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Revisiting lowest possible surface energy of a solid

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Revisiting lowest possible surface energy of a solid

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Abstract

The solid–vapor surface energy cannot be determined directly from the contact angle data because the Young equation includes three unknown interfacial energies. While the liquid–vapor energy is usually known, different theories can be used to exclude the solid–liquid energy, such as Antonoff, Zisman, Fowkes, and Owens and Wendt theories. These theories yield significantly different results for the solid–vapor surface energy. We revisit the claim that the lowest surface energy is 6.7 mJ m^{-2} of $\text{C}_{20}\text{F}_{42}$, while polytetrafluoroethylene's surface energy is 22 mJ m^{-2} . These numbers can change significantly if a different theory is used.

Materials with low surface energies are widely used to control surface properties, for example, to reduce adhesion and produce of self-cleaning, superhydrophobic, oleophobic, ice-phobic, omniphobic and anti-fouling coatings [1]. Fluorocarbons and fluorine polymers usually have low surface energies due to the inert fluorine groups $-\text{CF}_3$ and $-\text{CF}_2$. Extensive research has been done to determine the surface energies of these compounds and to estimate the lowest possible surface energy. It has been argued that no material with a smooth surface can have a contact angle (CA) greater than 119° [2]; furthermore, only reentrant surface roughness can provide robust oleophobicity [3]. In certain exotic cases, such as chemically active interfaces, even negative effective surface energies has been reported [4–6]; however, these are non-equilibrium cases, while a conventional definition of the surface energy implies an interface at equilibrium.

One of the most popular methods of determining the surface energy is the CA measurement (the goniometry). The problem with determining the surface energy using CA data is that according to the Young equation,

$$\cos \theta = \frac{\gamma_{\text{SV}} - \gamma_{\text{SL}}}{\gamma_{\text{LV}}} \quad (1)$$

the CA is dependent upon three unknown parameters: solid–vapor, solid–liquid, and liquid–vapor surface energies. Although the value of the liquid–vapor energy is usually known (thus, for water at room temperature $\gamma_{\text{LV}} = 72.8 \text{ mJ m}^{-2}$), there are still two unknown parameters, γ_{SV} and γ_{SL} , which should be determined from the only one experimentally measured value of the CA.

Various strategies have been proposed to overcome this difficulty. Antonoff [7, 8] suggested that the surface tension at the interface is the absolute value of the difference between the surface energies of liquid and solid in equilibrium state,

$$\gamma_{\text{SL}} = |\gamma_{\text{SV}} - \gamma_{\text{LV}}|. \quad (2)$$

With this relation and equation (1), γ_{SV} and γ_{SL} can be easily calculated. The physical reasoning behind Antonoff's rule is that the surface energy is due to missing bonds of atoms/molecules at the surface. When two materials come into contact, they form new bonds and one with lower energy (fewer bonds available) partially compensates for missing bonds in the other material. For two surfaces of the same material, all bonds are filled and the interfacial energy is zero.

Fox and Zisman [9, 10] introduced the concept of the critical surface energy of wetting γ_c , the surface energy of the liquid that just spreads on the solid. It is essentially γ_{LV} when $\cos \theta = 1$. From equation (1) $\gamma_c = \gamma_{\text{SV}} - \gamma_{\text{SL}}$, provided that $\gamma_{\text{SL}} = 0$ for the liquid just spreading, $\gamma_{\text{SV}} = \gamma_c$. However, as the authors pointed out, their approach provides a very rough approximation of the solid–liquid surface energy as a function of the solid–vapor surface energy.

