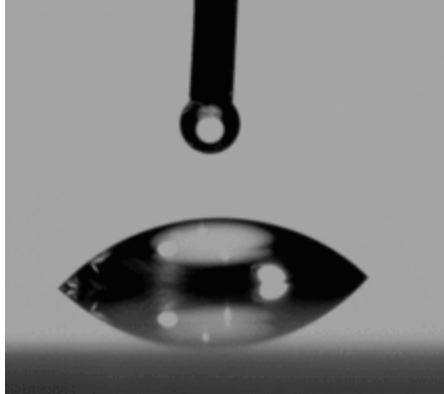# Surface energy

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[Contact angle](#) measurements can be used to determine the surface energy of a material. Here, a drop of water on glass.

Surface energy, or **interface energy**, quantifies the disruption of intermolecular bonds that occur when a surface is created. In the [physics](#) of [solids](#), surfaces must be intrinsically less energetically favorable than the bulk of a material (the molecules on the surface have more energy compared with the molecules in the bulk of the material), otherwise there would be a driving force for surfaces to be created, removing the bulk of the material (see [sublimation](#)). The surface energy may therefore be defined as the excess energy at the surface of a material compared to the bulk.

For a liquid, the [surface tension](#) (force per unit length) and the **surface energy density** are identical. Water has a surface energy density of 0.072 J/m^2 and a surface tension of 0.072 N/m; the units are equivalent. When a solution is formed comprising a mixture of two liquids or dissolved molecules, the surface tension of the primary liquid can deviate from corresponding pure liquid values. This phenomenon can be described by the [Gibbs isotherm](#).

Cutting a solid body into pieces disrupts its bonds, and therefore consumes energy. If the cutting is done reversibly (see [reversible](#)), then [conservation of energy](#) means that the energy consumed by the cutting process will be equal to the energy inherent in the two new surfaces created. The unit surface energy of a material would therefore be half of its energy of [cohesion](#), all other things being equal; in practice, this is true only for a surface freshly prepared in vacuum. Surfaces often change their form away from the simple "cleaved bond" model just implied above. They are found to be highly dynamic regions, which readily rearrange or react, so that energy is often reduced by such processes as [passivation](#) or [adsorption](#).

Determination of surface energy

Measuring the surface energy of a solid

The surface energy of a liquid may be measured by stretching a liquid membrane (which increases the surface area and hence the surface energy). In that case, in order to increase the surface area of a mass of liquid by an amount, δA, a quantity of work, γδA, is needed (where γ is the surface energy density of the liquid). However, such a method cannot be used to measure the surface energy of a solid because stretching of a solid membrane induces elastic energy in the bulk in addition to increasing the surface energy.

The surface energy of a solid is usually measured at high temperatures. At such temperatures the solid creeps and even though the surface area changes, the volume remains approximately constant. If γ is the surface energy density of a cylindrical rod of radius r and length l at high temperature and a constant uniaxial tension P, then at equilibrium, the variation of the total Helmholtz free energy vanishes and we have

$$\delta F = -P\ \delta l + \gamma\ \delta A = 0 \qquad \Longrightarrow \qquad \gamma = P\frac{\delta l}{\delta A}$$

where F is the Helmholtz free energy and A is the surface area of the rod:

$$A = 2\pi r^2 + 2\pi rl \qquad \Longrightarrow \qquad \delta A = 4\pi r\delta r + 2\pi l\delta r + 2\pi r\delta l$$

Also, since the volume (V) of the rod remains constant, the variation (δV) of the volume is zero, i.e.,

$$V = \pi r^2 l = \text{constant} \qquad \Longrightarrow \qquad \delta V = 2\pi rl\delta r + \pi r^2\delta l = 0 \implies \delta r = -\frac{r}{2l}\delta l\ .$$

Therefore, the surface energy density can be expressed as

$$\gamma = \frac{Pl}{\pi r(l - 2r)}\ .$$

The surface energy density of the solid can be computed by measuring P, r, and l at equilibrium.

