



A density depletion model for the interfacial tension between immiscible liquids



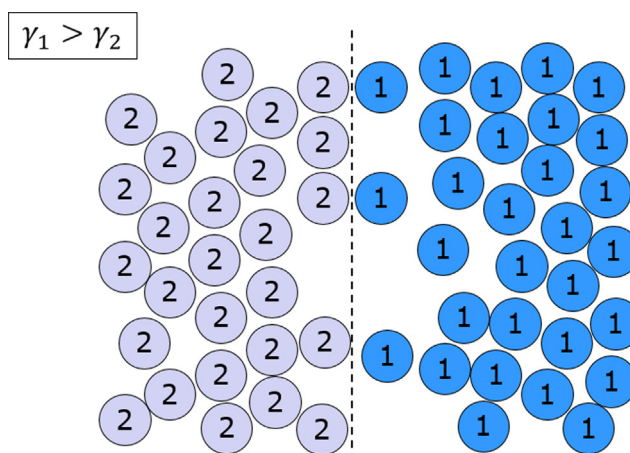
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HIGHLIGHTS

- Contact angle patterns are described by a model for liquid density depletion.
- The same model can be extended to describe liquid–liquid interfacial tensions.
- Deviation of data from the model increases with mutual solubility of liquids.

GRAPHICAL ABSTRACT



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ABSTRACT

A simple model for density depletion of organic liquid molecules at an interface with a lower-energy solid is revised. The model is then extended to immiscible liquid–liquid systems and used to develop a relationship between the surface tensions of pure liquids and the interfacial tension between them. Calculations are compared to literature data for contact angles and interfacial tensions, and the effect of partial miscibility between liquids on their interfacial tension is examined.

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1. Introduction

The boundary region between two phases contains excess free energy that is manifested as a surface or interfacial tension. Surface

and interfacial tensions play important roles in applications such as emulsions, non-adhesive coatings, and oil recovery. The interfacial tension between oil and water is closely related to the hydrophobic effect that has a profound influence in cell biology.

In the case of an interface between a liquid and a solid, the surface and interfacial tensions are related by Young's equation:

$$\gamma_S = \gamma_L \cos \theta + \gamma_{SL}, \quad (1)$$

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where γ_S is the solid surface tension, γ_L is the liquid surface tension, γ_{SL} is the solid-liquid interfacial tension, and θ is the contact angle.

Since the surface tensions γ_S and γ_L arise from solid–solid and liquid–liquid molecular interactions respectively, and the interfacial tension γ_{SL} arises from solid-liquid molecular interactions, it is natural to ask if γ_{SL} could be expressible in terms of γ_S and γ_L (independently of Young's equation). If such a relationship existed, and were substituted into Young's equation, the contact angle θ would become a function of γ_S and γ_L only, and the contact angles of different liquids on the same solid would be a function of γ_L only. This has indeed been found to be the case for many organic liquids and low-energy solids [1].

One example among several of such a relationship between surface and interfacial tensions in solid-liquid systems is

$$\gamma_{SL} = \gamma_L + \gamma_S - 2\sqrt{\gamma_L\gamma_S} [1 - \beta(\gamma_L - \gamma_S)^2], \quad (2)$$

where $\beta = 105.7 \text{ m}^4/\text{J}^2$ is an empirical constant [2]. When substituted into Young's equation, Eq. (2) described a large body of contact angle data on low-energy surfaces.

In the separate case of an interface between two liquids, all of the surface and interfacial tensions are readily measurable. It may again be asked whether the liquid–liquid interfacial tension can be expressed as a function of the surface tensions of the individual liquids. Several such relationships have been proposed.

One well-known example is Antonow's rule:

$$\gamma_{12} = \gamma_{1(2)} - \gamma_{2(1)}, \quad (3)$$

where γ_{12} is the liquid–liquid interfacial tension, $\gamma_{1(2)}$ is the surface tension of liquid 1 (saturated with liquid 2), $\gamma_{2(1)}$ is the surface tension of liquid 2 (saturated with liquid 1), and liquid 1 has the higher surface tension. While it is often a good approximation, Antonow's rule is valid only when liquid 2 spreads completely on liquid 1. In that case, when liquid 1 is saturated with liquid 2, the liquid 1/air interface effectively becomes a liquid 1/liquid 2 interface and a liquid 2/air interface, leading to Eq. (3).

Girifalco and Good [3] proposed the following relationship between surface and interfacial tensions of liquids:

$$\gamma_{12} = \gamma_1 + \gamma_2 - 2\Phi\sqrt{\gamma_1\gamma_2}, \quad (4)$$

where γ_1 and γ_2 are the surface tensions of pure liquid 1 and pure liquid 2, respectively. From experimental data, they found that the parameter Φ fell in different ranges between 0.31 and 1.15 depending on the nature of the intermolecular forces in each liquid.

