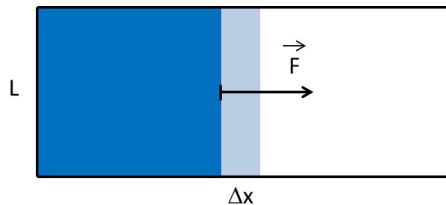


Krüss DSA-30 Surface Free Energy Theory

Version of 2024-11-20.

1. Introduction

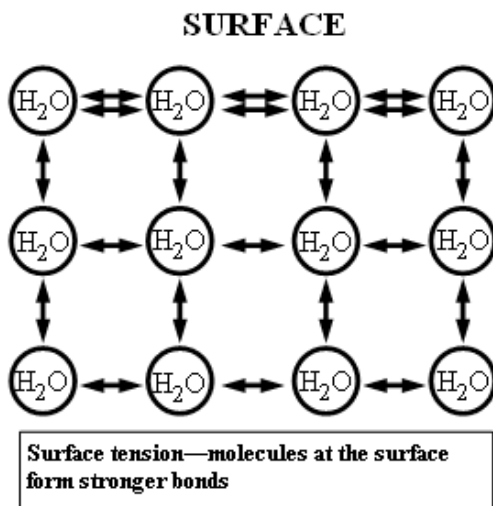
Surface tension describes the cohesion of molecules or atoms at the surface of a liquid or solid. It is tied to the force needed to stretch a surface. It is sometimes called (mostly for solids) surface energy and **defined as the work that is required to build a unit area of a particular surface.**



$$\gamma = \frac{F}{L} = \frac{W}{L\Delta x}$$

The units of surface tension are *free energy per unit area*, [J/m^2] or *force per unit length*, [N/m].

Surface tension is linked to several known physics experiment: For instance, molecules at the surface of a liquid forms stronger bonds than the molecules inside the liquid. This explains why, despite their weight, some objects can float on water while they sink at the bottom when they are fully immersed.



2. Surface Tension Components

To be more accurate, a surface is truly an interface between a liquid and a gas where the gas molecules also interact, although weakly, with the liquid molecules. Generally, surface tension values indicate the surface tension of the substance (liquid or solid) with surrounding air at 25°C.

The surface tension of a substance is most of the time separated in several “components” that are tied to the type of physical interactions between its molecule/atoms. As such the surface tension can be seen as a sum of components:

$$\gamma = \gamma^D + \gamma^P + \gamma^H + \gamma^i + \gamma^{AB} + \dots,$$

where γ^D = dispersion (London) forces, γ^P = polar forces, γ^H = hydrogen bridge forces, γ^i = induction (Debye) forces, γ^{AB} = acid-base forces, ... Note that the additivity of the force components is an assumption proposed by FOWKES which has been discussed and criticized heavily in the literature.

Work of cohesion and Work of adhesion

Adhesion express how well two substances stick together and cohesion express how well

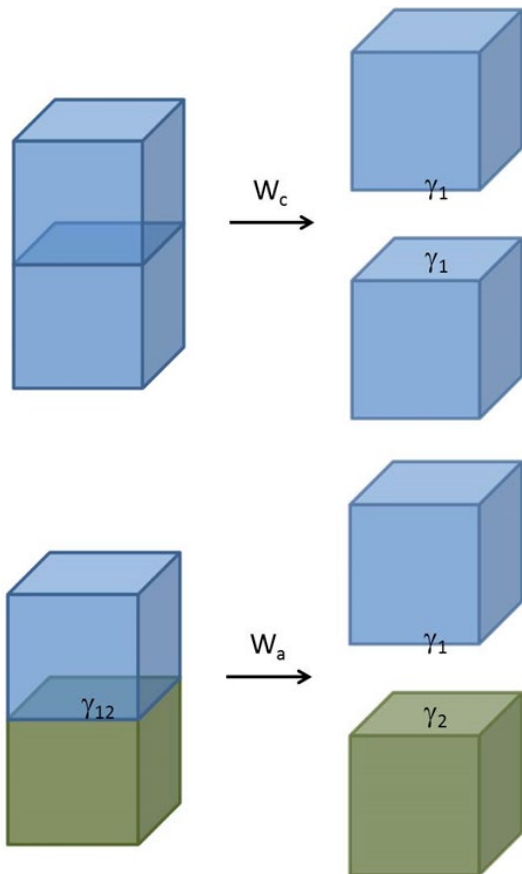
a substance maintains cohesion (“stick with itself”). Let’s consider a single substance that we cleave forming two identical surfaces of surface tension γ_1 . The work of cohesion is the work required to cleave the substance and create two identical unit area. According to the definition of the surface tension, we have:

$$W_c = 2 * \gamma_1$$

The work of cohesion is the work required to break the interface between two substances and create two surfaces of unit area. By definition, we have:

