Chapter 7
Determination of Solid Surface Tension by Contact Angle

Abstract In this chapter, approaches to determine solid surface tension by contact angle are briefly reviewed and assessed. These approaches include the Zisman method, various versions of the surface tension component methods, and the equation of state methods. The Zisman method is an empirical approach based on the relationship between the cosine of the contact angle and the surface tensions of the test liquids. The approach allows the determination of the critical surface tension of the solid. However, it is limited to low surface energy surfaces as data points from high surface tension liquids deviate from linearity due to polar and H-bonding interactions. The surface tension component approach is pioneered by Fowkes who assumed that (1) surface tension can be partitioned into individual independent components and (2) the work of adhesion can be expressed as the geometric means of the surface tension components. The original Fowkes method only considered dispersion interaction, and the methodology has been extended to include polar and H-bonding interactions in the extended Fowkes method or electron donor and acceptor interactions in the vOCG method. The equation of state assumes that the interfacial liquid–solid surface tension depends on the surface tension of the liquid and solid only. The interface surface tension was obtained by curve fitting with contact angle data and adjustable parameters. While the equation of state approach has been improved and three different versions have been developed, the basic thermodynamic assumption and the methodology were seriously challenged by many researchers in the field. It is important to note that both surface tension component methods and equation of state methods are semiempirical and that there are many assumptions in each methodology. Both approaches inherit a reversible work-of-adhesion assumption from Dupre. Specifically, for two immiscible liquids, the free energy change at the interface is equated to the interfacial tension of the newly formed interface subtracted by the surface tensions of the precursor liquids. The validity of this assumption is always questionable when one of the components is solid as the surface molecules or segments in solid have no mobility during any interfacial interaction. In view of this questionable assumption and the semiempirical nature of the contact angle approach, we propose a simpler and more direct approach to move forward. Since the motivation of determining surface tension is to be able to predict surface wettability and adhesion, we suggest measuring the advancing and receding angle of the solid surface instead. They have recently been shown to correlate to wettability and adhesion, respectively, by force measurements.

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7.1 Introduction

Solid surface energy is one of the basic physical properties for solid like density, melting point, refractive index, dielectric constant, modulus, etc. It is a very important material property for anyone, who is interested in interfacial interaction between a solid and another material. The industrial needs are very diverse. While the obvious applications are paints, coatings, and adhesives, the less obvious ones actually have much higher economic values to date. They include cleaning in the semiconductor industry, printing in printed electronic device manufacturing, aerospace, shipping, mining, pharmaceuticals, and so on. Generally speaking, a high surface energy material will be more reactive and stickier and vice versa. Such property is thought to originate from interactions at the atomic and molecular level and has not been accessible for direct measurement [1]. About 200 years ago, Young [2] studied liquid wetting on solid surface and found that an angle is formed at the three-phase contact line as a result of the mechanical equilibrium between the liquid surface tension (γ_{LV}), solid surface tension (γ_{SV}), and liquid–solid interfacial tension (γ_{SL}). His description has become the famous Young's equation (Eq. 7.1), and the subject was detailed in Chap. 3 in this book.

$$\gamma_{\mathrm{SV}} = \gamma_{\mathrm{LV}} \cdot \cos\boldsymbol{\theta} + \gamma_{\mathrm{SL}} \tag{7.1}$$

The Young's equation is problematic because only two out of four quantities (γ_{LV} and $\boldsymbol{\theta}$) can be determined experimentally. Dupre [3] later introduced the concepts of reversible work of cohesion (W^{coh}) and work of adhesion (W^{ad}) between two liquids. A concept diagram is depicted in Fig. 7.1. Hypothetically, when two cylinders of the same liquid are brought together (Fig. 7.1a), the free energy change per unit area ($\Delta G_{11}^{\mathrm{coh}}$) is the free energy of cohesion and is equaled to the negative of work of cohesion and can be expressed as

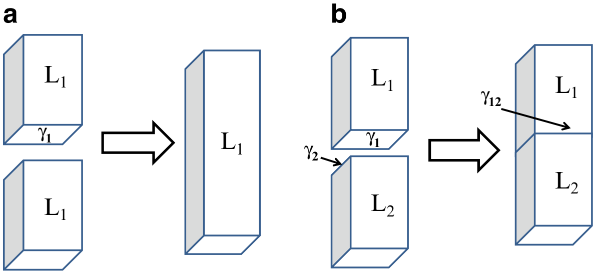

Fig. 7.1 Diagram illustration of the concepts of reversible work of (**a**) cohesion and (**b**) adhesion

$$\Delta G_{11}^{\mathrm{coh}} = -2\gamma_1 = -W_{11}^{\mathrm{coh}} \tag{7.2}$$

where γ_1 and W_{11}^{coh} are the surface tension and work of cohesion for L_1, respectively.

