  $\beta$ , and  $x_i^\alpha$  and  $x_i^\beta$  are the molar fractions of component  $i$  in the phases  $\alpha$  and  $\beta$ , respectively. For a binary system constituted by matrix molecules A and an arbitrary solute  $i$  dissolved in phase  $\alpha$ , the superficial tension can be derived from eq 56 giving the following result:

$$\gamma^\sigma = - (N_A^{\sigma A}) RT \ln \left( 1 - \frac{K_i^{\alpha} x_i^{\alpha}}{1 + \nu_i K_i^{\alpha} x_i^{\alpha}} \right) + \gamma_0^\sigma \quad (58)$$

This expression, after some arithmetic manipulation and assuming that  $y_A^{\sigma A} N_A^{\sigma A} \cong y_i^{\sigma A} N_i^{\sigma A}$ , i.e.,  $\nu_i \cong 1$ , reproduces Szyszkowski's<sup>11</sup> isotherm.

$$\gamma^\sigma = (N_A^{\sigma A}) RT \ln(1 + K_i^{\alpha} x_i^{\alpha}) + \gamma_0^\sigma \quad (59)$$

## Conclusions

The thermodynamic model of a fluid/liquid interface was presented. Among its most relevant characteristics are the following: (i) It includes a redistribution of elastic energy between formerly isolated phases when they are joined together to form an interface. (ii) The description of the system suggested by Sugimoto<sup>10,11</sup> is fully adopted. In that view (Figure 1), the interface consists of two subphases, each one adjacent to a bulk phase. Each subphase can store potential energy, and the interfacial energy can be expressed as a sum of two terms, each belonging to a subphase. (iii) The equalization of chemical potential as a condition of equilibrium (or quasi equilibrium) is maintained. Equalizing the chemical potential of the absorbent between the bulk phases and the interface reproduces the adsorption isotherms most frequently used. (iv) The interfacial tension can be expressed in terms of the activity of only one component of the system at the interface.

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## Appendix A: Meaning of the Elastic Field

When an elastic field produced by a normal tension  $\tau$  ( $=F/A$ ), propagates in a continuous media along the  $z$  axis, the unitary deformation  $\varphi$  can be expressed as<sup>21</sup>

$$\varphi = \frac{\partial \Psi}{\partial z} \quad (A.I.1)$$

where  $\Psi$  is the deformation field. The relation between the normal tension and the unitary deformation is usually written as

$$\tau = Y\varphi = Y \frac{\partial \Psi}{\partial z} \quad (A.I.2)$$

where  $Y$  is the Young's elasticity modulus and

$$F = YA \frac{\partial \Psi}{\partial z} \quad (A.I.3)$$

which looks very familiar for the case of one spring:

$$F = K \frac{\partial \Psi}{\partial z} \quad (A.I.4)$$

where  $K$  is the elasticity modulus of the spring system, and is simply related to the force constant  $k$  as  $K = kL$ , where  $L$  is the spring length.

If the dissipation of a deformation field over a macroscopic continuous plane located at  $z$ , with width  $\delta_\pi$ , were considered, the force that acts on that plane would be

$$F_\pi = k_\pi \delta_\pi \frac{\partial \Psi}{\partial z} \quad (A.I.5)$$

In this last expression,  $k_\pi$  is an effective force constant for plane  $\pi$  in direction  $z$ . Taking into consideration that the energy that is distributed in this plane to deform it is the same energy that the planes stores, we arrive to a more general relationship

$$-\frac{\partial(g(z)^2 H_\pi A_\pi \delta_\pi)}{\partial z} = k_\pi \delta_\pi \frac{\partial \Psi}{\partial z} \quad (A.I.6)$$

