

# Comments

## Comments on Some Recent Papers on Interfacial Tension and Contact Angles

It is well-known that the field of contact angle measurements and surface energetic's calculations is still highly debated and controversial. This is true despite the deceptive simplicity of the basic experiment involved (the measurement of the contact angle between a liquid and a solid). We believe it is of interest to drive the attention of *Langmuir's* readership to two recent papers published in this journal. In our view, these papers are good examples of the "subtle" problems which can be encountered in the field of contact angle and surface tension, and their critical reading can offer many a hint for interesting reflections.

The two papers ((A) Makkonen, L. *Langmuir* 2000, 16, 7669–7672. (B) Öner, D.; McCarthy, T. J. *Langmuir* 2000, 16, 7777–7782.) are extremely interesting and well-written papers; in both cases, however, we believe that starting from some exact considerations some partially erroneous conclusions are reached.

(A) The first paper deals with the problem of the strong differences found in the measurements of surface free energies of solids on the basis of the Gibbs–Thomson equation (GTE)<sup>1</sup> with respect to other methods as the acid–base or surface tension components approach (STC)<sup>2</sup> or the equation of state (EQS) method;<sup>3</sup> both GTE and STC or EQS are used by many researchers in similar but independent fields of research. In fact the first one is dominant for metals, molecular solids, and ionic solids, while the others are used mainly in the fields of polymers and liquids. When, rarely, the two methods are used to evaluate the properties of the same material, the results are different by 1 or 2 orders of magnitude.

This is a very proper observation, indeed. A spectacular consequence is the following: applying the Gibbs–Thomson approach, the solid–liquid interfacial energy of water is estimated between 16 and 44 mJ/m<sup>2</sup>,<sup>4–5</sup> and consequently the ice surface free energy is between 96 and 120 mJ/m<sup>2</sup>. From the perspective of contact angles, the situation is completely different. In fact the equilibrium contact angle of liquid water on ice is between 12 and 24°,<sup>6</sup> and thus the solid appears to possess a surface free energy lower than the liquid, about 70 mJ/m<sup>2</sup> vs 75.8 mJ/m<sup>2</sup> for liquid water at 0 °C. The numerical values of ice surface free energy in this case are calculated from semiempirical theories, as the EQS or the STC, but the experimental result of positive contact angle is independent of the applied theory and it is hard to be explained in terms of GTE. In fact if ice has a surface free energy so much higher than that of water, the consequence would

be the "spreading" of liquid water on ice or, at least, a zero contact angle!

It is worth noting that the existence of a finite contact angle of water on ice (as well as of other common liquids on their solid face) has an important role also in another debate, on the existence of the so-called "surface melting"<sup>7</sup> (whose effective existence could eventually solve even the present puzzle).

The different results obtained by GTE and through the STC and EQS methods however are in Makkonen's opinion proof that these last theories are wrong.

In our opinion there is a different answer to this problem. It is only worth noting that both EQS and STC are semiempirical theories, able to fit a considerable number of experimental data; further, STC is an example of the so-called "linear free energy relationships" (LFER), widely and successfully used in many fields of physical organic chemistry;<sup>8</sup> EQS has been repeatedly considered as theoretically wrong.<sup>9</sup>

On the other hand the question is not the general theoretical validity of the GTE but the exact conditions of its validity and of its proper use. Some important objections have been raised by Moi and Neumann in a very interesting chapter of ref 3; they start from the consideration that if a solid material is not a crystal, with a shape which respects the Gibbs–Wulff theorem, then the common procedure to prove GTE is not strictly applicable to it. This point of view has been accepted by Makkonen, who has tried to develop two more general proofs of the GTE, based on thermodynamic and mechanical considerations, to make GTE independent of the objections of Moi and Neumann.

However it is our opinion that in these new proofs some unreasonable approximations are made.

In the *thermodynamic* derivation Makkonen writes (eq 10 of A)

$$\Delta G_v = -\Delta S_f \Delta T \quad (1)$$

where the quantity on the left is the difference between the free energy per unit volume between the liquid and the solid state and on the right we have the entropy of fusion and the temperature difference between the planar and curved materials. This equality is not generally valid. In fact he quotes the previous equation from the book by Kurz and Fisher,<sup>10</sup> p 176, in which it is clearly written that the previous approximated equation could be valid only if the specific heat of liquid and solid phases are the same. Fisher restricts this assumption to the metals; however it is not valid for many other materials. Two examples can be interesting: water and hydrocarbons, for which the solid and liquid heat capacities are strongly different, in an approximated ratio of 1:2, and even their

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(1) Kulkarni, N.; Dehoff, R. T. *Acta Mater.* 1997, 45, 4963–4968.

