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# How Thermodynamics Drives Wet-out in Adhesive Bonding: Correcting Common Misconceptions

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#### Abstract

The traditional maxim that one should keep the adhesive surface energy below that of the substrate to ensure wet-out is shown to be a false and often counter-productive constraint in designing superior adhesive bonds. The confusion stems from the failure to carefully distinguish the one-substrate problem (coating) from the two-substrate problem (adhesive bonding). When two substrates are bonded the adhesive will almost invariably be driven to wet them out, even if the adhesive is of much higher surface energy than the substrates. The driving force is the elimination of the condensed phase/air interfaces in favor of condensed phase/condensed phase interfaces. Experiments are conducted to demonstrate that high surface energy liquids and adhesives will easily wet low surface energy substrates when sandwiched between them. The standard mathematical formalism for the free energy change of coating, bonding liquid adhesives, and bonding PSA tapes is developed to clarify the thermodynamic distinctions between these very different processes. It is shown that for spontaneous, thermodynamically driven, wet-out the contact angle the adhesive (PSA) tape. These forgiving criteria are readily met in practice, and are far less stringent than the 0° contact angle required for spontaneous spreading in a coating process.

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#### Keywords

Wet-out, wetting, wicking, surface energy, excess free energy

#### 1. Introduction

Review of the literature on adhesion frequently begins with a detailed discussion of surface energy and its importance for adhesion. However, this formalism is used to draw a false conclusion — that the surface energy of the adhesive needs to be lower than that of the substrates for wet-out to occur spontaneously, i.e., to be driven by thermodynamics. This false constraint impedes the development of optimum adhesives by distracting the formulator's focus from the real obstacles to bond-

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ing low-surface-energy substrates (e.g., the presence of lubricants and mold release agents, the blooming of low-molecular-weight materials, lack of interpenetration, etc.).

This error in conventional thinking arises from the failure to distinguish the important difference between bonding (two substrates) and coating (one substrate). For a liquid adhesive this is the difference between wicking and spreading. For a coating liquid to spread spontaneously over a surface requires a contact angle  $(\theta)$ of  $0^{\circ}$ . By contrast, for a liquid adhesive to spontaneously wick between two substrates requires only that  $\theta$  is less than 90°. A solid adhesive, such as a PSA, i.e., one that has already been spread over one of the substrates, will be thermodynamically driven to wet-out a second substrate provided only that  $\theta < 180^{\circ}$  [1]. These criteria for thermodynamically driven wet-out in adhesive bonding are readily met in practice even for very-high-surface-energy adhesives and very-low-surface-energy substrates. An illustrative example is the common transfer-coating process of making PSA tapes using water-borne adhesives. In this continuous process the adhesive is coated onto a silicone release liner (low surface energy, approx. 20 mJ/m<sup>2</sup>), dried and then bonded to a backing (often film or paper). The process races against dewetting after the coating step. That is, drying and thus solidification of the adhesive must be sufficiently rapid that insignificant dewetting occurs on the low surface energy liner. However, dewetting is not a concern once the tape is formed (i.e., adhesive between backing and release liner). Thermodynamics favors wet-out of the low surface energy release liner by the high surface energy adhesive once the adhesive is sandwiched with the backing.

The adhesive technologist recognizes the critical importance of wetting-out the substrates and the kinetic obstacles to achieving this intimate contact (e.g., high adhesive viscosity, setting or cure, rough surfaces, heat loss, etc.). This article sets out to show that thermodynamic resistance to wet-out is not an issue the adhesive technologist needs to be concerned with. In virtually all practical bonding situations thermodynamic framework for distinguishing between coating, bonding liquid adhesives and bonding PSA tapes is developed, drawing solely from traditional wetting theory. Experiments are then described which demonstrate that high-surface-energy adhesives readily wet low-surface-energy substrates in a bonding (two-substrate) process.