and so

$$g(z)^2 H_\pi A_\pi \delta_\pi = A_\pi \delta_\pi \int_{z-\frac{\delta_\pi}{2}}^{z+\frac{\delta_\pi}{2}} \frac{\partial(g(z)^2 H_\pi)}{\partial z} dz = k_\pi \delta_\pi \int_{z-\frac{\delta_\pi}{2}}^{z+\frac{\delta_\pi}{2}} \frac{\partial \Psi}{\partial z} dz \quad (A.I.7)$$

which once evaluated gives

$$g(z)^2 H_\pi A_\pi \delta_\pi = k_\pi \delta_\pi \left( \Psi \left( z + \frac{\delta_\pi}{2} \right) - \Psi \left( z - \frac{\delta_\pi}{2} \right) \right) \quad (A.I.8)$$

Because  $\Psi(z)$  is a smooth continuous function, it can be developed in Taylor series up to first order for length  $\delta_\pi/2$  around  $z$ , giving the following expression

$$g(z)^2 H_\pi A_\pi \delta_\pi = k_\pi \delta_\pi \left( \frac{\partial \Psi(z)}{\partial z} \right) \delta_\pi = k_\pi \delta_\pi^2 \left( \frac{\partial \Psi(z)}{\partial z} \right) \quad (A.I.9)$$

This equation allows us to associate the proposed elastic field with a deformation field. According to eq A.I.9, the modulus of such field  $g(z)$  is equal to

$$g(z) = \sqrt{\frac{k_\pi \delta_\pi}{A_\pi H_\pi} \left( \frac{\partial \Psi(z)}{\partial z} \right)} \quad (A.I.10)$$

## Appendix B: Surface Tension

In terms of the present theory, the interfacial tension is equal to the sum of the elastic energy accumulated within each contributing mesoscopic plane  $\pi_k$ . Thus, the free energy of subphase  $\sigma_A$  is equal to

$$A^{\sigma A} \Delta \gamma^{\sigma A} = \sum_k A^{\pi_k} \Delta \gamma^{\pi_k} \quad (B.1)$$

Substituting eq 30 on the right-hand side of eq B.1

$$A^{\sigma_A} \Delta \gamma^{\sigma_A} = \sum_k \sum_i g_{\alpha}^2(z) h_i(z) \Delta n_i^{\pi_k} \quad (\text{B.2})$$

Once equilibrium is attained, a profile in the molar density of species  $i$  from the bulk phase  $\alpha$  ( $z = -\infty$ ) up to the interface ( $z = 0$ ) is created. It is represented by the quantity  $N_i(z) y_i(z)$  which is strongly dependent on position  $z$

$$\Delta n_i^{\pi_k} = A^{\pi_k} N_i(z) y_i(z) \Delta z_{\pi_k} \quad (\text{B.3})$$

where  $\Delta z_{\pi_k}$  is the width of plane  $\pi_k$ .

If the sum in eq B.2 is substituted by an integral over infinite planes of with  $dz$  from bulk  $\alpha$  ( $z = -\infty$ ) up to the interface ( $z = 0$ )

$$A^{\sigma_A} \Delta \gamma^{\sigma_A} = \int_{-\infty}^0 A_z \sum_i g_{\alpha}^2(z) h_i(z) N_i y_i dz \quad (\text{B.4})$$

where  $A_z$  is the area of an infinitesimal plane  $\pi_k(z)$  located at  $z$ .

In the case of an interface,  $\sigma = \sigma_A + \sigma_B$ , the integration of eq B.4 extends from bulk  $\alpha$  ( $z = -\infty$ ) to bulk  $\beta$  ( $z = +\infty$ ), giving

$$A^{\sigma} \Delta \gamma^{\sigma} = \int_{-\infty}^{+\infty} A_z \sum_i g_{\alpha}^2(z) h_i(z) N_i y_i dz \quad (\text{B.5})$$

where  $\varphi$  is equal to  $\alpha$  ( $-\infty < z - \epsilon$ ) or  $\beta$  ( $+\epsilon < z < +\infty$ ) depending on the position of the plane in  $z$ .

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