Similarly, when two cylinders of immiscible liquids are brought together (Fig. 7.1b), the free energy change per unit area would be $\Delta G_{12}^{\mathrm{ad}}$ and is equaled to the negative of work of adhesion. More importantly, the free energy change can be equated as the interfacial tension of the newly formed interface subtracted by the surface tensions of the precursor liquids.

$$\Delta G_{12}^{\mathrm{ad}} = \gamma_{12} - \gamma_1 - \gamma_2 = -W_{12}^{\mathrm{ad}} \tag{7.3}$$

where γ_2 is the surface tension of L_2 and γ_{12} is the interfacial tension between L_1 and L_2.

Now if one assumes that L_1 is a liquid and L_2 is a solid (S) and combines Eqs. (7.1) and (7.3), the work of adhesion between a liquid and a solid surface ($W_{\mathrm{SL}}^{\mathrm{ad}}$) is given by Eq. (7.4), which becomes known as the Young–Dupre equation [4]:

$$W_{\mathrm{SL}}^{\mathrm{ad}} = \gamma_{\mathrm{LV}}\left(1 + \cos\boldsymbol{\theta}\right) \tag{7.4}$$

This derivation opens the possibility of studying γ_{SL} through $W_{\mathrm{SL}}^{\mathrm{ad}}$, which can now be determined by measuring $\boldsymbol{\theta}$ with a known liquid. Solid surface tension γ_{SV} is no longer inaccessible. Many theories and models had been studied to develop the expressions for work of adhesion W_{SL} and the corresponding interfacial tension γ_{SL}. One of the objectives of this chapter is to provide a brief overview of some key approaches for the estimation of solid surface tension through contact angle measurements. The different approaches are assessed and discussed. It is important to point out that solid surface energy and surface tension have been used interchangeably in recent literature. They are actually known to be two distinct quantities in solid [5–7], and the quantity derived from contact angle is solid surface tension. The fundamental issues around surface tension versus surface energy and the methodology of using contact angle to determine solid surface tension will be discussed, and a path forward is proposed.

7.2 Approaches to Determine Solid Surface Tension by Contact Angle

7.2.1 Zisman Method

In 1950, Fox and Zisman [8] reported their study of the wettability of poly(tetrafluoroethylene) (PTFE) with *n*-alkanes, di(*n*-alkyl)ethers, *n*-alkylbenzenes, and many other liquids. A linear relationship between the cosine of the contact angle ($\cos\boldsymbol{\theta}$) and the surface tension of the liquid (γ_{LV}) for the *n*-alkane solvents was obtained (Fig. 7.2). Similar plots were also obtained for di(*n*-alkyl)ethers and

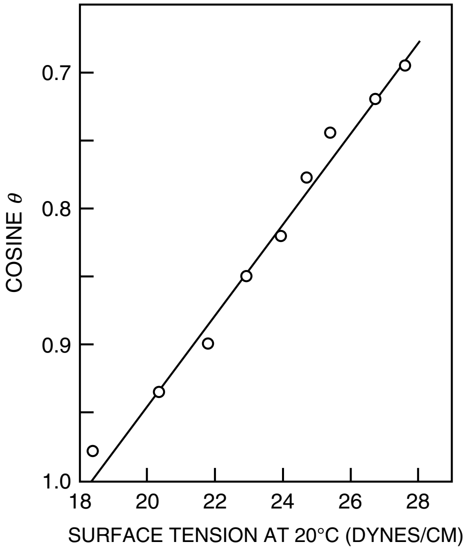

Fig. 7.2 Plot of cos*θ* against surface tension for a series of *n*-alkanes on PTFE (reproduced with permission from [8], copyright 1950 Elsevier)

n-alkylbenzenes [9]. When the plot in Fig. 7.2 is extended to a much larger solvent set, including other halocarbons, ketones, esters, amides, and water, the plot is no longer linear (see Fig. 3.15 in Chap. 3). Zisman [9] attributed the linear portion of the relationship to the van der Waals force interaction between *n*-alkanes and the PTFE surface. The deviation from linearity for high surface tension liquids was attributed to stronger intermolecular interactions, such as dipolar interactions and H-bonding, in these solvents. The intercept at $\cos\theta = 1.0$ is at ~18 mN/m and is defined as critical surface tension (γ_C) of the solid. Liquids with surface tensions lower than γ_C will fully wet the solid surface, while liquids with higher surface tensions than γ_C will form a finite contact angle on the solid surface. In other words, the critical surface tension is the highest surface tension which the liquid fully wets the solid surface. This critical surface tension is found to be empirically close to the solid surface tension. The plot in Fig. 7.2 is now known as the Zisman plot in literature and has become one of the methods to estimate the surface tension of solid surface.