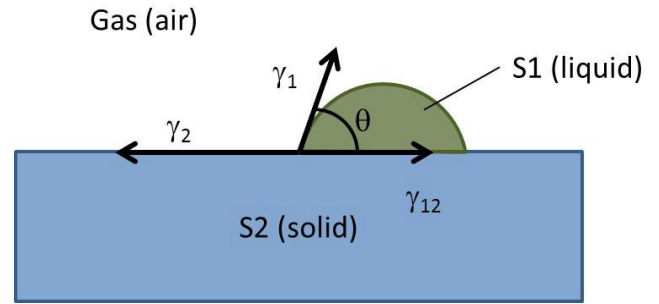
$$W_a = \gamma_1 + \gamma_2 - \gamma_{12} \quad (1),$$

where γ_{12} is the interfacial tension between both substances.



3. The Young-Dupree Equation

Let’s consider a liquid bubble on a surface. At the triple point (intersection of the three phases), the sum of forces equals zero (equilibrium). This gives the **Young’s Equation**:



$$\gamma_2 = \gamma_1 * \cos(\theta) + \gamma_{12} \quad (2)$$

By combining, equation (1) and (2), we get the **Young-Dupree equation** for the work of adhesion:

$$W_a = \gamma_1 * (1 + \cos(\theta)) \quad (3)$$

4. Models

The Krüss DSA-30 system records the contact angle between the solid surface of interest and a set of probe liquids. All the models that are used in the Krüss DSA4 software combine the **Young-Dupree Equation (3)** and an expression for the interfacial tension in terms of the surface tension components of the two substances that are in contact. The liquids that are used must have known surface tension components and the number of probe liquids should, at minimum, match the number of components. Having more liquids will improve the precision of the measurement.

1) *FOWKES and OWRK (Owens, Wendt, Rabel & Kaeble) methods (two liquids minimum)*

These two models assume that the surface tension of a substance can be separated in two main components, the dispersive γ^D and polar γ^P components.

In their model, the work of adhesion is expressed as the sum of the geometric means of the two substances for each type of components:

$$W_a = W_a^D + W_a^P, \text{ where } W_a^D = 2 \cdot (\gamma_1^D \gamma_2^D)^{\frac{1}{2}} \text{ and } W_a^P = 2 \cdot (\gamma_1^P \gamma_2^P)^{\frac{1}{2}} \quad (4)$$

The interfacial tension between the liquid and the solid is then expressed using the following expression:

$$\gamma_{12} = \gamma_1 + \gamma_2 - 2 \cdot (\gamma_1^D \gamma_2^D)^{\frac{1}{2}} - 2 \cdot (\gamma_1^P \gamma_2^P)^{\frac{1}{2}}$$

By combining equation (3) and (4), we find:

$$(\gamma_1^D + \gamma_1^P) * (1 + \cos(\theta)) = 2 \cdot (\gamma_1^D \gamma_2^D)^{\frac{1}{2}} + 2 \cdot (\gamma_1^P \gamma_2^P)^{\frac{1}{2}} \quad (5)$$

where the two unknowns are the solid surface energy components. If two liquids are used in the experiment, the solid surface energy can be calculated using two similar equations (5), one for each liquid.

The FOWKES and OWRK use the same physical model but differ in the mathematical solving of the equations (5). In particular, the FOWKES method requires that one of the test liquid has no polar component (diiodomethane is used in this case). Details of the calculation can be found in the literature. In most cases, the two methods will give the same results.

2) WU method (two liquids minimum)

The WU method uses the same components of the surface tension that previous methods.

However, in this case, the work of adhesion is expressed as the sum of the harmonic means of the two substances for each type of components:

$$W_a = W_a^D + W_a^P, \text{ where } W_a^D = 2 \cdot \frac{2 \cdot \gamma_1^D \gamma_2^D}{\gamma_1^D + \gamma_2^D} \text{ and } W_a^P = 2 \cdot \frac{2 \cdot \gamma_1^P \gamma_2^P}{\gamma_1^P + \gamma_2^P} \quad (6)$$

This new expression of the work of adhesion is then combined with the Young-Dupree equation (3) to produce an equation with the two components of the surface energy of the solid. With the use of two liquids, the surface energy of the wafer can be determined. According to Wu, his model is more adapted to low energy surfaces such as polymers.

3) Extended FOWKES (three liquids minimum)

The extended FOWKES model assumes that the surface tension of a substance can be separated in three main components, the dispersive γ^D , polar γ^P and hydrogen-bond γ^H . Hydrogen bridge bonds are short-range polar interactions (H^+ / H^-).