#### 2. Experimental

### 2.1. Wet-Out of Liquids

Two silicone-coated release liners obtained from Akrosil (Menasha, WI, USA) were used. The bottom substrate was a polyethylene film-coated paper and the top substrate was a clear poly(ethylene terephthalate) (PET) film (38  $\mu$ m thick). In each case the silicone-coated surfaces were placed against the liquid. The surface energy of the bottom liner was determined to be 20 mJ/m<sup>2</sup> based on contact angle

measurements of water (111°) and methylene iodide (83°). The calculation used the harmonic mean approximation [2] for estimating the interfacial energy between the solid and liquid using the polar and dispersion components of these liquids (for water,  $\gamma^{d}$  was taken as 22.1 mJ/m<sup>2</sup> and  $\gamma^{p}$  was taken as 50.7 mJ/m<sup>2</sup>, whereas the respective values used for methylene iodide were 48.5 and 2.3 mJ/m<sup>2</sup>). The software of the VCA 2000 video contact angle machine (from AST Products, Billerica, MA, USA) was used to make this calculation. The determined value of 20.1 mJ/m<sup>2</sup> ( $\gamma^{d} = 18.2 \text{ mJ/m}^{2}$  and  $\gamma^{p} = 1.9 \text{ mJ/m}^{2}$ ) is typical for silicone [3].

Two organic liquids with higher surface energy were used, mineral oil (Kaydol from Witco, with a molecular weight of approx. 450 g/mol, and a surface energy of about 29 mJ/m<sup>2</sup> [3]) and methylene iodide (surface energy of about 51 mJ/m<sup>2</sup> [4], obtained from Sigma Aldrich). A drop of liquid was placed on the silicone release paper. The contact angle was 83° for methylene iodide and 62° for mineral oil. Placing a second piece of silicone-coated PET on top of either of these drops resulted in immediate and spontaneous wet-out to the edge of the second liner (see Fig. 1). The weight of the liner was only 0.0710 g, exerting a pressure of only 0.48 Pa, infinitesimal compared to conventional bonding processes (approx. 1 MPa). When pure water (approx. 72 mJ/m<sup>2</sup>) was used the drop spread to about 1.5-times its original diameter (see Fig. 2A), but did not continue to flow. Pressing lightly with a finger spread this water layer easily and it stayed spread for the one minute that it was allowed to stand. A water-based emulsion adhesive designed for bonding wood



**Figure 1.** A drop of mineral oil ( $\gamma \sim 29 \text{ mJ/m}^2$ ) wet-out a siliconized release paper ( $\gamma \sim 20 \text{ mJ/m}^2$ ) when a clear siliconized release liner was placed on top. This image was taken after 5 minutes. After 40 min the oil had spread to the edge of the top liner and stopped. Methylene iodide ( $\gamma = 51 \text{ mJ/m}^2$ ), due to its low viscosity, wets out in a few seconds. Wet-out is so complete that the image shows no contrast. The dime is shown as a reference for size and also aided the camera in focusing.



(A)





**Figure 2.** Drops of distilled water ( $\gamma \sim 72 \text{ mJ/m}^2$ ) on siliconized release paper ( $\gamma \sim 20 \text{ mJ/m}^2$ ) (A) expanded only slightly and immediately when a clear silicone release liner was placed on top, and did not wick further due to a high contact angle of 111° (>90°). In (B) it is shown that a light finger pressure spread the water substantially between the silicone substrates and this water layer did not dewet significantly in the 60 seconds it was allowed to stand.

(proprietary product available from National Starch and Chemical Bridgewater, NJ, USA) wet out between silicone liners to several times the initial drop area despite its relatively high viscosity (approx. 1300 cP) and evaporation on the free edge as

the adhesive spreads (see Fig. 3A). This adhesive is stabilized by poly(vinyl alcohol) (88% hydrolyzed poly(vinyl acetate)), not with surfactant. Once wicking had stopped, the layers were peeled apart to reveal a liquid center (which rapidly dewet) and a solidified edge ring (see Fig. 3B).