Surface wettability depends strongly on molecular interactions between liquid and the solid surface. In 1953, Ellison, Fox, and Zisman [10] reported a wetting study of three adsorbed monolayers with different end groups with *n*-alkanes, along with a PTFE film. The end groups from the adsorbed monolayers are CH_3, CHF_2, and CF_3. The main functional group on the PTFE film is CF_2. The Zisman plot for the study is depicted in Fig. 7.3. From the intercepts at $\cos\theta = 1.0$, these authors found that the critical surface tensions of the surface constituents decrease in the following order: $CH_3 > CF_2 > CHF_2 > CF_3$. From the intercept at $\cos\theta = 1$, the critical surface tension for the CF_3 head group was determined to be ~6 mN/m. This is very similar to the surface free energy value of *n*-perfluoroeicosane ($C_{20}F_{42}$), which is

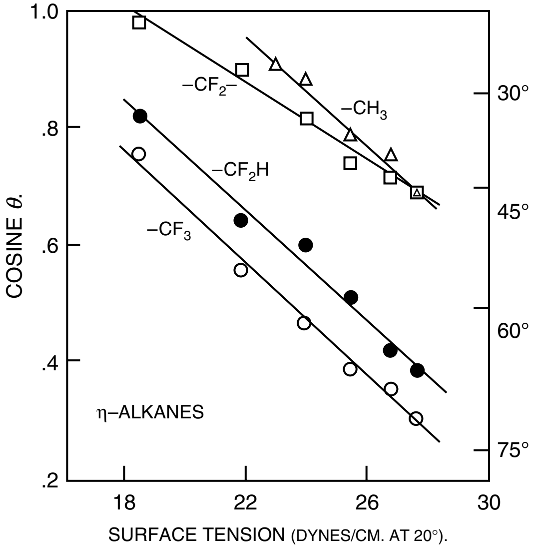

Fig. 7.3 Plot of wettability data for adsorbed monolayers with CH_3, CF_2H, and CH_3 end group and PTFE film with *n*-alkanes (reproduced with permission from [10], copyright 1953 The American Chemical Society)

6.7 mN/m, determined by Nishino et al. using the dynamic contact angles of water and diiodomethane [11]. The results demonstrate that the Zisman plot can be used to determine the surface tension of different chemical constituents on the solid surface. Indeed, the critical surface tensions of different chemical constituents from surfaces of fluorocarbon, hydrocarbon, chlorocarbon, and nitrated hydrocarbon polymers have been determined [12].

It is important to point out that the Zisman critical surface tension analysis is only limited to low surface energy surfaces and alkane solvents, where van de Waals force is the prime interaction. Many exceptions were found with polar and H-bonding solvents. Despite this limitation, the Zisman analysis remains as one of the useful tools to estimate the surface tension of low surface energy material to date [13].

7.2.2 Surface Tension Component Methods

Fowkes method. Fowkes [14–16] was the pioneer proposing partition of surface tension. He assumed that the surface tension of a solid or liquid is a sum of independent components, which addresses specific molecular interaction individually. For example, γ_{SV} can have a number of contributors and is given by

$$\gamma_{\mathrm{SV}} = \gamma_{\mathrm{SV}}^{\mathrm{d}} + \gamma_{\mathrm{SV}}^{\mathrm{p}} + \gamma_{\mathrm{SV}}^{\mathrm{h}} + \gamma_{\mathrm{SV}}^{\mathrm{i}} + \gamma_{\mathrm{SV}}^{\mathrm{ab}} \tag{7.5}$$

where $\gamma_{\mathrm{SV}}^{\mathrm{d}}$, $\gamma_{\mathrm{SV}}^{\mathrm{p}}$, $\gamma_{\mathrm{SV}}^{\mathrm{h}}$, $\gamma_{\mathrm{SV}}^{\mathrm{i}}$, $\gamma_{\mathrm{SV}}^{\mathrm{ab}}$ represent contributions from the dispersion, dipole–dipole interaction, hydrogen bonding, induced dipole–dipole interaction, and acid–base components, for example.