A different approach was taken by Fowkes [11], who suggested that the surface energy of any material is proportional to the energy of interacting dipole molecules and, therefore, to the square of the electric polar moment: $\gamma_1 \sim (p_1)^2$, $\gamma_2 \sim (p_2)^2$. When two materials come into contact, the surface energy of each is amended by subtracting a geometric average term,

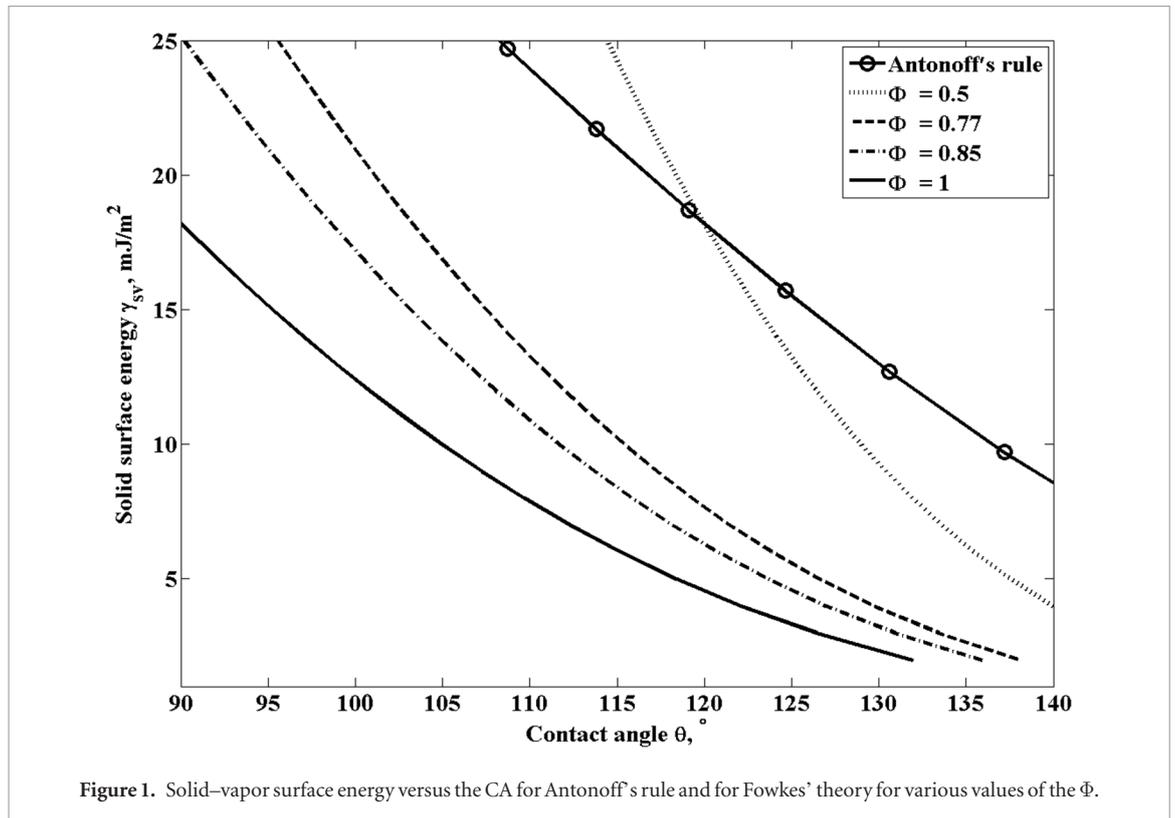


Figure 1. Solid–vapor surface energy versus the CA for Antonoff's rule and for Fowkes' theory for various values of the Φ .

corresponding to the interaction energy of the two, namely, $p_1 p_2 \sim (\gamma_1 \gamma_2)^{1/2}$. Therefore, the total energy of the interface between two materials is given by the sum of their surface energies with the amendments, $\gamma_{12} = \gamma_1 + \gamma_2 - 2(\gamma_1 \gamma_2)^{1/2}$, and thus

$$\gamma_{SL} = \gamma_{SV} + \gamma_{LV} - 2(\gamma_{SV} \gamma_{LV})^{1/2}. \quad (3)$$

Obviously, equations (2) and (3) are in contradiction with each other; however, different sets of experimental data are available supporting both. The main shortcoming of Fowkes' theory is that it does not take into account that intermolecular forces consist of components of different nature.