## 2.2. Wet-Out of a Pressure Sensitive Adhesive

Teflon-coated aluminum plates were obtained from Scientific Machine and Supply (Middlesex, NJ, USA). The contact angles with water and methylene iodide were 114° and 82°, respectively. These values lead to a surface energy of 17 mJ/m<sup>2</sup>, calculated as described in Section 2.1. This value is slightly below that for the silicone release liners, as expected based on literature data for these polymeric surfaces [5].

A solution of acrylic pressure sensitive adhesive, 80-1057 (available from National Starch and Chemical Co., Bridgewater, NJ, USA), was coated onto a silicone release liner and dried. The dried thickness of this pressure sensitive film was 25  $\mu$ m. The film exhibited a contact angle of 86° with water. Methylene iodide would rapidly swell the acrylic and so contact angle was not measured with this liquid. The dried film was bonded to a 50  $\mu$ m thick PET backing film to make a pressure sensitive tape. A paper cutter was used to cut a square of this tape, the silicone release liner was removed, and the tape was draped down onto a Teflon-coated plate with no pressure applied. Only small points of contact were initially present (Fig. 4A). However, over time the tape was observed to progressively wet out the Teflon to make intimate contact (see Fig. 4B and 4C). Between observations, the plate was kept in a laboratory drawer.

#### 3. Theory

#### 3.1. Practical Aspects

It is clear from the experiments shown above that the addition of a second substrate (i.e. the difference between coating and bonding) has a dramatic effect. Wet-out is driven thermodynamically by the second substrate's presence. The molecular interactions in condensed phases (liquids (l) or solids (s)) are much stronger than in gases where the molecules are much further apart (density of an ideal gas is  $0.0012 \text{ g/cm}^3 vs$ . approx. 1 for common organic liquids). Coating a solid with a liquid does not produce a net decrease in the area of condensed phase exposed to air (substrate exposure to air is replaced by coating exposure to air). Bonding, on the other hand, eliminates the air exposure of the substrates on the bonding faces and replaces it with a condensed phase (the adhesive). Thus, bonding intrinsically has a strong thermodynamic driving force, whereas coating does not.

#### 3.2. Mathematical Framework

The formalism developed by Pocius [6] is used. The focus is on simple equations and materials which behave ideally since the point is to compare expected outcomes



(A)



(B)

**Figure 3.** Drops of a water-based PVOH-stabilized emulsion adhesive on siliconized release paper ( $\gamma \sim 20 \text{ mJ/m}^2$ ). In (A) drops spread when a small piece of clear silicone release liner was placed on top of them. Spreading was halted after about three minutes due to drying at the air-exposed edge. In (B) the top liner was lifted after 21 min to reveal a liquid core of emulsion that immediately dewet when unbonded, and also revealed the dried adhesive ring that had formed around the edge of the two bonded layers.



(A)



(B)

**Figure 4.** A pressure sensitive acrylic tape (25- $\mu$ m thick adhesive film on a 50- $\mu$ m PET backing) laid down onto a Teflon-coated aluminum plate with no pressure. It exhibited only point contacts initially (A), but had wet-out roughly one third its surface area overnight (B), and after 2 weeks the majority of the tape area had wet-out (C).



Figure 4. (Continued.)

for three different situations (coating, liquid adhesive bonding and PSA bonding) rather than on the materials themselves.

The surface energy,  $\gamma$ , is the increase in free energy *G* with surface area  $\Omega$  at constant *P*, *T* and *N<sub>i</sub>* (number of mol of each ingredient *i*). Surface energy of material 1 in air,  $\gamma_{1,air} \equiv (\partial G/\partial \Omega)_{P,T,N_i}$  and is a positive number.