In the original Fowkes model [14], only dispersion component of the surface tension was considered, which is caused by London dispersion force. The London dispersion forces arise from the interaction of fluctuating electronic dipoles with induced dipoles in neighboring atoms or molecules [15]. It exists in all type of materials and always presents as an attractive force at the liquid–solid interface. The work of adhesion from dispersion interaction has been proved thermodynamically to take the form of the geometric mean according to the Berthelot mixing rule [17, 18].

$$W_{\mathrm{SL}}^{\mathrm{d}} = \sqrt{W_{\mathrm{SV}}^{\mathrm{d}} \cdot W_{\mathrm{LV}}^{\mathrm{d}}} \tag{7.6}$$

Therefore, according to Eq. (7.3), the liquid–solid interfacial tensions can be expressed as

$$\gamma_{\mathrm{SL}} = \gamma_{\mathrm{SV}} + \gamma_{\mathrm{LV}} - 2\sqrt{\gamma_{\mathrm{SV}}^{\mathrm{d}} \cdot \gamma_{\mathrm{LV}}^{\mathrm{d}}} \tag{7.7}$$

If the solid surface has only a dispersion component, $\gamma_{\mathrm{SV}} = \gamma_{\mathrm{SV}}^{\mathrm{d}}$. By combining the Young–Dupre equation (Eq. 7.4) and the definition of work of adhesion (Eq. 7.2), γ_{SV} can be expressed as

$$\gamma_{\mathrm{SV}} = \gamma_{\mathrm{SV}}^{\mathrm{d}} = \frac{\gamma_{\mathrm{LV}}^{2}}{4\gamma_{\mathrm{LV}}^{\mathrm{d}}} \cdot (1 + \cos\theta)^{2} \tag{7.8}$$

From Eq. (7.8), the solid surface tension (γ_{SV}) can be calculated by measuring the contact angle $\boldsymbol{\theta}$ with a liquid whose γ_{LV} value is known.

Owens–Wendt–Rabel–Kaelble (*OWRK*) *method*. Owens and Wendt [19] modified the Fowkes model by assuming that solid surface tension and liquid surface tensions are composed of two components, namely, a dispersion component and a hydrogen-bonding component. The nondispersive interaction was included into the hydrogen-bonding component. Nearly at the same time, Rabel [20] and Kaelble [21] also published a very similar equation by partitioning the solid surface tension into dispersion and polar components. Subsequent researchers called this as the OWRK method, and γ_{SV} and γ_{LV} can be expressed as

$$\begin{aligned} \gamma_{\mathrm{SV}} &= \gamma_{\mathrm{SV}}^{\mathrm{d}} + \gamma_{\mathrm{SV}}^{\mathrm{p}} \\ \gamma_{\mathrm{LV}} &= \gamma_{\mathrm{LV}}^{\mathrm{d}} + \gamma_{\mathrm{LV}}^{\mathrm{p}} \end{aligned} \tag{7.9}$$

Similar to Eq. (7.7), the interfacial liquid–solid surface tension can be derived by assuming that the polar component has a geometric mean form, although dipole–dipole interactions follow the rule of geometric mean [15] and hydrogen-bonding interactions are probably not [15, 16, 22].

$$\gamma_{\mathrm{SL}} = \gamma_{\mathrm{SV}} + \gamma_{\mathrm{LV}} - 2\sqrt{\gamma_{\mathrm{SV}}^{\mathrm{d}} \cdot \gamma_{\mathrm{LV}}^{\mathrm{d}}} - 2\sqrt{\gamma_{\mathrm{SV}}^{\mathrm{p}} \cdot \gamma_{\mathrm{LV}}^{\mathrm{p}}} \tag{7.10}$$

By combining with the Young–Dupre equation (Eq. 7.4), we have

$$\gamma_{\mathrm{LV}}\left(1+\cos\theta\right)=2\sqrt{\gamma_{\mathrm{SV}}^{\mathrm{d}}\cdot\gamma_{\mathrm{LV}}^{\mathrm{d}}}+2\sqrt{\gamma_{\mathrm{SV}}^{\mathrm{p}}\cdot\gamma_{\mathrm{LV}}^{\mathrm{p}}} \tag{7.11}$$

There are two unknowns, $\gamma_{\mathrm{SV}}^{\mathrm{d}}$ and $\gamma_{\mathrm{SV}}^{\mathrm{p}}$, in Eq. (7.11). They can be calculated by determining the contact angles with two different test liquids with known $\gamma_{\mathrm{LV}}^{\mathrm{d}}$ and $\gamma_{\mathrm{LV}}^{\mathrm{p}}$ values. γ_{SV} will be just the sum of $\gamma_{\mathrm{SV}}^{\mathrm{d}}$ and $\gamma_{\mathrm{SV}}^{\mathrm{p}}$. Since two test liquids are required, this method is also called the two-liquid method.