(2) Good, R. J.; van Oss, C. J. In *Modern Approaches to Wettability Theory and Applications*; Schrader, M. E., Loeb, G. I., Eds.; Plenum Press: New York, 1992; pp 1–28.

(3) In *Applied Surface Thermodynamics*; Neumann, A. W., Spelt, J. K., Eds.; Marcel Dekker: New York, 1996.

(4) Ketcham, W. M.; Hobbs, P. V. *Philos. Mag.* 1969, 19, 1161–1173.

(5) Jones, D. R. H. *J. Mater. Sci.* 1974, 9, 1–17.

(6) Knight, C. A. *J. Colloid Interface Sci.* 1966, 25, 280–284.

(7) Wettlaufer, J. S. *Philos. Trans. R. Soc. London* 1999, A357, 3403–3425.

(8) Abraham, M. H. *Chem. Soc. Rev.* 1993, 22, 73–83.

(9) Morrison, I. D. *Langmuir* 1991, 7, 1833–1836.

(10) Kurz, W.; Fisher, D. J. *Fundamentals of solidification*; Trans. Technol. Publ.: Enfield, NH, 1986.

difference is not a constant with the temperature.<sup>11</sup> Thus the new thermodynamic proof of Makkonen is not generally valid.

It is worth noting that the original equations of Fisher are already approximated, because the author considers that the fusion enthalpy does not change with the fusion temperature, which is strictly false. This point deserves further considerations.

To prove GTE, one, classically, considers two systems with different curvatures,  $K$ , at a constant pressure in  $\alpha$  and  $\beta$  phases, writing the following equation (e.g., eq 46 of ref 1)

$$-\Delta S dT - 2\gamma V^{S=\beta} dK = 0 \cdots (dP^{\alpha=L} = 0) \quad (2)$$

from the application of the Gibbs–Duhem equation to this system.

From this, one extracts the following:

$$dT = -\frac{2\gamma V^{S=\beta} dK}{\Delta S} = -\frac{2\gamma TV^{S=\beta} dK}{\Delta h} \quad (3)$$

But in doing so we have separated the variables and their corresponding functions and we are considering that none of the functions on the right depends on the curvature. Strictly speaking all the functions on the right depend on the temperature and on the curvature; on the other hand these quantities are connected and are not independent variables. The fact that the solid density and the fusion entropy or, equivalently, the unit volume enthalpy depend on the temperature, especially considering that the temperature change can be of tens of degrees, is not strange; moreover the interfacial energy *must* decrease with the temperature for stability reasons.<sup>12</sup> Some results which confirm this dependence appear in ref 13, from whose data a linear dependence of the enthalpy on the temperature can be recalculated.

As a conclusion, strictly speaking, all the thermodynamic quantities cannot be simply transferred on the right of the equation; the correct form of the Gibbs–Thomson equation is thus the following:

$$\int_{K=0, T=T_0}^{K,T} \frac{\Delta S}{2V^{S=\beta}} dT = \int_{K=0, T=T}^{K,T} d(\gamma K) \quad (4a)$$

or equivalently

$$\int_{K=0, T=T_0}^{K,T} \frac{\Delta h_V}{2T} dT = \int_{K=0, T=T_0}^{K,T} d(\gamma K) \quad (4b)$$

where, to integrate the left-hand side, we need at least the approximate dependence on the temperature of the used thermodynamic functions; in the right-hand side we can integrate the function product differential by parts. In this way the appearance of the GTE is a bit different, as consequently also the obtained numerical results:

$$\int_{K=0, T=T_0}^{K,T} \frac{\Delta h_V}{2T} dT = \gamma_{sl,T} K_T \quad (5)$$

As to the new *mechanical* proof, reference is made to the “Gibbs–Duhem” equation (eq 5 of the cited paper), defined as

$$\Delta P = -\frac{\Delta TL_M}{T_M} \quad (6)$$

where the quantities are referred to the melting of a unit volume of a solid. It would be probably more correct to call this equation the Clapeyron or modified Clapeyron equation, which is a particular case of the original differential Gibbs–Duhem equation. However, in the Clapeyron equation the use of  $\Delta$  operator is referred to the difference between the solid and liquid state (e.g.,  $L_M$  is a  $\Delta$  quantity, the difference between the liquid and solid enthalpy). The application of the  $\Delta$  operator to the pressure and temperature corresponds once again to assume that the extensive quantity  $L_M$  is not function of the intensive variables; i.e., the fusion enthalpy per unit volume is constant with respect to the temperature, which again is not strictly valid, as previously discussed.