The energy of interaction between two molecules of material 1 is given by  $\chi_{11}$  and is a negative number (decrease in free energy). Pocius employs a lattice model which is useful for simplicity. The coordination number *z* is lower at the surface (s) than in the bulk (b), i.e.,  $z_s < z_b$ , since air is only 1/1000th as dense as condensed materials. Thus using a lattice model expression for the increase in free energy gives:

$$\gamma_{1,air} = ((z_s - z_b)/2 \propto) \chi_{11},$$
 (1)

where  $\propto$  is the area/molecule on the surface. Since  $z_s - z_b$  is negative, as is  $\chi_{11}$ , then  $\gamma_{1,air}$  is positive, i.e., it is undesirable to create more surface area exposed to air. The interfacial energy between two dissimilar condensed phase materials is then written as:

$$\gamma_{12} = k \bigg( \chi_{12} - \frac{1}{2} (\chi_{11} + \chi_{22}) \bigg), \tag{2}$$

where k is a lattice constant. The interaction between two materials can be very complex, and many 'mixing rules' have been proposed. For simplicity we assume that the interaction between the two condensed materials can be represented by an arithmetic mean of their self-interactions:

$$\chi_{12} = \frac{1}{2}(\chi_{11} + \chi_{22}). \tag{3}$$

Inserting equation (3) into equation (2) gives  $\gamma_{12} = 0$  for the ideal (arithmetic mean) case!

This is a very important point. What it says is that if the materials can interact with each other as the average of their self-interactions then replacing their self-interactions with their mutual interactions has no effect on the free energy of the system. This sounds redundant, but it is common to forget that the interface energy between condensed phases should be vastly lower than between a condensed phase and air. For any *x*, *y* condensed phases,  $\gamma_{x,air}$  will always be positive, whereas  $\gamma_{x,y}$  can be either positive or negative. Positive values indicate the two materials prefer themselves, whereas negative values indicate they prefer each other. A better way to think of  $\gamma_{x,y}$  is as an excess free energy of bonding. Complementary interactions produce negative values and antagonistic interactions produce positive values. Ideally it is zero.

Using the nomenclature above we consider three processes: coating, bonding a liquid adhesive and bonding a tape to another surface. The free energy change/area for each of these processes is given by:

Free energy change/area = Work/area of process  
= 
$$\sum$$
 free energy/area of products  
-  $\sum$  free energy/area of reactants.

Recall a process is thermodynamically favorable if the total free energy change is negative.

### 3.2.1. Case I — Coating a Surface (Free Surface upon Completion)

Scheme 1 gives a misleading representation of the relative surface areas. In reality we can ignore the initial surface area of the coating material in comparison to its final surface area. For example, imagine coating 1 m<sup>2</sup> of substrate with a 50  $\mu$ m coating. 50  $\mu$ m is about 50 g/m<sup>2</sup>, assuming a density of 1 g/cm<sup>3</sup>; thus, the initial sphere of coating material has 0.0066 m<sup>2</sup> of surface, which is less than 1% of the area exposed to air after coating (1 m<sup>2</sup>). We also assume we can ignore changes in



Scheme 1.

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the bulk properties. Then for this coating process

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Free energy change/area = 
$$(\gamma_{1,2} + \gamma_{2,air}) - \gamma_{1,air}$$
 (4a)

$$= \gamma_{2,air} - \gamma_{1,air}$$
 in the ideal case ( $\gamma_{1,2} = 0$ ). (4b)

Equation (4b) states that a coating (2) will try to dewet, only if its surface energy is greater than that of the substrate. This is the basis of the statement: low surface energy wets high.

In terms of contact angles, a material which spreads spontaneously exhibits an equilibrium contact angle of  $0^{\circ}$ . While this is intuitively obvious, it can be shown mathematically by introducing the Young equation [7]

$$\cos\theta = (\gamma_{1,\text{air}} - \gamma_{1,2})/\gamma_{2,\text{air}},\tag{5}$$

which is a force balance relating the contact angle to the surface energy terms. Rearranging equation (5) provides an expression for the interfacial energy

$$\gamma_{1,2} = \gamma_{1,\text{air}} - \gamma_{2,\text{air}} \cos \theta. \tag{6}$$

Inserting equation (6) into equation (4a) gives

Free energy change/area = 
$$\gamma_{2,air}(1 - \cos\theta)$$
, (7)

which states that the free energy can never be negative, and can only be in equilibrium when  $\theta = 0^{\circ}$ . In reality the process is initially driven (negative free energy) due to the driving force for eliminating the surface area of the initial drop of coating material. Once  $\theta = 0^{\circ}$ , equilibrium is reached.