Extended Fowkes method. Kitazaki et al. [23] further refined the OWRK model by splitting the dipole–dipole interactions into polar and H-bonding interactions. Accordingly, both γ_{SV} and γ_{LV} comprise three components: *d* for dispersion, *p* for polar, and *h* for H-bonding (Eq. 7.13), and they all take the form of geometrical mean (Eqs. 7.14 and 7.15).

$$\begin{gathered}\gamma_{\mathrm{SV}}=\gamma_{\mathrm{SV}}^{\mathrm{d}}+\gamma_{\mathrm{SV}}^{\mathrm{p}}+\gamma_{\mathrm{SV}}^{\mathrm{h}}\\ \gamma_{\mathrm{LV}}=\gamma_{\mathrm{LV}}^{\mathrm{d}}+\gamma_{\mathrm{LV}}^{\mathrm{p}}+\gamma_{\mathrm{LV}}^{\mathrm{h}}\end{gathered} \tag{7.13}$$

$$\gamma_{\mathrm{SL}}=\gamma_{\mathrm{SV}}+\gamma_{\mathrm{LV}}-2\sqrt{\gamma_{\mathrm{SV}}^{\mathrm{d}}\cdot\gamma_{\mathrm{LV}}^{\mathrm{d}}}-2\sqrt{\gamma_{\mathrm{SV}}^{\mathrm{p}}\cdot\gamma_{\mathrm{LV}}^{\mathrm{p}}}-2\sqrt{\gamma_{\mathrm{SV}}^{\mathrm{h}}\cdot\gamma_{\mathrm{LV}}^{\mathrm{h}}} \tag{7.14}$$

$$\gamma_{\mathrm{LV}}\left(1+\cos\theta\right)=2\sqrt{\gamma_{\mathrm{SV}}^{\mathrm{d}}\cdot\gamma_{\mathrm{LV}}^{\mathrm{d}}}+2\sqrt{\gamma_{\mathrm{SV}}^{\mathrm{p}}\cdot\gamma_{\mathrm{LV}}^{\mathrm{p}}}+2\sqrt{\gamma_{\mathrm{SV}}^{\mathrm{h}}\cdot\gamma_{\mathrm{LV}}^{\mathrm{h}}} \tag{7.15}$$

There are three unknowns in the solid surface tension, $\gamma_{\mathrm{SV}}^{\mathrm{d}}$, $\gamma_{\mathrm{SV}}^{\mathrm{p}}$, and $\gamma_{\mathrm{SV}}^{\mathrm{h}}$ in Eq. (7.15). To calculate γ_{SV}, one can use three test liquids with known $\gamma_{\mathrm{LV}}^{\mathrm{d}}$, $\gamma_{\mathrm{LV}}^{\mathrm{p}}$, and $\gamma_{\mathrm{LV}}^{\mathrm{h}}$ values. The component solid surface tensions can be determined from the three contact angles, and γ_{SV} is simply the sum of the three components. This method is also known as the three-liquid method.

van Oss, *Chaudhury*, *and Good (vOCG) model*. van Oss et al. [24–26] proposed a slightly different approach to partition the surface tensions in order to address hydrogen-bonding interactions. In the vOCG model, the surface tensions compose of (a) an apolar component of the interfacial tension γ^{LW} (Lifshitz–van der Waals interactions, including dispersion, dipole–dipole interaction, and induced dipole–dipole interactions) and (b) a short range surface tension γ^{AB} including hydrogen-bonding interactions. The solid and liquid surface tensions are given by

$$\begin{gathered}\gamma_{\mathrm{SV}}=\gamma_{\mathrm{SV}}^{\mathrm{LW}}+\gamma_{\mathrm{SV}}^{\mathrm{AB}}\\ \gamma_{\mathrm{LV}}=\gamma_{\mathrm{LV}}^{\mathrm{LW}}+\gamma_{\mathrm{LV}}^{\mathrm{AB}}\end{gathered} \tag{7.16}$$

where $\gamma_{\mathrm{SV}}^{\mathrm{AB}}=2\sqrt{\gamma_{\mathrm{SV}}^{+}\cdot\gamma_{\mathrm{SV}}^{-}}$ and $\gamma_{\mathrm{LV}}^{\mathrm{AB}}=2\sqrt{\gamma_{\mathrm{LV}}^{+}\cdot\gamma_{\mathrm{LV}}^{-}}$. γ_{SV}^{+} and γ_{SV}^{-} γ_{LV}^{+} and γ_{LV}^{-} are the electron acceptor (Lewis acid) and electron donor (Lewis base) for the solid and liquid, respectively.

