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Theory for Interfacial Tension of Partially Miscible Liquids

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Abstract

The aim of this work is to study the problem of the existence of a fundamental relation between the interfacial tension of a system of two partially miscible liquids and the surface tensions of the pure substances. It is shown that these properties cannot be correlated from the physical point of view. However, an accurate relation between them may be developed using a mathematical artifact. In the light of this work, the basis of the empirical formula of Girifalco and Good is examined. The weakness of this formula as well as the approximation leading to it are exposed and discussed and, a new equation connecting interfacial and surface tensions is proposed.

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I. Introduction

There is a considerable interest in the understanding of inhomogeneous systems, i.e., two-phase systems, fluids in contact with a solid or subjected to an external potential, etc. This is because:

(i) From the fundamental point of view, it is of interest to know how to explain the phenomena related to the inhomogeneity of the system.

(ii) From the technical point of view, that may help to predict the properties of such systems. Indeed, the most vital fluids in our lives (water, oils, hydrocarbons, etc) exist in nature, in reserves or while in transportation in the state of confined systems. Some of these fluids are partially immiscible.

In these cases therefore, the adsorption, the interfacial tension and the surface tensions are, among others, important properties that one has to know. Unfortunately, the interparticle potentials for realistic fluids are often unknown. Hence one has to predict the behaviour of such systems using the general properties of the intermolecular potential functions (i.e., the magnitude of the potential functions, their range and the manner in which they decrease).

The study of the two-phase fluids (i.e., liquid-gas or liquid-liquid) is probably the most complex one. For this reason, few fundamental results are available in this area.¹⁻² For instance, to predict the interfacial tension and the surface tensions for two-phase systems, empirical formulae^{3,4} are widely used:

(i) Macleod's formula³ and its various versions are often applied to the studies of liquid-vapour systems. (For more details, see for instance, reference 5).

(ii) In the case of two-partially miscible liquids, a and b , the formula of Girifalco and Good⁴ is used. This equation is based on an analysis consisting in the assumption that the interactions between particles satisfy the so called Berthelot combining rule. According to this combining rule the potentials, assumed to be universal functions, are such that the magnitude of the interactions between two particles of different species is equal to the geometric mean of the magnitudes of the two interactions between identical particles. The interfacial tension, γ , is then written in the form:

$$\gamma = \gamma_a + \gamma_b - 2K(\gamma_a\gamma_b)^{1/2}, \quad (1)$$

where γ_a and γ_b are, respectively, the surface tensions of the pure liquids a and b , and K is a constant depending on the nature of the system (see, for example, reference 4).

The formula of Girifalco and Good as well as the formula of Macleod, besides having very simple analytical forms, give results in good agreement with experiments for several fluids. These qualities make them widely used and their understanding is of great interest. The formula of Macleod has been derived^{6,7} using the thermodynamic equation relating the surface tension, γ_a , of the system to its superficial internal energy, u_a ,

$$u_a = S(\gamma_a - T \partial_T \gamma_a). \quad (2)$$

$$\begin{aligned}\gamma_b^* &= (\Delta\rho_b/\Delta\rho_b^0)^2 \gamma_b \\ &= \beta^2 \gamma_b.\end{aligned}\tag{15b}$$

Concerning the function $\Phi_{qb}^{(1,2)}$, using equations (9) and (12) it may be written:

$$\Phi_{a/b}^{(1,2)} = (\rho_{ab}^{(1,2)} \partial_{r_{12}} w_{ab}^{(1,2)}) / (\rho_{aa}^{(1,2)} \partial_{r_{12}} w_{aa}^{(1,2)}).\tag{16}$$

Using equation (13) and averaging over z_1 and z_2 , equation (16) takes the form:

$$\begin{aligned}\Phi_{a/b}^{(1,2)} &= (\sigma_{ad}/\sigma_{ab}) (\Delta\rho_a/\Delta\rho_a^0) (\Delta\rho_b/\Delta\rho_b^0) \{ [1/2(\rho_b^j + \rho_b^i) g_{ab}(r_{12}^{ab})] \partial_{r_{12}^{ab}} w_{ab}(r_{12}^{ab}) / \\ &\quad [1/2(\rho_a^j + \rho_a^i) g_{aa}(r_{12}^{aa})] \partial_{r_{12}^{aa}} w_{aa}(r_{12}^{aa}) \}.\end{aligned}\tag{17}$$