However, the main wrong point of the mechanical proof is the confusion between the surface stress and the surface tension. Surface tension is a scalar quantity, corresponding to the work required to reversibly form a unit area of new surface, but it can also be considered as the modulus of a vector, considered as isotropic in a liquid, whose direction is tangent to the liquid surface and whose versus opposes to the formation of a new surface.

This formation is considered in a liquid as a “plastic” process. It is worth noting that in a “structured” liquid, such as water, the formation of new surface can probably contain both plastic and “elastic” components (see the famous experiment of Berthelot and the measurements of the Young modulus of liquid water<sup>14</sup>). Following the definition given by many authors<sup>3,15</sup>

$$f_{ij} = \gamma \delta_{ij} + \frac{\partial \gamma}{\partial \epsilon_{ij}} \quad (7)$$

where  $f_{ij}$  is the surface stress,  $\gamma$  is the surface tension,  $\delta_{ij}$  is the Kronecker delta, and  $\epsilon_{ij}$  is the surface strain tensor; the surface stress is the work required to increase a unit area of a surface by stress, it is a tensor and depends on the elastic deformations. In a solid the elastic components for the formation of new surface are predominant. Moiré and Neumann stress as in the plastic process the surface molecule density is a constant, while in the elastic process the total number of molecules is constant, but not their surface density. Makkonen considers, on the contrary, that in a solid only the surface tension exists, which can be considered as the modulus of a force always parallel to the solid surface.

He justifies this opinion by the consideration that no stress can exist in a crystal in equilibrium with its liquid. Actually, the stresses present in the solids have so many consequences as to constitute an important part of material science; they are classified in the following way:<sup>16</sup> (1) macrostresses, or I-kind stresses, that act over macroscopic regions and are generally caused by any applied or residual macroscopic elastic and plastic deformation; (2) microstresses, or II-kind stresses, which act on submillimeter regions, such as grains, caused by elastic incompatibility of different grains in single phase material, different plastic deformations, or thermal expansion coefficient of phases in multiphase materials. Both of these stresses

(11) *CRC Handbook of Chemistry and Physics*, CRC NetBase; Lide D. R., Ed.; Chapman & Hall: London, 1999.

(12) Defay, R.; Prigogine, I.; Bellemans, A. *Surface Tension and Adsorption*; Longmans, Green & Co.: London, 1966.

(13) Jackson, C. L.; McKenna, G. B. *J. Chem. Phys.* **1990**, *93*, 9002–9010.

(14) Jones, W. M.; Overton, G. D. N.; Trevena, D. H. *J. Phys. D: Appl. Phys.* **1981**, *14*, 1283–1291.

(15) Cherry, B. W. *Polymer Surfaces*; Cambridge University Press: Cambridge, 1981; Chapter 1, p 3.

(16) Bunge, H.-J. *Texture Analysis in Materials Science*; Butterworth & Co: London, 1982.

cause a shift of the diffraction X-rays lines, because the deformation is homogeneous through all the sampling volume. (3) Differently, the III-kind stresses or micro-stresses are visible in the line broadening of the X-rays diffraction lines, because they are caused by localized inhomogeneous deformation associated with structural defects even in the single grains.

This well-founded classification of stresses shows that the hypothesis of Makkonen is very weak and that it can be wrong not only when two grains meet but also in the single grain case; his hypothesis could eventually be true only for a single crystal, not for a crystal groove, where two crystal surfaces must meet.

It is worthy to remember that literature extensively discussed the use of the term "surface tension" for a solid;<sup>15</sup> a commonly accepted conclusion is that for a solid it is not correct to use this concept in an "equilibrium" context; in the majority of the journals it is practically forbidden to use the term "surface tension" as referred to the surface of a solid. In a crystalline solid, to move an atom or a molecule from the bulk to the surface cannot be made in a quasistatic, reversible way, because, contrary to what happens in the liquid state, strong bonds exist. As a result, the concept of surface tension for a solid is invalid.

The question could be posed for certain amorphous materials with weak intermolecular bonds at a  $T > T_g$ , as it is true for many polymers. But also in these cases it is commonly allowed to use the concept of "surface free energy" or generically of surface energy, due to the practical impossibility to consider "quasistatic" processes on a current laboratory time scale.