The work of adhesion $W_{\mathrm{SL}}^{\mathrm{AB}}$ and the interfacial surface tensions $\gamma_{\mathrm{SL}}^{\mathrm{AB}}$ and γ_{SL} can be derived from molecular orbital theory [27, 28]:

$$W_{\mathrm{SL}}^{\mathrm{AB}}=2\sqrt{\gamma_{\mathrm{SV}}^{+}\cdot\gamma_{\mathrm{LV}}^{-}}+2\sqrt{\gamma_{\mathrm{SV}}^{-}\cdot\gamma_{\mathrm{LV}}^{+}} \tag{7.17}$$

$$\gamma_{SL}^{AB} = \gamma_{SV}^{AB} + \gamma_{LV}^{AB} - 2\sqrt{\gamma_{SV}^{+} \cdot \gamma_{LV}^{-}} - 2\sqrt{\gamma_{SV}^{-} \cdot \gamma_{LV}^{+}} \tag{7.18}$$

$$\gamma_{SL} = \gamma_{SV} + \gamma_{LV} - 2\sqrt{\gamma_{SV}^{LW} \cdot \gamma_{LV}^{LW}} - 2\sqrt{\gamma_{SV}^{+} \cdot \gamma_{LV}^{-}} - 2\sqrt{\gamma_{SV}^{-} \cdot \gamma_{LV}^{+}} \tag{7.19}$$

From the Young–Dupre equation in Eq. (7.4), the relationship between contact angle and the surface tension components can be written as

$$\gamma_{LV}\left(1+\cos\theta\right) = 2\sqrt{\gamma_{SV}^{LW} \cdot \gamma_{LV}^{LW}} + 2\sqrt{\gamma_{SV}^{+} \cdot \gamma_{LV}^{-}} + 2\sqrt{\gamma_{SV}^{-} \cdot \gamma_{LV}^{+}} \tag{7.20}$$

There are three unknowns in the solid surface tension, γ_{SV}^{LW}, γ_{SV}^{+}, and γ_{SV}^{-}. Experimentally, they can be calculated by measuring the contact angles with three liquids with known γ_{LV}^{LW}, γ_{LV}^{+}, and γ_{LV}^{-} values.

In addition to the methods discussed above, there are a few other solid surface tension determination methods, such as the Wu method [29, 30] and the Schultz methods [31, 32], which also fall into the category of partitioning surface tensions into independent components. Wu used the harmonic means to describe the interfacial surface tension instead of the geometric mean, based on a few slightly different assumptions to derive the equations for Wu's model. The Schultz methods can be considered as a special case of the extended Fowkes method. The contact angle of a polar liquid (usually water) on the solid is conducted in another nonpolar liquid medium (e.g., pure hydrocarbon compounds), or the contact angle of a nonpolar liquid on the solid is measured in another polar liquid medium.

7.2.3 Equation of State

The method of equation of state is totally different from all the surface tension component methods described in Sect. 7.2.2. The equation of state method assumes that the interfacial surface tension γ_{SL} depends on the surface tension of the liquid γ_{LV} and solid γ_{SV} only, i.e., $\gamma_{SL} = f\left(\gamma_{SV}, \gamma_{LV}\right)$. The method was mainly developed in Neumann's laboratory [33–37]. Neumann et al. formulated three versions of the equation of state. The first version was based on Zisman's data comprising eight solid surfaces with low surface tensions [33, 34]. According to Girifalco and Good [38], the liquid–solid interfacial surface tension between dissimilar molecules can be formulated as

$$\gamma_{SL} = \gamma_{SV} + \gamma_{LV} - 2\varphi_{SL} \cdot \sqrt{\gamma_{SV} \cdot \gamma_{LV}} \tag{7.21}$$

$\varphi_{SL}$is a characteristic constant of the system and is equaled to one when the interactions are from similar types of molecules and not much difference between γ_{SV} and γ_{LV}, which is the Berthelot's combining rule. However, in most situations φ_{SL} is an unknown when measuring solid surface tension. Neumann et al. [33, 34] performed a curve fitting to obtain the relationship of φ_{SL} and interfacial tension γ_{SL} by assuming that solid surface tension equals to the critical surface tension determined from the Zisman plot (Eq. 7.22). Eventually the explicit expression of γ_{SL} is derived by combining Eqs. (7.21) and (7.22).

$$\varphi_{\mathrm{SL}} = -0.00775\gamma_{\mathrm{SL}} + 1 \tag{7.22}$$

$$\gamma_{\mathrm{SL}} = \frac{\left(\sqrt{\gamma_{\mathrm{LV}}} - \sqrt{\gamma_{\mathrm{SV}}}\right)^2}{1 - 0.015\sqrt{\gamma_{\mathrm{SV}} \cdot \gamma_{\mathrm{LV}}}} \tag{7.23}$$

Then this relationship can be used to determine the solid surface tension (γ_{SV}) using only one liquid with known surface tension.