The density of the fluid b is now assumed to be equal to $1/2(\rho_b^j + \rho_b^i)$, $1/2(\rho_b^j + \rho_b^i) g_{ab}(r_{12}^{ab})$ is the probability density to find one particle of species b at the distance r_{12}^{ab} from a given particle of species a where $r_{12}^{\mu\nu}$ is the distance between the two particles 1 and 2 of species μ and ν expressed in unit $\sigma_{\mu\nu}$. We have:

$$r_{12}^{\mu\nu} = r_{12} / \sigma_{\mu\nu}.\tag{18}$$

Introducing the approximations:

$$\{ 1/2[(\rho_b^j + \rho_b^i) g_{ab}(r_{12}^{ab})] / [1/2[(\rho_a^j + \rho_a^i) g_{aa}(r_{12}^{aa})]] \} \overset{\circ}{\Delta} \{ (\rho_b^j + \rho_b^i) / (\rho_a^j + \rho_a^i) \} (\sigma_{ad}/\sigma_{ab})^3,\tag{19a}$$

$$\partial_{r_{12}^{ab}} w_{ab}(r_{12}^{ab}) / \partial_{r_{12}^{aa}} w_{aa}(r_{12}^{aa}) \overset{\circ}{\Delta} 1,\tag{19b}$$

$\Phi_{a/b}^{(1,2)}$ in equation (16) becomes:

$$\Phi_{a/b}^{(1,2)} \overset{\circ}{\Delta} (\Delta\rho_a/\Delta\rho_a^0) (\Delta\rho_b/\Delta\rho_b^0) [(\rho_b^j + \rho_b^i) / (\rho_a^j + \rho_a^i)] (\sigma_{ad}/\sigma_{ab})^4.\tag{20}$$

By symmetry, we can write for $\Phi_{b/a}^{(1,2)}$:

$$\Phi_{b/a}^{(1,2)} \overset{\circ}{\Delta} (\Delta\rho_a/\Delta\rho_a^0) (\Delta\rho_b/\Delta\rho_b^0) [(\rho_a^j + \rho_a^i) / (\rho_b^j + \rho_b^i)] (\sigma_{bb}/\sigma_{ab})^4.\tag{21}$$

Equations (20) and (21) together with (9) lead to:

$$\gamma_{ab}^* \overset{\circ}{\Delta} -2 (\Delta\rho_a/\Delta\rho_a^0) (\Delta\rho_b/\Delta\rho_b^0) (\sigma_{aa} \sigma_{bb} / \sigma_{ab}^2)^2 (\gamma_a^* \gamma_b^*)^{1/2}$$

$$= -2 \alpha \beta K (\gamma_a \gamma_b)^{1/2}. \quad (22)$$

Using equations (7), (15a), (15b) and (22), the interfacial tension for a system of two partially immiscible liquids takes the form:

$$\begin{aligned} \gamma &= (\Delta\rho_a/\Delta\rho^0)^2 \gamma_a + (\Delta\rho_b/\Delta\rho^0)^2 \gamma_b - 2(\sigma_{aa}\sigma_{bb}/\sigma_{ab}^2)^2 (\Delta\rho_a \Delta\rho_b / (\Delta\rho_a^0 \Delta\rho_b^0)) (\gamma_a \gamma_b)^{1/2} \\ \gamma &= \alpha^2 \gamma_a + \beta^2 \gamma_b - 2\alpha\beta K (\gamma_a \gamma_b)^{1/2}. \end{aligned} \quad (23)$$

It should be noted that:

(i) Two differences exit between this equation and that proposed by Girifalco and Good:

First, in equation (23), γ_a^* and γ_b^* are associated with the coefficients $(\Delta\rho_a/\Delta\rho_a^0)^2$ and $(\Delta\rho_b/\Delta\rho_b^0)^2$, respectively. These two coefficients replaced by 1 in Girifalco and Good equation.