*3.2.2. Case II — Bonding Two Surfaces with a Bead or Drop of Adhesive (Scheme 2)* 

Free energy change/area = 
$$2\gamma_{1,2} - 2\gamma_{1,air}$$
 (8a)

$$= -2\gamma_{1,\text{air}}$$
 in the ideal case  $(\gamma_{1,2} = 0)$ . (8b)

Unless the materials have highly antagonistic interactions (e.g. pure water (mostly polar interactions) between silicones (mostly non-polar)) they will stay wet-out. The surface energy of the adhesive is irrelevant except as it influences  $\gamma_{1,2}$ .

As above, the criterion can be put in terms of contact angles by inserting the Young equation (6) for  $\gamma_{1,2}$  into equation (8a) yielding

Free energy change/area = 
$$-2\gamma_{2,air}\cos\theta$$
, (9)

which is only negative and, thus, thermodynamically driven, if  $\theta < 90^{\circ}$ . This criterion is that for wicking [8].



ostrate, 1

Scheme 2.

Adhesive, 2 (tape with backing)



Scheme 3.

#### *3.2.3. Case III — Bonding a Tape to Another Surface (Scheme 3)*

Free energy change/area = 
$$\gamma_{1,2} - (\gamma_{1,air} + \gamma_{2,air})$$
 (10a)

 $= -(\gamma_{1,air} + \gamma_{2,air})$  in the ideal case  $(\gamma_{1,2} = 0)$ . (10b)

The adhesive is driven to wet-out unless the surfaces have highly antagonistic interactions (large positive  $\gamma_{1,2}$ ). Note that, since the adhesive on the tape is solid and the substrate is rarely smooth, the elastic memory of the adhesive will resist the surface energy forces which are driving wet-out. The elastic modulus of the backing also resists any deformation of the tape. Commonly, a pressure sensitive adhesive will build adhesion over time to a rough surface.

Converting again to contact angles by inserting the Young equation (6) for  $\gamma_{1,2}$  into equation (10a) yields

Free energy change/area = 
$$-\gamma_{2,air}(1 + \cos\theta)$$
 (11)

which implies that thermodynamics drives wetting (negative free energy) provided only that  $\theta < 180^{\circ}$ . This situation is even more forgiving than Case II. The adhesive would have to be so repelled by the surface as to want to be a perfect ball on the substrate. In fact it is difficult to even imagine a situation where wetting was not being driven.

What drives bonding in Cases II and III is the reduction of air/solid interfaces in preference for condensed phase/solid interfaces across which van der Waals forces (and other types) can act.

#### 4. Results and Discussion

#### 4.1. Case II — Bonding Two Surfaces with a Bead or Drop of Adhesive

The experiments involving mineral oil and methylene iodide between silicone release liners demonstrate clearly that wicking and not spreading is the key criterion for thermodynamically driven wet-out. Mineral oil, with a surface energy of about 29 mJ/m<sup>2</sup> [3] wets-out between silicone liners (about 20 mJ/m<sup>2</sup>) spontaneously and completely due to wicking forces (contact angle  $62^{\circ}$ ), see Fig. 1. Once the oil has wicked to the edge of the top sheet of release liner it stops and remains in this fully wet-out configuration indefinitely, never spreading beyond the edge. In contrast, a drop of oil on a single silicone liner will remain as a bead on this surface indefinitely and never spread. Similarly methylene iodide, which has a surface energy of about  $51 \text{ mJ/m}^2$  and a contact angle of  $83^\circ$  on silicone wets out completely between silicone liners within a few seconds. Wet-out is more rapid due to the lower viscosity of methylene iodide *vs*. mineral oil (approx. 450 Da). The surface energy of methylene iodide is higher than most conventional liquid adhesives. If methylene iodide is driven to wick out completely between silicone surfaces then it is a safe assumption that wicking forces are also driving wet-out for liquid adhesives between any set of real substrates.