There are two other equations of state formulated from larger data set of surfaces and testing liquids [35–37].

$$W_{\mathrm{SL}} = 2 \cdot \sqrt{\gamma_{\mathrm{SV}} \cdot \gamma_{\mathrm{LV}}} \cdot \mathrm{e}^{-\beta(\gamma_{\mathrm{LV}} - \gamma_{\mathrm{SV}})^2} \tag{7.24}$$

$$\gamma_{\mathrm{SL}} = \gamma_{\mathrm{SV}} + \gamma_{\mathrm{LV}} - 2 \cdot \sqrt{\gamma_{\mathrm{SV}} \cdot \gamma_{\mathrm{LV}}} \cdot \mathrm{e}^{-\beta(\gamma_{\mathrm{LV}} - \gamma_{\mathrm{SV}})^2} \tag{7.25}$$

where $\beta = 0.0001247\,(\mathrm{m}^2/\mathrm{mJ})^2$.

$$W_{\mathrm{SL}} = 2 \cdot \sqrt{\gamma_{\mathrm{SV}} \cdot \gamma_{\mathrm{LV}}} \cdot \left(1 - \beta_1 \cdot (\gamma_{\mathrm{LV}} - \gamma_{\mathrm{SV}})^2\right) \tag{7.26}$$

$$\gamma_{\mathrm{SL}} = \gamma_{\mathrm{SV}} + \gamma_{\mathrm{LV}} - 2 \cdot \sqrt{\gamma_{\mathrm{SV}} \cdot \gamma_{\mathrm{LV}}} \cdot \left(1 - \beta_1 \cdot (\gamma_{\mathrm{LV}} - \gamma_{\mathrm{SV}})^2\right) \tag{7.27}$$

where $\beta_1 = 0.0001057\,(\mathrm{m}^2/\mathrm{mJ})^2$.

The coefficients β and β_1 are determined experimentally by measuring the contact angles on 15 solid surfaces with a series of testing liquids. Kwok and Neumann [36, 37] also suggested to adjust the coefficients and the solid surface tension simultaneously to get more precise calculation of the solid surface tension. They further demonstrated that despite the different formulations and coefficients, the three equations of states have yielded the same γ_{SV} values, based on various set of experimental contact angles [36, 37].

7.2.4 Assessment of the Different Methods

In summary, there are three basic approaches to use contact angle data to determine the surface tensions of solid surfaces. These approaches are the Zisman method, the surface tension component methods, and the equation of state. Within these three approaches, there are many variants. It is reasonable to wonder the merit, accuracy, and limitation of some of the methods. The Zisman method is an empirical approach based on the correlation between the cosines of the contact angles on a solid surface versus the surface tensions of the test liquids. With alkanes, linear plots are usually obtained, and the critical solid surface tension (γ_{C}) is determined by extrapolating the plot to $\cos\boldsymbol{\theta} = 1.0$. Zisman never claimed γ_C is γ_{SV}, although some in the literature assumed so. The analysis is limited to alkanes as the plots tend to depart from linear due to polar and H-bonding interactions. Zisman et al. also observed many exceptions during their studies with higher energy surfaces owing to specific interactions. In a sense, the Zisman approach is limited to low surface energy surfaces where the van de Waals interaction is dominant [9].

The differences between the surface tension component methods and the equation of state method are very distinct, and there have been significant debates in the literature between these two approaches [36, 37, 39–45]. The equation of state method is an empirical fitting method by assuming that the liquid–solid interfacial surface tension is a function of the solid and liquid surface tension only. The thermodynamic argument of the approach has been heavily criticized first by Morrison [42], who conducted a thermodynamic analysis and concluded that the equation of state is thermodynamically erroneous. Siboni and coworkers [45] later questioned the thermodynamic justification of the theory, particularly the calculation of the degree of freedom for a two-component three-phase system, as well as the approximation used in deriving the equation. They concluded that both of the theory and the approximation are highly questionable, if not wrong. In fact, Good felt so strongly about the incorrectness of the approach that he withdrew his support of the work he coauthored earlier [18, 34].

From the molecular interaction standpoint, the equation of state did not consider any polar, hydrogen bond, or acid–base interactions in formulating φ_{SL}. Therefore, it may be inadequate to illustrate the interfacial tensions between the solid and liquid phases [18]. Strong evidences have been reported for the existence of molecular interactions at the liquid–solid interface. For example, Fowkes et al. [40] were able to observe interfacial van der Waals and Lewis acid–base interactions directly as chemical shifts in infrared and NMR spectra. These are the direct evidences that γ_{SL} should be a function of some molecular interactions, not just γ_{SV} and γ_{LV} as shown in Eq. (7.21). Inspired by the interactions between two immiscible polar liquids [38], theoretical attempts were made to predict the value of φ_{SL} from the molecular properties, e.g., dipole moment, polarizability, and ionization energy of the solid and liquid phases [18, 41]. Although promising results were obtained, notable exceptions to the correlation, e.g., aromatic compounds, could not be resolved except by involving interactions with hydrogen bonds [41].