Similar as the FOWKES model, the work of adhesion is expressed as the sum of the geometric means of the two substances for each type of components:

$$W_a = W_a^D + W_a^P + W_a^H, \text{ where } W_a^i = 2 \cdot (\gamma_1^i \gamma_2^i)^{\frac{1}{2}}$$

In this case, with three unknown components for the surface energy of the solid, three tests liquids with known surface tension are now required for the contact angle measurement in order to solve the equations. This model can be used with the standard liquids installed on the Krüss DSA-30 but is not recommended with other liquids as the hydrogen-bond γ^H component is not measured in most liquid database.

4) The GOOD, van OSS, CHAUDHURY (GvOC) acid-base (AB) model (three liquids minimum)

In the case where the surface is expected to have weak polar but strong hydrogen bridge interactions, the model of OSS & GOOD may be more suited. The OSS & GOOD model assumes that the surface tension of a substance can also be separated in two main components, the Lifschitz-Van der Waals γ^{LW} component (dispersive & polar interactions), and the acid-base γ^{AB} component (short-range acid-base interactions due to hydrogen-bridge (H^+ / H^-)).

The acid-base component γ^{AB} is then separated into acid and base component depending on the tendency of the substance to give or take electrons. This relation is used:

$$\gamma^{AB} = 2 * \sqrt{\gamma^+ \gamma^-}$$

Liquids with both acid and base components are called **bipolar** (mainly water) and liquids with a strong acid or base component are

called **monopolar**. In the case of the AB model, the work of adhesion is described with this equation:

$$W_a = W_a^{LW} + W_a^{AB},$$

$$\text{where } W_a^{LW} = 2 \cdot (\gamma_1^{LW} \gamma_2^{LW})^{\frac{1}{2}} \text{ and } W_a^{AB} = 2 \cdot (\gamma_1^+ \gamma_2^-)^{\frac{1}{2}} + 2 \cdot (\gamma_1^- \gamma_2^+)^{\frac{1}{2}}$$

In this case, with three unknown components for the surface energy of the solid, three tests liquids with known surface tension are now required for the contact angle measurement in order to solve the equations.

In contrast with the extended FOWKES method, the AB model has been used by many authors to characterize polymer surfaces and the γ^{LW} , γ^+ and γ^- can be found for several liquids (see papers from *Lee & al.* or *Siboni & al.*).

5) *The Equation of State (EOS) method (single liquid)*

The equation of state theory (also called Neuman's model) completely disregards the separation of the surface tension into components and the interfacial tension is not expressed as a function of these components. The surface energy of the solid γ_2 can be expressed as a function of the contact angle and the surface tension of the liquid. The relation is expressed as follow:

$$\gamma_2 = \gamma_1 * \cos(\theta) = -1 + 2 \sqrt{\frac{\gamma_2}{\gamma_1}} \cdot e^{-\beta(\gamma_1 - \gamma_2)^2},$$

where $\beta = 0.000115 \text{ (mJ /m}^2\text{)}^2$. This method gives accurate results only for non-polar and low energy surfaces. It is used mostly to characterize polymer surfaces with solvents. It is not accurate at all and not recommended for semiconductor surfaces tested with water (for wetting experiments).

6) *The Zisman method (multiple liquids)*

Similar to the Equation of State method, the Zisman approach is mainly accurate for low-energy polymers with no polar components, such as polyethylene. It does not work on treated polymers that present some degree of

polarity (e.g. PMMA, polyimides ...). The method involves measuring the contact angle of several liquids on the test sample, and plotting the cosine of the contact angle versus the surface tension of the probe liquids used in the experiment. The surface energy of the sample equals the highest surface tension of any liquid that fully wets the surface. It is found by interpolation of the plot above to $\cos(\theta) = 1$.

5. References

- 1) F. M. Fowkes, J. Phys. Chem. **66**, 382, 1962.
- 2) J. Lyklema, Colloids Surf. A **156**, 413, 1999.
- 3) C. J. van Oss, R. J. Good, and M. K. Chaudhury, J. Colloid Interface Sci. **111**, 378, 1986.
- 4) C. Della Volpe, and S. Siboni, J. Colloid Interface Sci. **195**, 121, 1997.
- 5) L.-H. Lee, Langmuir **12**, 1681, 1996.
- 6) C.A. Ward, and A.W. Neumann, J. Colloid Interface Sci. **49**, 286, 1974.
- 7) J. H. Clint, Curr. Opin. Colloid Interface Sci. **6**, 28, 2000.
- 8) D. E. Packham, International Journal of Adhesion & Adhesives **23**, 437, 2003.
- 9) E. Chibowski, and R. Perea-Carpio, Advances in Colloid and Interface Science **98**, 245, 2002.
- 10) M. Zenkiewicz, Journal of Achievements in Materials and Manufacturing Engineering **24**, 137, 2007.