Apart of this particular case (long time scale for amorphous materials with weak intermolecular bonds at  $T > T_g$ ) the use of the term "surface tension" for a solid can be a misleading concept.

A last point can be raised about the experimental determinations. In the common contact angle measurements the radius of curvature of solid surfaces is very high or infinite, samples must be extremely flat and this is a fundamental condition to obtain meaningful values: roughness can invalidate each result;<sup>18</sup> on the contrary, the radius of curvature of the particles used in the experimental evaluations of GTE is extremely small, even of the order of a few nanometers. In nucleation experiments the question could be: is thermodynamics valid when a very low number of particles is involved? In other cases, as in grain groove experiments (e.g., see the wonderful image of Figure 9 by Hardy<sup>18</sup>) the curvature estimated by optical methods (whose resolution cannot be better than half-a-micrometer, due to the diffraction limit) can differ from the "local" microscopic or nanoscopic curvature at molecular scale, which can possibly be extremely different.

In both cases the presence of roughness may induce significant errors.

(B) The second paper treats the problem of the relation between the hydrophobicity and the exact topography of the surface. To do this the authors refer to a result first obtained by Furnidge.<sup>19</sup> Studying the mechanical equilibrium conditions for liquid droplets on tilted surfaces in a gravity field, he found the following equation:

$$\frac{mg(\sin \alpha)}{w} = \gamma_{LV}(\cos \theta_R - \cos \theta_A) \quad (8)$$

where  $g$  is the gravity,  $m$  the mass of the drop,  $\alpha$  is tilting

of the plane with respect to the horizontal,  $\gamma_{LV}$  is the surface tension of the liquid,  $\theta_A$  and  $\theta_R$  are the advancing and receding angles, respectively, and  $w$  is the width of the drop along a line parallel to the plane and perpendicular to the its maximum inclination direction.

They conclude as follows (page 7777): "It is clear from this equation that the difference between advancing and receding contact angles (hysteresis) and not the absolute values of the contact angles is important to hydrophobicity."

This sentence is seriously wrong and misleading.

Unfortunately the concept of hydrophobicity/hydrophilicity does not have a clear and unique definition, and it is often used for very different and contradictory phenomena; however it is more commonly defined with respect to the work of adhesion,<sup>20</sup> with the formation or the elimination of interfacial area, a process quite different from the motion of a drop on a tilted surface, which appears as a process more correlated with the concept of "friction", with a constant value of interfacial area. The work of adhesion is calculated from the equation

$$W_{adh} = \gamma_{LV}(1 + \cos \theta_{equ}) \quad (9)$$

which is defined using an equilibrium value of contact angle. Suppose one has two different equilibrium contact angles of water on two different surfaces, then a higher angle will correspond to a more hydrophobic surface and to a lower work of adhesion.

Considering a "real" surface, with the hysteresis of contact angles, claims for the characterization of the corresponding equilibrium value of contact angle; there is no commonly accepted method to do this, at the moment; however an approximated equation has been repeatedly proposed<sup>21</sup> as

$$\cos \theta_{equ} = 0.5 \cos \theta_{adv} + 0.5 \cos \theta_{rec} \quad (10)$$

Suppose now to know all the three values, the advancing, receding, and equilibrium contact angles, one can evaluate both the work of adhesion and the sliding conditions in a gravity environment (obviously in this second case one needs also to measure the tilting angle of the plane and/or the lateral size of the drop).

In the quoted paper the authors compare the situation of droplets on two different surfaces: on surface A, the drop has  $\theta_A = \theta_R = 70^\circ$ ; on surface B, the drop has  $\theta_A = 120^\circ$  and  $\theta_R = 80^\circ$ . Using basic terminology of contact angle measurement, one would say that the first surface is a "Young" or ideal surface, showing no hysteresis (i.e., perfectly flat and homogeneous), with an equilibrium or Young angle equal to the advancing and receding one. Surface B is a real rough and/or heterogeneous surface with an advancing and receding angle, whose equilibrium angle is intermediate and can be estimated from the previous equation (or measured through an opportune experimental set) as about  $\theta_{equ} = 99.4^\circ$ .<sup>21</sup>

On the first one the work of adhesion is greater and to detach the drop from an horizontal plane is more energetically expensive. However, in a gravity environment the drop can easily slip (without detaching) if the plane is tilted, even by an infinitesimal angle; on the second one the adhesion work is lower, but the drop does not move until the plane is tilted at a critical value, given by Furnidge's equation. This can appear strange, but it is

(17) Morra, M.; Della Volpe, C. Letter to the editor *J. Biomed. Mater. Res.* **1998**, *42*, 473–474.