Second, in equation (23), the term $(\gamma_a \gamma_b)^{1/2}$ is associated with the coefficient $-2(\sigma_{aa}\sigma_{bb}/\sigma_{ab}^2)^2 (\Delta\rho_a \Delta\rho_b / (\Delta\rho_a^0 \Delta\rho_b^0))$; whereas it is associated with the coefficient $-2(\sigma_{aa}\sigma_{bb}/\sigma_{ab}^2)$ in the equation of Girifalco and Good.

(ii) Besides the arising in equation (23) of the terms $\Delta\rho_a$ and $\Delta\rho_b$ which guarantee that the three components γ_a^* , γ_b^* and γ_{ab}^* go to zero when the temperature of the system tends to its critical value, the approaches leading to these two equations are completely different.

(iii) The factor δ in equation (6) is very small. Few per cents are enough to create vacancies between particles a and b leading to the split of the system into two phases. It follows that:

First, δ plays an indirect role in the arising of the interfacial phenomena, i.e., due to to the split of the system into two phases, the particles will not be distributed uniformly and the interfacial tension arises.

Second, in equation, (23) σ_{ab} can be replaced by $(\sigma_{aa} + \sigma_{bb})/2$. The direct (macroscopic) effect of δ can be neglected.

(iv) If the liquid b in the binary mixture is now replaced by a system of n liquids which mix together but not miscible with the liquid a , equation (23) becomes:

$$\gamma = (\Delta\rho_a/\Delta\rho_a^0)^2 \gamma_a + \sum_{i \leq i \leq n} \left\{ (\Delta\rho_i/\Delta\rho_i^0)^2 \gamma_i - 2(\sigma_{aa}\sigma_{ii}/\sigma_{ai}^2)^{1/2} (\Delta\rho_a \Delta\rho_i / (\Delta\rho_a^0 \Delta\rho_i^0)) (\gamma_a \gamma_i)^{1/2} \right\}. \quad (24)$$

Because of the approximation used, it is expected that the less miscible the liquids are the better this approximation becomes.

B. General case

We now turn back to the more general case of molecular fluids. The particle-particle potential, $w(i,j)$, has the form given by equation (3). It follows that its derivative with

respect to the surface area will take a form a little different from equation (12):

$$(\partial_s w_{\mu\nu}(i,j))_V = (1/2S) \mathbf{r}_{ij}^* \cdot \partial_{\mathbf{r}_{ij}} w_{\mu\nu}(i,j), \quad (25)$$

in which the vector \mathbf{r}_{ij}^* and the operator $\mathbf{r}_{ij}^* \cdot \partial_{\mathbf{r}_{ij}}$ are defined respectively by:

$$\mathbf{r}_{ij}^* = (x_{ij}, y_{ij}, -2z_{ij}), \quad (26a)$$

$$\mathbf{r}_{ij}^* \cdot \partial_{\mathbf{r}_{ij}} = (x_{ij} \partial_{x_{ij}}, y_{ij} \partial_{y_{ij}}, -2z_{ij} \partial_{z_{ij}}). \quad (26b)$$

For simplify the estimation of the different terms $\Phi_{aa}(1,2)$, $\Phi_{bb}(1,2)$, $\Phi_{a/b}(1,2)$ and $\Phi_{b/a}(1,2)$, it is convenient to write the molecular pair-potential as a sum of simple-fluid potential terms. Such a decomposition can be obtained by introducing the site-site interaction model. The molecular potential becomes:

$$w(i,j) = \sum_{m,n} v(i_m j_n), \quad (27)$$

where the site-site interaction, $v(i_m j_n)$, depends only on the distance between the sites under consideration. It can be written in the form:

$$v(i_m j_n) = v(r_{i_m j_n} / \sigma_{mn}), \quad (28)$$

σ_{mn} is the hard core parameter associate to these sites. Two particles of different species should have at least one couple of sites whose pair-potentials' hard core parameters, σ_{aa} , σ_{bb} and σ_{ab} , satisfy the condition (6). The decomposition given by equation (27) is:

(i) attractive. Because intuitively, it is natural to write that the interactions between two molecules are equal to the sum of the interactions between their different particles.