An extension of the Fowkes' theory was suggested by Grifalco and Good [12] and Owens and Wendt [13], who assumed that the surface tension as a sum of two independent contributions corresponding to the polar and dispersion forces, $\gamma = \gamma_d + \gamma_p$. Consequently, the interfacial energy is given by

$$\gamma_{SL} = \gamma_{SV} + \gamma_{LV} - 2(\gamma_{SV}^d \gamma_{LV}^d)^{1/2} - 2(\gamma_{SV}^p \gamma_{LV}^p)^{1/2} \quad (4)$$

or

$$\gamma_{SL} = \gamma_{SV} + \gamma_{LV} - 2\Phi \sqrt{\gamma_{SV} \gamma_{LV}} \quad (5)$$

where $0 \leq \Phi \leq 1$ is a parameter characterizing dispersion-polar cross-interaction [14],

$$\Phi = \frac{\sqrt{\gamma_{SV}^d \gamma_{LV}^d} + \sqrt{\gamma_{SV}^p \gamma_{LV}^p}}{\sqrt{\gamma_{SV} \gamma_{LV}}}. \quad (6)$$

In most cases, Φ is close to the unity. In the limit of $\Phi = 1$, equation (5) becomes equation (3)

corresponding to the case when only dispersion forces are present (e.g. non-polar molecules). An interesting geometric interpretation of equations (2) and (5) exists with equation (2) being related to the triangle rule and equation (5) to the cosine law [15].

Note that the derivation of equation (5) is based on a number of assumptions, namely, that (i) there are only two components of the intermolecular force—the dispersion and polar, (ii) both these components are independent and additive, and (iii) they both obey the 'Coulomb law' geometric mean rule. Besides that, additional components of the intermolecular forces can exist, thus, Shalel-Levanon and Marmur [16] suggested a theory on the basis of the Lewis acid–base interaction. A different method was proposed by Drummond *et al* [17], who utilized dielectric data and theoretical predictions of van der Waals (dispersion) interaction and that the lowest known surface free energies of all bulk homogeneous polymeric solids is provided by polytetrafluoroethylene (PTFE).

Furthermore, it has been argued in the textbook literature, that the polar component of the surface energy of water is primarily an entropic one due to the rearrangement of the H₂O molecular network of H-bonds in the surface layer [18], and therefore the assumption of the geometric mean is not valid. Similarly, a computational simulation by Dalvia and Rosky [19] has shown that the hydrophobicity of fluorocarbons is due to the extra work of cavity formation to accommodate a fluorocarbon, compared to a hydrocarbon, and that it is not offset by enhanced energetic interactions with water.

Table 1. Calculation of the surface energy of the PTFE and C₂₀F₄₂.

CA	Water		Methylene iodide	
	PTFE	109°	88°	
	C ₂₀ F ₄₂	119°	107°	
Liquid–vapor surface energy (mJ m ⁻²)				
		Dispersion	Polar	Total
	Water	21.8	51	72.8
	Methylene iodide	49.5	1.3	50.8
Solid vapor surface energy (mJ m ⁻²)				
		Dispersion	Polar	Total
	PTFE	12.64	1.24	13.9
	C ₂₀ F ₄₂	5.67	1.14	6.8
Solid liquid surface energy (mJ m ⁻²)				
		Water	Methylene iodide	
	PTFE	37.6	12.1	
	C ₂₀ F ₄₂	42.1	21.6	

It is clear from the above, that one must be cautious when converting the CA data into the solid–vapor surface energy. Depending on what theory is assumed to be valid and values of parameters, the same value of the CA may result in a very different value of γ_{SV} . Thus, using equations (1) and (5) CA = 120° corresponds to $\gamma_{SV} = 5 \text{ mJ m}^{-1}$ for $\Phi = 1$, $\gamma_{SV} = 8 \text{ mJ m}^{-1}$ for $\Phi = 0.77$, and $\gamma_{SV} = 18.2 \text{ mJ m}^{-1}$ for Antonoff's rule (figure 1). Besides the simple goniometry, alternative methods of determining the liquid–solid adhesion include measuring the lateral adhesion force and require more sophisticated equipment, such as the centrifugal adhesion balance [20].