This method is valid only if the solid is isotropic, meaning the surface energy is the same for all crystallographic orientations. While this is only strictly true for amorphous solids (glass) and liquids, isotropy is a good approximation for many other materials. In particular, if the sample is polygranular (most metals) or made by powder sintering (most ceramics) this is a good approximation.

In the case of single-crystal materials, such as natural gemstones, anisotropy in the surface energy leads to faceting. The shape of the crystal (assuming equilibrium growth conditions) is related to the surface energy by the Wulff construction. The surface energy of the facets can thus be found to within a scaling constant by measuring the relative sizes of the facets.

Calculating the surface energy of a deformed solid

In the deformation of solids, surface energy can be treated as the "energy required to create one unit of surface area", and is a function of the difference between the total energies of the system before and after the deformation:

$$\gamma = \frac{1}{A}(E_1 - E_0)$$

Calculation of surface energy from first principles (for example, density functional theory) is an alternative approach to measurement. Surface energy is estimated from the following variables: width of the d-band, the number of valence d-electrons, and the coordination number of atoms at the surface and in the bulk of the solid.[1]

**Calculating the surface formation energy of a crystalline solid**

In density functional theory, surface energy can be calculated from the following expression

$$\gamma = \frac{E_{slab} - N \cdot E_{bulk}}{2A}$$

where E_{slab} is the total energy of surface slab obtained using density functional theory. N is the number of atoms in the surface slab. E_{bulk} is the bulk energy per atom. A is the surface area. For a slab, we have two surfaces and they are of the same type, which is reflected by the number 2 in the denominator. To guarantee this, we need to create the slab carefully to make sure that the upper and lower surfaces are of the same type.

Estimating surface energy from the heat of sublimation

To estimate the surface energy of a pure, uniform material, an individual molecular component of the material can be modeled as a cube. In order to move a cube from the bulk of a material to the surface, energy is required. This energy cost is incorporated into the surface energy of the material, which is quantified by:
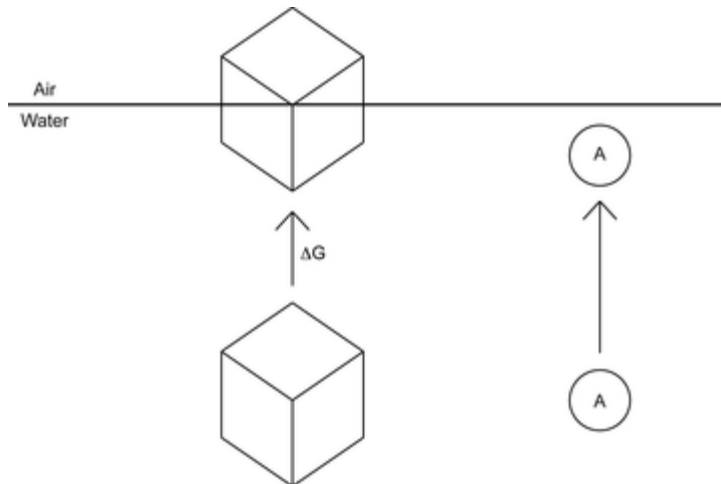
Cube Model. The cube model can be used to model pure, uniform materials or an individual molecular component to estimate their surface energy.

$$\gamma = \frac{(z_\sigma - z_\beta)\frac{W_{AA}}{2}}{a_0}$$

where z_σ and z_β are coordination numbers corresponding to the surface and the bulk regions of the material, and are equal to 5 and 6, respectively; a_0 is the surface area of an individual molecule, and W_{AA} is the pairwise intermolecular energy.