(ii) exact. Because the pair-potential can be decomposed in any way, the only requirement is that the whole potential should be realistic.

The use of the site-site interaction model is supported by the good agreement with the results obtained from the molecular dynamics and the experiments.¹⁸ The theory related to this model has been recently reformulated and the results obtained are in good agreement with the numerical simulations in both cases of low and high temperatures.¹⁹

Using the same arguments as in the case of simple fluids, equations (14a) and (14b) and, therefore equations (15a) and (15b), can be extended to the general case. Concerning the approximation of the functions $\Phi_{a/b}(1,2)$ and $\Phi_{b/a}(1,2)$ in equation (9), results obtained for pure molecular fluids^{19,20} can easily be extended to their mixtures. The molecular pair-distribution functions in the mixture *a-b* can be written as:

$$g_{\mu\nu}(1,2) = \prod_{m^s 1} \prod_{n^s \dot{A}} g^0(1_m, 2_n) \Psi_{\mu\nu}(1,2), \quad (29)$$

where the products over m and n are extended to all the sites of the particles 1 of species μ and 2 of species ν , $g_{\mu\nu}(1,2)$ stands for the molecular pair-distribution function, $g^0(1_m, 2_n)$ are the pair-distribution functions in a mixture of simple liquids whose particles are identical to the sites of the particles 1 and 2, and $\Psi_{\mu\nu}(1,2)$ is a function converging rapidly to unity. An estimation for the functions $\Phi_{a/b}(1,2)$ and $\Phi_{b/a}(1,2)$ can be obtained by: (i) neglecting the functions, $\Psi_{\mu\nu}(1,2)$ and, (ii) for a given molecule, each site is replaced by a uniform distribution of sites over a sphere centered on one of the molecule sites. In the case where the liquid a has spherical molecules and b has linear molecules consisting of k sites of equal hard core diameter, σ_{ss} , we can write:

$$\Phi_{a/b}(1,2) \dot{A} (\Delta\rho_a/\Delta\rho_a^0) (\Delta\rho_b/\Delta\rho_b^0) [(\rho_b^j + \rho_b^s)/(\rho_a^j + \rho_a^s)] (\sigma_{aa}/\sigma_{ab})^3 (\sigma_{aa}/\sigma_{as}) (k+2)/2. \quad (30)$$

$$\Phi_{b/a}(1,2) \dot{A} (\Delta\rho_a/\Delta\rho_a^0) (\Delta\rho_b/\Delta\rho_b^0) [(\rho_a^j + \rho_a^s)/(\rho_b^j + \rho_b^s)] (\sigma_{bb}/\sigma_{ab})^3 (\sigma_{ss}/\sigma_{as}) \{ (k+2)/[4\{1 + (k+2)^2/4\}] \}, \quad (31)$$

where σ_{bb} is the parameter associated with the spherical molecule equivalent to those of the liquid b and σ_{as} characterizes the interaction site-molecule a . Equations(30) and (31) together with (9) lead to:

$$\begin{aligned} \gamma_{ab}^* \dot{A} & -2 (\Delta\rho_a/\Delta\rho_a^0) (\Delta\rho_b/\Delta\rho_b^0) (\sigma_{aa} \sigma_{bb}/\sigma_{ab}^2)^{3/2} (\sigma_{aa} \sigma_{ss}/\sigma_{as}^2)^{1/2} (2(1 + 4/(k+2)^2))^{-1/2} (\gamma_a \gamma_b)^{1/2} \\ & = -2 \alpha \beta K (\gamma_a \gamma_b)^{1/2}. \end{aligned} \quad (32)$$

The interfacial tension has the same form as in equation(23) i.e.,

$$\gamma = \alpha^2 \gamma_a + \beta^2 \gamma_b - 2\alpha\beta K (\gamma_a \gamma_b)^{1/2}, \quad (33)$$

where the coefficient K is now different that obtained for simple liquids and given by equation (22).