To test the assertion above, a water-based emulsion adhesive designed to bond wood (a relatively high energy surface) was tested between the same silicone liners (see Fig. 3). This emulsion is stabilized with poly(vinyl alcohol) (88% hydrolyzed poly(vinyl acetate)) not with surfactant. Even this water-based adhesive wicks between silicone liners (contact angle =  $86^{\circ}$ ). Wicking is slow due to the high viscosity of the adhesive (1300 cP) and is stopped by drying along the air-exposed edge of the adhesive after about 3 min. That drying is halting the wicking process is demonstrated by the dried edge ring apparent upon removing the top liner (see Fig. 3B).

Water was tested as the most extreme case. In the case of pure water, the drop flattened as the second silicone layer was applied, but wicking did not take place. Note that, most water-based adhesives have surface energies much lower than pure water due to the adhesive itself (if dissolved in the water phase) or surface active stabilizers (if the adhesive is dispersed in the water in the form of an emulsion). Case II is simply capillary action between sheets rather than in a tube. Capillary action is driven if the contact angle of the liquid on the solid surface is  $<90^{\circ}$ . Thus methylene iodide spontaneously wets out the gap between silicone liners completely ( $83^{\circ}$ ), whereas water does not ( $111^{\circ}$ ). It is interesting to consider the resistance to wetting provided by the water. The capillary pressure is given by [8]:

$$P_{\rm c} = (-2\gamma_{2,\rm air}\cos\theta)/r = (51.6 \text{ mJ/m}^2)/r \text{ for water on silicone,} (12)$$

where *r* is the radius of the capillary.

This equation can be used to predict what pressure would be required to force the water to wet out to a reasonable thickness. A pressure of only 4 kPa (0.6 psi) would be required to press the water down to a gap of 25  $\mu$ m. Thus, even when capillarity is working against wet-out its resistance is weak. In fact, the water layer could easily be pressed to spread out further with light finger pressure. Upon removing the pressure the water remained spread (see Fig. 2B), although given enough time it would have dewet. Most bonding processes could easily overcome this resistance to wetting, although it would be a very unusual situation in which a 72 mJ/m<sup>2</sup> surface energy adhesive was being applied to 19 mJ/m<sup>2</sup> surface energy substrates. Under typical circumstances, capillarity is favorable towards wet-out, but one should always check, if possible, that the contact angle is <90° to be sure.

The measured contact angles for water and methylene iodide can be compared to theoretical predictions using the Young equation (equation (5)) and the theory of

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Fowkes [3] for estimating  $\gamma_{1,2}$ . This theory is based on the assumption that polar interactions across surfaces are not possible, only dispersion interactions. It takes the form:

$$\gamma_{1,2} = \gamma_1 + \gamma_2 - 2(\gamma_1^d \gamma_2^d)^{1/2}.$$
(13)

Thus water molecules lose most of their interactions upon being placed at an interface as the polar and dispersion components of its surface energy are about 50 mJ/m<sup>2</sup> and 22 mJ/m<sup>2</sup> respectively. Almost 70% of the cohesive energy of water is from polar interactions which are lost to molecules placed at an interface, in Fowkes's theory. Certainly this assumption is likely to be valid when the other side of the interface is silicone. Using the values for silicone and water given in the Experimental section, we obtain a value for  $\gamma_{1,2}$  of 53 mJ/m<sup>2</sup>, a very large value indeed, which predicts a contact angle of 111° using equation (5). This value is not far from the experimental value of 111°. Using the same equation for methylene iodide on silicone predicts a much lower value of  $\gamma_{1,2}$  (11 mJ/m<sup>2</sup>) and a contact angle of 80°, close to the 83° observed.

In summary, these experiments demonstrate that even the most polar adhesives (water-based) are driven to wet-out extremely low surface energy substrates (silicone-coated release liner). Thus, in most all practical bonding situations wet-out is thermodynamically favored.