The surface tension component method assumes that surface tension can be partitioned into different components, which address different intermolecular interactions individually. The overall surface tension will be the sum of all the components according to the linear free energy relationship. In the original Fowkes method [14], only the dispersion interaction is considered. The component method has been subsequently extended to include polar component and later divided the polar component into dipolar interaction and H-bonding interaction. The vOCG model appeared as a refined version of the surface tension component methodology. It assumes the existence of both additive and nonadditive components. The Lifshitz–van der Waals component (γ^{LW}) is additive, and the electron donor and acceptor components (γ^- and γ^+) are nonadditive. The solid surface tension (γ_{SV}) can be calculated by using three liquids with known γ^{LW}, γ^- and γ^+ values. Since this is a semiempirical approach, the calculated value may vary a little depending on the choice of liquid set [44]. In general, the vOCG method considers all type of molecular interactions and is probably suitable for general use. If there is certainty that the solid surface has dispersion component only, the Fowkes model and the Zisman plot can be used as well.

7.3 Fundamental Issues and Outlook

7.3.1 Solid Surface Energy Versus Surface Tension

Due to simplicity, contact angle measurement has been widely used to determine surface energy of solid. It is important to point out that most people are interested in the surface energy of the solid not surface tension. The assumption is that the higher the surface energy, the stickier the surface and vice versa. Johnson [7] noted in 1959 that the terms surface energy, surface free energy, and surface tension had been used interchangeably and as desired by authors. This practice unfortunately has not been changed today. In any event, surface energy and surface tension are two distinct quantities in solid [5–7], and what's determined from contact angle measurement is surface tension. The cause of this confusion can be traced back to Dupre [3], who hypothesized the reversibility of the work of adhesion between two dissimilar materials. If these two materials are immiscible liquids such as that shown in Fig. 7.1b, the free energy change per unit area at the interface would be equaled to the surface tension of the newly formed interface minus the surface tensions of the two precursor liquids (Eq. 7.3). Unlike liquid, molecules at the surface or interface of a solid have little mobility during interfacial interactions. The extension of the work-of-adhesion assumption to a one-solid, one-liquid system may not be justifiable. In fact, Girifalco and Good [38] had pointed this out nearly six decades ago. The solid surface tension (γ_{SV}) value calculated from contact angle is hence questionable.

7.3.2 Which Contact Angle One Should Use?

As pointed out in Chap. 3, there are at least four measurable contact angles for a given liquid–solid system. They are the static (or Young's) angle $\boldsymbol{\theta}$, the advancing and receding angle $\boldsymbol{\theta}_A$ and $\boldsymbol{\theta}_R$, and the equilibrium angle $\boldsymbol{\theta}_{eq}$. The first three angles are from the metastable wetting states. The latter is from a thermodynamically stable state, which is populated through appropriate vibration of the Young's sessile droplet. Survey of the solid surface tension literature suggests that most of the solid surface tensions were determined from $\boldsymbol{\theta}$, which is from a metastable state. Should one recalculate all the surface tension numbers using $\boldsymbol{\theta}_{eq}$ as suggested by Marmur et al. [46] and Della Volpe et al. [47]? This really challenges the legitimacy of all solid surface tension numbers in the literature.

7.3.3 Path Forward

The motivation of determining solid surface energy or more precisely solid surface tension is to use the number to predict wettability and adhesion and sometimes infer molecular interactions. While contact angle is a very simple measurement, as briefly overviewed in Sect. 7.2, the methodologies employed to calculate the surface tension are actually not straightforward. They are mostly semiempirical. There are assumptions over assumptions and some of which have yet to be validated! The fundamental question one may ask is: is surface tension the correct quantity one needs to predict wettability and adhesion? We actually got the answer from Fowkes, who pioneered the surface tension component approach. He concluded in one of his papers that surface energy is actually not of any importance for surface and interfacial studies [40]. Using the microbalance technique, Samuel, Zhao, and Law [48] showed that surface wettability can be predicted from the advancing contact angle $\boldsymbol{\theta}_{\mathrm{A}}$, the larger the $\boldsymbol{\theta}_{\mathrm{A}}$, the lower the wettability. In the same study, they also showed that surface adhesion is correlating to $\boldsymbol{\theta}_{\mathrm{R}}$, the smaller the $\boldsymbol{\theta}_{\mathrm{R}}$, the stronger the surface adhesion. Since the whole objective of determining surface tension (energy) is to be able to predict surface wettability and adhesion interaction, we recommend everyone to simply measure $\boldsymbol{\theta}_{\mathrm{A}}$ and $\boldsymbol{\theta}_{\mathrm{R}}$ instead.

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