Lecture 7a: 5 October 2005. 2003

Blakely, J.M., *Introduction to the Properties of Crystal Surfaces*, 261 pp., Pergamon
Press, Oxford, 1973.
Guéguen, Y., and V. Palciauskas, *Introduction to the Physics of Rocks*, 294 pp., Princeton
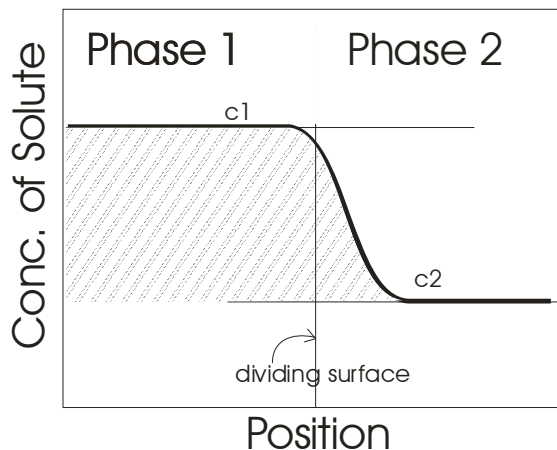University Press, Princeton, NJ, 1994.

Surface Energy, Surface Tension and Fracture Surface Energy

Surface Energy

Surface tension is the work to create unit area of new surface:

$$\gamma \triangleq \lim_{dA \to 0.0} \frac{dW}{dA}$$

Grain boundary or surface segregation:

Notice there is an excess amount of
material
$n_s = n_{total} - (n_1 + n_2)$ where n_i is the
number of moles of phase *i* if the
material were homogeneous.

The specific molar excess per unit area is
$$\Gamma = \frac{d(n_1 + n_2)}{dA}$$

Then at constant T and V, work done is
the Helmholtz Free Energy:

$$dF_{total} = d(F_1 + F_2) + dF_s = \gamma \, dA$$
$$= \mu \cdot d(n_1 + n_2) + dF_s$$

then from the definition of Γ, and expressing the parameters as specific,
i.e. per unit area,

$$\gamma = f_s - \mu$$

Conclusions:

*Suface tension, γ, (a measurable quantity) is not necessarily
= specific surface free energy, especially if segregation
occurs*

It seems that $\frac{d\gamma}{dT} < 0$ from experimental measurements,

although not a lot of data exist.

Values of $\gamma \approx 1\text{-}10\ J/m^2\ (0.4\text{-}4.0ev\ or\ 1\text{-}10\ x10^3\ ergs/cm^2\ )$

Intersection of Three Surfaces

Blakely, J. M., Introduction to the Properties of Crystal Surfaces, Chapt. 1&2, Pergamon
Press, Oxford, U. K., 1973.
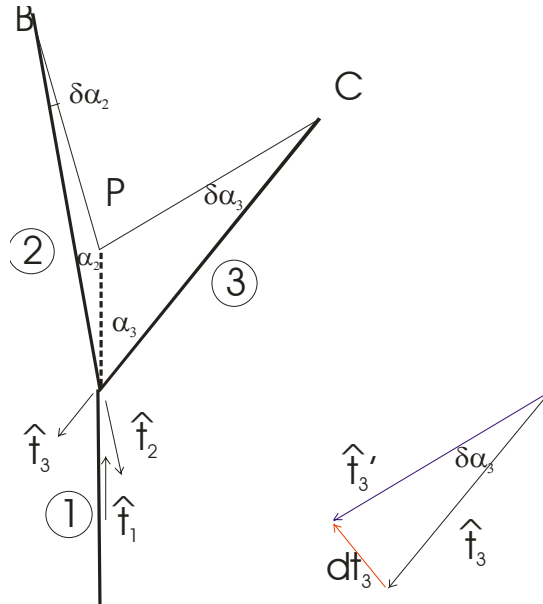
Suppose three interfaces meet. Consider a small displacement from the equilibrium configuration. For example, if boundary 1 grows a bit. Then

$$dF = \gamma \, dA + A \, d\gamma$$

$$dF^{surface} = \gamma_1(OP) + \gamma_2(BP - BO) + \gamma_3(CP -$$

$$+ \frac{\partial \gamma_2}{\partial \alpha_2} \delta\alpha_2 (BP) + \frac{\partial \gamma}{\partial \alpha}$$

Assume that the ensemble is approaching equilibrium and that $dF^{surface} = 0$.

$$0 = \gamma_1 \hat{\mathbf{t}}_1 + \gamma_2 \hat{\mathbf{t}}_2 + \gamma_3 \hat{\mathbf{t}}_3 + \frac{\partial \gamma_2}{\partial \alpha_2} \frac{\hat{\mathbf{t}}_3 \times \hat{\mathbf{t}}_2 \times \hat{\mathbf{t}}_1}{\left|\hat{\mathbf{t}}_3 \times \hat{\mathbf{t}}_2 \times \hat{\mathbf{t}}_1\right|} + \frac{\partial \gamma_3}{\partial \alpha_3} \frac{\hat{\mathbf{t}}_1 \times \hat{\mathbf{t}}_2 \times \hat{\mathbf{t}}_3}{\left|\hat{\mathbf{t}}_1 \times \hat{\mathbf{t}}_2 \times \hat{\mathbf{t}}_3\right|}$$

Conclusions: Two forces arise:

First, capillarity forces that are tangent to the surface at each point and are proportional to the magnitude of the surface tension.

Second, torque forces that are perpendicular to the surface and tend to rotate the surface normal into a new direction. These forces may be thought of as causing faceting. In the case of fracture surfaces, the torque terms would arise whenever the material had a good cleavage.

Capillarity Forces and Laplace's Equation

Suppose that the volume occupied by phase 1 increases slightly.

$V_{total} = V_1 + V_2$ and $dV_2 = -dV_1$
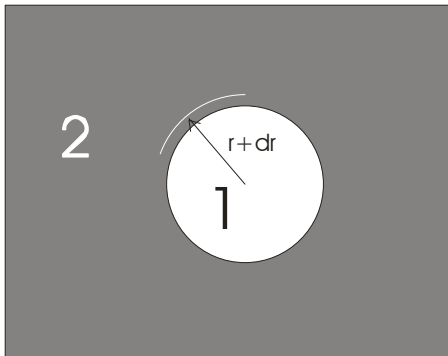
The total work done is the change in the PdV work plus a surface (interface) energy term; if the process is reversible then the sum is 0:

$-P_1 dV_1 - P_2 dV_2 + \gamma dA = 0$

Originally, $V_1 = \dfrac{4}{3}\pi r^3$ so $dV_1 = 4\pi r^2 dr$ and $dA = 8\pi r dr$

So $\boxed{P_1 - P_2 = \dfrac{2\gamma}{r}}$

In general, for a surface or interface that is not spherical
Should insert

$\dfrac{1}{r_m} = \dfrac{1}{2}\left(\dfrac{1}{r_1} + \dfrac{1}{r_2}\right)$ where $r_{1,2}$ are the principal radii of curvature.