#### 4.2. Case III — Bonding a Tape to Another Surface

The acrylic PSA tape shown in Fig. 4A initially did not wet-out the Teflon plate because the tape and plate are not perfectly flat, part of which is due to the edges being curled down slightly by the process of cutting the tape. No visible wet-out occurred in the first hour after applying the tape. However, by the next morning, roughly one-third of the tape had wet-out the Teflon (Fig. 4B), and within 2 weeks the vast majority of the area was bonded (Fig. 4C). Given enough time, even the trapped air pockets will remove themselves as air diffuses out through the PET backing. The imperfections in the Teflon plate will not be wet out due to the thickness and rigidity of this PET backing. This result may not seem unusual, yet it is a clear example of how higher surface energy adhesives (86° contact angle with water) are thermodynamically driven to wet-out lower surface energy substrates (114° contact angle with water), which is contrary to conventional teaching.

Case III is the situation described by the familiar Dupre equation [7]. This equation is for the reverse process, where the work of adhesion  $(W_A)$  is the energy required to break a bond, considering only surface interactions.

$$W_{\rm A} = \gamma_{1,\rm air} + \gamma_{2,\rm air} - \gamma_{1,2} - \pi_{\rm e}.$$
 (14)

Here  $\pi_e$  is the equilibrium spreading pressure, which accounts for vapor adsorption onto the solid surface. This term is normally considered negligible for low surface energy substrates with higher surface energy adhesives, which are much less likely to adsorb on the surface, and, thus, becomes:

$$W_{\rm A} = \gamma_{1,\rm air} + \gamma_{2,\rm air} - \gamma_{1,2}. \tag{15}$$

The Dupre equation is written for debonding, and thus assumes the adhesive has already wet out the substrate and has solidified. This assertion is confirmed by noting that it is the negative (reverse process) of equation (10a). Thus, combining equation (15) with the Young equation for  $\gamma_{1,2}$ , equation (6), yields the famous Young–Dupre equation (16) which describes the debonding process of a solid adhesive from a solid surface (Case III in reverse).

$$W_{\rm A} = \gamma_{2,\rm air} (1 + \cos\theta). \tag{16}$$

Notice that in this case work is required to debond the substrates unless the contact angle is 180°. Never can spontaneous debonding take place. Air will never be preferred over another condensed surface, because no molecules are being moved from the bulk to an interface in this process; rather, the interfaces are already established. Tapes will be driven thermodynamically to wet out any surface to which they are applied. Further, the work of debonding will generally increase with the surface energy of the adhesive (equation (15)) and, thus, one should generally try to maximize the cohesive energy (twice the surface energy) of the adhesive that is used.

#### 5. Conclusions

In all practical bonding situations, the thermodynamics of wetting is working in the favor of the adhesive technologist, helping to drive wet-out of both tapes and liquids. This thermodynamic driving force for wetting exists even if the surface energy of the adhesive is much higher than the substrates. The second substrate present during bonding drives the wet-out. This reality was demonstrated by placing drops of mineral oil, methylene iodide, and a water-based adhesive between two low energy surfaces (siliconized release liners) and observing the spontaneous wetout of these higher surface energy materials. Bonding situations are much more forgiving than coating, where the old adage 'low surface energy wets high' still applies. For spontaneous, thermodynamically driven, spreading in a coating process the contact angle must be  $0^{\circ}$ . By contrast, for a liquid adhesive to spontaneously wick between two substrates requires only that  $\theta$  is less than 90°. A solid adhesive, such as a PSA, i.e., one that has already been spread over one of the substrates, will be thermodynamically driven to wet-out virtually any substrate, since all that is required is that  $\theta < 180^{\circ}$ . The traditional maxim that one should keep the adhesive surface energy below that of the substrate to ensure wet-out is shown to be a false and often counterproductive constraint in designing superior adhesive bonds. It is also suggested that a more descriptive term for the 'interfacial energy' is an 'excess free energy of bonding', acknowledging the fact that it can be positive or negative, and in the ideal case is zero.

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