IV. Concluding remarks

The purpose of this paper was to examine the problem of the existence of a fundamental relation between the interfacial tension of a system of two partially miscible liquids and their surface tensions. It has been seen that these properties cannot be physically correlated. However, because of the fact that in the two-phase systems: liquid-liquid a - b and the one-component a and b liquid-vapor, the transition regions are thin layers and the one-particle densities have the same behavior, the expression of the

interfacial tension can be mathematically approximated in such a way to express this property in term of γ_a and γ_b . The equation proposed differs from the Girifalco and Good equation from two points of view:

(i) The coefficients associated to the terms γ_a , γ_b and $(\gamma_a\gamma_b)^{1/2}$ in the expression of γ are different from the corresponding coefficients in equation (1).

(ii) The three contributions to the interfacial tension vanish independently when the temperature of the mixture reaches its critical value. Consequently γ becomes zero, as it should be, and without need of compensation between its different terms.

The accuracy of this equation is examined in the second part of this work.

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M-E Boudh-Hir and G.A. Mansoori
Theory for Interfacial Tension of Partially Miscible Liquids
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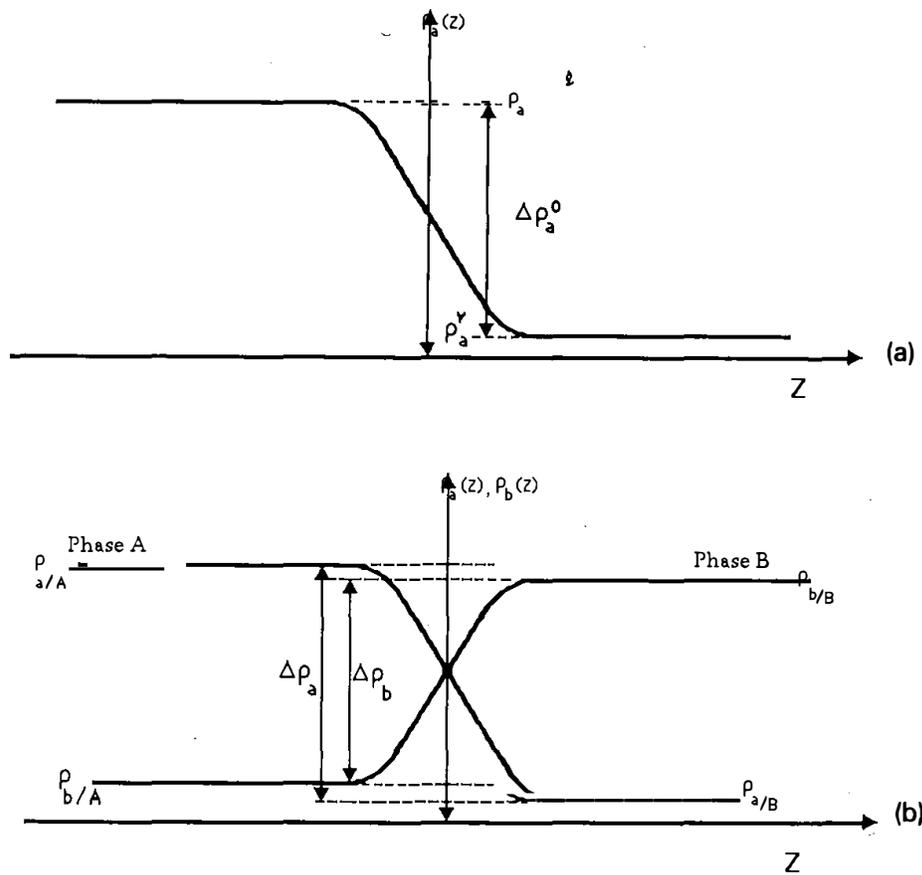


Figure 1. (a) One-particle density in liquid-vapour system. (b) One-particle density in liquid-liquid system.