Surface area can be determined by squaring the cube root of the volume of the molecule:

$$a_0 = V_{\text{molecule}}^{2/3} = \left(\frac{\bar{M}}{\rho N_A}\right)^{2/3}$$

Here, $\bar{M}$ corresponds to the molar mass of the molecule, ρ corresponds to the density, and N_A is [Avogadro's number](#).

In order to determine the pairwise intermolecular energy, all intermolecular forces in the material must be broken. This allows thorough investigation of the interactions that occur for single molecules. During sublimation of a substance, intermolecular forces between molecules are broken, resulting in a change in the material from solid to gas. For this reason, considering the enthalpy of sublimation can be useful in determining the pairwise intermolecular energy. Enthalpy of sublimation can be calculated by the following equation:

$$\Delta_{\text{sub}}H = \frac{-W_{AA}N_A z_b}{2}$$

Using empirically tabulated values for enthalpy of sublimation, it is possible to determine the pairwise intermolecular energy. Incorporating this value into the surface energy equation allows for the surface energy to be estimated.

The following equation can be used as a reasonable estimate for surface energy:

$$\gamma \approx \frac{(z_\sigma - z_\beta)(-\Delta_{\mathrm{sub}}H)}{a_0 N_A z_\beta}$$

Interfacial energy

The presence of an interface influences generally all thermodynamic parameters of a system. There are two models that are commonly used to demonstrate interfacial phenomena, which includes the Gibbs ideal interface model and the Guggenheim model. In order to demonstrate the thermodynamics of an interfacial system using the Gibb's model, the system can be divided into three parts: two immiscible liquids with volumes V_α and V_β and an infinitesimally thin boundary layer known as the Gibbs dividing plane (σ) separating these two volumes.
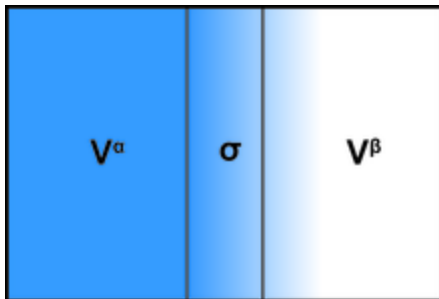
Guggenheim Model. An extended interphase (sigma) divides the two phases alpha and beta. Guggenheim takes into account the volume of the extended interfacial region, which is not as practical as the Gibbs model.
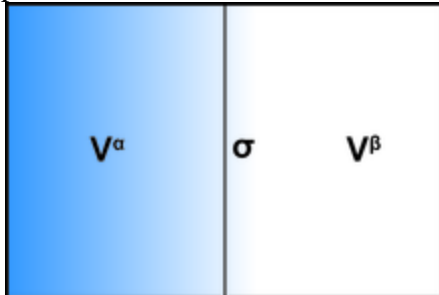
Gibbs Model. The Gibbs model assumes the interface to be ideal (no volume) so that the total volume of the system comprises only the alpha and beta phases.

The total volume of the system is:

$$V = V_\alpha + V_\beta$$

All extensive quantities of the system can be written as a sum of three components: bulk phase a, bulk phase b, and the interface, sigma. Some examples include internal energy (U), the number of molecules of the ith substance (n_i), and the entropy (S).

$$U = U_\alpha + U_\beta + U_\sigma$$

$$N_i = N_{i\alpha} + N_{i\beta} + N_{i\sigma}$$
$$S = S_\alpha + S_\beta + S_\sigma$$

While these quantities can vary between each component, the sum within the system remains constant. At the interface, these values may deviate from those present within the bulk phases. The concentration of molecules present at the interface can be defined as:

$$N_{i\sigma} = N_i - c_{i\alpha}V_\alpha - c_{i\beta}V_\beta$$

where $c_{i\alpha}$ and $c_{i\beta}$ represent the concentration of substance i in bulk phase α and β, respectively. It is beneficial to define a new term interfacial excess Γ_i which allows us to describe the number of molecules per unit area:

$$\Gamma_i = \frac{N_{i\alpha}}{A}$$