(18) Hardy, S. C. *Philos. Mag.* **1977**, *35*, 471–484.

(19) Furnidge, G. C. L. *J. Colloid Interface Sci.* **1962**, *17*, 309–324.

(20) Wu, S. *Polymer Interface and Adhesion*; Marcel Dekker, Inc.: New York, 1982.

(21) Della Volpe, C.; Maniglio, D.; Siboni, S.; Morra, M. *Oil Gas Sci. Technol.* **2001**, *56*, 9–22 and references therein.



important to consider that the phenomena described by the two equations are completely different.

The work of adhesion considers as initial states separated surfaces which are in contact in the final state and so measures the direct interaction of the liquid and solid; the Furnidge equation analyses a case in which the interaction surface is constant and reveals the presence of microscopic hindrances which can eventually put the system in metastable blocked states, local minima of energy, giving a "friction" effect!

The drop on surface A, the ideal one, must slide by definition; a perfectly flat and homogeneous surface does not give any hindrance to a sliding drop, independently on the value of its contact angle, but two different ideal surfaces, with two different contact angles with respect to water can be well classified with respect to their work of adhesion with water and considered less or more hydrophobic with respect to the energy necessary to detach the drop from the surface.

Consider, now, two real different surfaces (that is, two surfaces with contact angle hysteresis). Suppose, for the sake of simplicity, there are droplets of the same liquid on the surfaces with the same contact angle hysteresis but with different absolute values of the advancing and receding angles (and consequently of the equilibrium contact angle); what happens? Should they show the same behavior, according to the quoted paper? Let's consider some numerical values: on surface C the drop has, e.g.,  $\theta_A = 150^\circ$  and  $\theta_R = 120^\circ$  and  $\theta_{\text{equ}}$  of about  $133^\circ$ ; on surface D the drop has, e.g.,  $\theta_A = 60^\circ$  and  $\theta_R = 30^\circ$ , with an equilibrium angle,  $\theta_{\text{equ}}$ , of about  $47^\circ$ . In common terms the first surface is more hydrophobic than the second.

In this case the hysteresis effect, which corresponds to the right term of the Furnidge equation, is exactly the same, and this must be true also for the left term, but what is the value of  $w$ ? It is higher for case D, as one can intuitively conclude or calculate by using programs as Surface Evolver.<sup>22</sup> So not only is the adhesion work higher for the second case, but even for the drop to slip on the plane one obviously needs a value of  $\alpha$  for case D higher than the  $\alpha$  value in case C; the more hydrophilic plane should be more inclined to allow the drop to slip, as the intuitive concept of hydrophobicity, defined in the field of adhesion, claims.

(22) Surface Evolver is a free program developed at University of Minnesota, useful for the calculations of minimal energy surfaces; web address <http://www.susqu.edu/facstaff/b/brakke/>.

As a conclusion it is not possible to consider "only the hysteresis as important to hydrophobicity" in the case of sliding drops or in every other case, as claimed by the authors of the paper, first of all because the hydrophobicity is not related to the presence of hindrance on the surface but to the strength, number, and kind of molecular interactions between the surface and the liquid.

The sliding phenomenon does not immediately depend on the higher or lower hydrophobicity of the surface but on the existence of microscopic hindrances, due to surface roughness or heterogeneity which produces the hysteresis of contact angles. A Young ideal surface does not offer any hindrance to sliding drops, independently on its level of hydrophobicity or hydrophilicity. Hydrophobicity or hydrophilicity of the surfaces, defined from the work of adhesion, have an indirect effect on the sliding phenomenon; in fact, they express the intensity level of the forces acting between the liquid and the solid; greater forces present in the case of hydrophilic surfaces "push" the drop onto the surface and increase their reciprocal contact area, modifying the parameter  $w$ , the lateral size of the drop. This greater interfacial contact simply increases the number of total "hindrances" intrinsic of the interface, thus increasing the plane tilting necessary to move the drop.

In the friction between two solids, the real microscopic contact area is considered as a constant and does not appear in the corresponding equation; in the case of a liquid drop on a solid, the real microscopic contact area can strongly change with the hydrophobicity/hydrophilicity of the surface, and it is expressed by the lateral drop size, which increases with hydrophilicity and the decrease of equilibrium contact angle; in this analogy the hysteresis is the equivalent of the friction coefficient and it is completely independent of the hydrophobicity/hydrophilicity of the surface.

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