Nishino *et al* [2] reported that the maximum possible water CA with a smooth solid material is 119°. This was achieved for *n*-Perfluoroeicosan (C₂₀F₄₂)-coated glass. The authors noted that ‘closest hexagonal packed –CF₃ groups’ provide the lowest possible surface energy. In other words, there are no chemical groups with lower surface energies. The paper further claims that the value of the solid–air surface energy for *n*-Perfluoroeicosan is 6.7 mJ m⁻² and that ‘this value is much smaller than that (22 mJ m⁻²) of PTFE’. PTFE or Polytetrafluoroethylene better known under its commercial name ‘Teflon’ is a famous non-sticky low adhesion polymer material consisting of the same elements—carbon and fluorine—with the formula (C₂F₄)_{*n*}. Water CA on smooth PTFE surfaces have been reported to vary from 109° to 114° [21], and even higher. The results may depend on the measurement technique and on the accuracy of the experiments as well as on smoothness of the surface. Even assuming the value of 109° one can ask, why such close values of the CA for PTFE and C₂₀F₄₂, namely, 109° and 119°, result in such drastically different values of the surfaces energy for these two materials, namely, $\gamma_{SV} = 22 \text{ mJ m}^{-2}$ and $\gamma_{SV} = 6.7 \text{ mJ m}^{-2}$?

To decouple the effects of dispersion and polar forces, Nishino *et al* [2] investigated wetting of C₂₀F₄₂ by two liquids: predominantly polar water and predominantly non-polar methylene iodide

(CH₂I₂) presumably having $\gamma_{LV} = 50.8 \text{ mJ m}^{-2}$. Using equation (1), water CA = 119° provides the value of $\gamma_{SV} - \gamma_{SWater} = -35.29 \text{ mJ m}^{-2}$, while methylene iodide CA = 107° yields $\gamma_{SV} - \gamma_{SMethylene iodide} = -14.85 \text{ mJ m}^{-2}$. To find the value of γ_{SV} , it is necessary to know the interface energy of the solid and liquid. Nishino *et al* [2] adopted the model by Owens and Wendt [13], i.e. equation (4), to calculate the surface energy using water versus methylene iodide data [13]. Note that the value of the surface tensions for methylene iodide, $\gamma_{LV} = 50.8 \text{ mJ m}^{-2}$ is known with a large uncertainty. According to Owens and Wendt, their original data had the accuracy of $\pm 9 \text{ mJ m}^{-2}$ or about $\pm 20\%$.

The results of the calculation of the surface energy of the PTFE and C₂₀F₄₂ are presented in table 1 using the equation (4), Owens and Wendt theory. The value of CA = 88° [10] of methylene iodide on PTFE is used, the calculated PTFE solid–vapor energy is $\gamma_{SV} = 13.9 \text{ mJ m}^{-2}$, which is much smaller than the claimed value of 22 mJ m⁻². Owens and Wendt note that there is alternative measurement value of CA = 77° [13] of methylene Iodide on PTFE. This value yields $\gamma_{SV} = 19.1 \text{ mJ m}^{-2}$. Wetting of PTFE by glycerol (CA = 86.8°) and glycol (CA = 76.6°) yields $\gamma_{SV} = 23.0 \text{ mJ m}^{-2}$ and $\gamma_{SV} = 24.6 \text{ mJ m}^{-2}$, respectively.

We conclude from the above that there are three significant sources of error for the surface energy determination from the CA data. First, the theory is based on a large number of assumptions about the intermolecular interactions. Depending on the assumptions the results are different. Thus, the value of water CA = 120° corresponds to the range of energies between $\gamma_{SV} = 5.0 \text{ mJ m}^{-1}$ and $\gamma_{SV} = 18.2 \text{ mJ m}^{-1}$, depending on which model is used. Second, even when the same theory is used consistently, the CA data for different non-polar liquids provide different results. Thus, methylene iodide, glycerol, and glycol on PTFE data yield surface energy in the range between $\gamma_{SV} = 13.9 \text{ mJ m}^{-2}$ and $\gamma_{SV} = 24.6 \text{ mJ m}^{-2}$. Third, even for water, the CA experimental data is not always

consistent, e.g. CA of water on PTFE is in a range between 109° to 114° . Given that no physical explanation has been provided why the interfacial energy of the $(C_2F_4)_n$ molecules is larger than that of $C_{20}F_{42}$, it is questionable whether the solid-air surface energy of the n -Perfluoroicosane is indeed more than three times lower than that of the PTFE.

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