Fowkes [4] expressed the interfacial tension between a polar or metallic liquid 1 and a dispersive liquid 2 as

$$\gamma_{12} = \gamma_1 + \gamma_2 - 2\sqrt{\gamma_1^d\gamma_2}, \quad (5)$$

where γ_1^d is the contribution of dispersive forces to the surface tension of liquid 1. Values of γ_1^d for water and mercury were found from their respective interfacial tensions with various hydrocarbon liquids. Generalizations of Fowkes' theory have introduced additional contributions to the surface tension of each liquid, which are also found from interfacial tension data [5].

Finally, beginning from the Gibbs model of an interface, Marmur and Valal [6] developed a general theoretical equation and then reduced it to the following empirical correlation:

$$\gamma_{12} = \frac{\cosh(\gamma_1/\gamma_0)\gamma_1^{1-m} - \cosh(\gamma_2/\gamma_0)\gamma_2^{1-m}}{\cosh(\gamma_{ef}/\gamma_0)\gamma_{ef}^{-m}}, \quad (6)$$

where

$$\gamma_{ef} = \gamma_1 + \gamma_2 - \eta\gamma_1^n\gamma_2^{1-n}, \quad (7)$$

and $\gamma_0 = 42.121 \text{ mJ/m}^2$, $\eta = 0.83755$, $m = 0.93884$, and $n = 0.94965$ were optimized on a set of interfacial tension data for both

immiscible and partially miscible systems. Interestingly, Marmur and Valal [6] also found that Eq. (2) for solid-liquid interfaces, with S as a second liquid, gave a reasonable approximation for liquid–liquid interfacial tensions, provided a higher value of $\beta = 191.712 \text{ m}^4/\text{J}^2$ was used.

For solid-liquid systems, the empirical relationship between surface and interfacial tensions that is implied by contact angle data has been derived in approximate form from a consideration of molecular interactions. Calculations were based on a combining rule for interactions between unlike molecules, and a computational [7] or analytical [8] model of the depletion of liquid molecules adjacent to a lower-energy solid surface.

In the work described here, the analytical model [8] for density depletion at a solid-liquid interface was revisited, and then extended to the case of an interface between two immiscible liquids, in order to explain the observation of Marmur and Valal [6].

2. Interface between a liquid and a solid

Liquid molecules adjacent to a lower-energy solid surface experience a net attraction back into the liquid, generating a depletion in the liquid density at the interface. The density depletion of water at hydrophobic surfaces has been observed experimentally [9].

Using the geometric mean combining rule and accounting for the liquid density depletion leads to the following first-order approximation for the tension at a solid–liquid interface [8]:

$$\gamma_{SL} = \gamma_L + \gamma_S - 2\rho\sqrt{\gamma_L\gamma_S}, \quad (8)$$

where ρ is the density of the liquid adjacent to the solid, normalized by the bulk liquid density. This ratio of densities can be expressed as

$$\rho = e^{-\Delta E/k_B T}, \quad (9)$$

where ΔE is the energy difference per atom between the interface and the bulk liquid, k_B is Boltzmann's constant, and T is temperature. In Ref. [8], ΔE was written as $\gamma_{SL} \times \delta^2$, where δ is the size of an atom. However, the energy change per unit area experienced by liquid atoms in moving from the bulk to the interface is not γ_{SL} , which also counts the energy change of the solid, but approximately $\gamma_L - (\gamma_L\gamma_S)^{1/2}$; and the space occupied by a liquid atom in the interface, when corrected for the density depletion, is not δ^2 but δ^2/ρ , if the interfacial region of the liquid is modelled as a monolayer. Therefore,

$$\rho \approx e^{-(\gamma_L - \sqrt{\gamma_L\gamma_S})\delta^2/\rho k_B T}. \quad (10)$$

Eq. (10) generally has three solutions for ρ in the interval [0,1]: $\rho = 0$, corresponding to no interface; a middle, unstable value; and a large, stable value. Taking the large value of ρ and inserting it into Eq. (8) gives a relationship between the surface and interfacial tensions in a solid-liquid system. Substituting for γ_{SL} using Young's equation then gives a relation between the surface tensions γ_L and contact angles θ of different liquids on a given solid surface (fixed γ_S).

Fig. 1 shows fits of Eq. (8) (lines) to experimental contact angles [10] for a variety of organic liquids on three low-energy solid surfaces at room temperature. (The use of advancing contact angles like these with Young's equation is discussed in Ref. [8] and references therein.) For each surface, the atomic size δ and the solid surface tension γ_S were varied to fit the data. The optimized values are listed in Table 1. The values for δ were consistent and appropriate for an atomic dimension. The density ratio ρ from Eq. (9), an intermediate result in each calculation, ranged from 0.6 to 1, with the higher values, corresponding to the least depletion, occurring for the liquids of lowest contact angles.

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