

## 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.

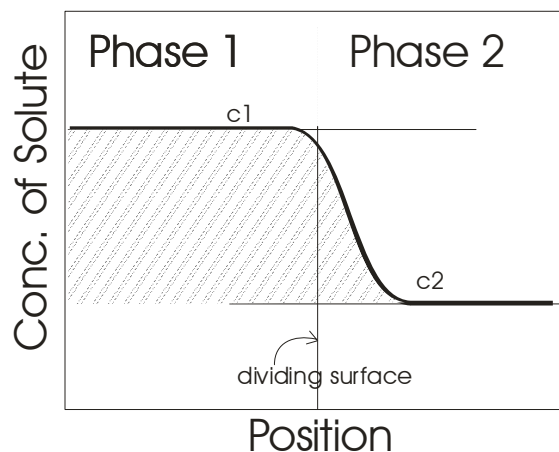
## Surface Energy, Surface Tension and Fracture Surface Energy

### Surface Energy

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

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

### 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:

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

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

$$\gamma = f_s - \mu$$

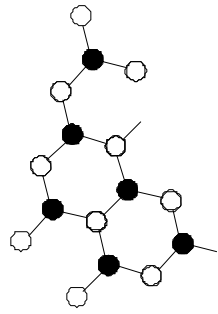
### Conclusions:

*Surface tension,  $\gamma$ , (a measurable quantity) is not necessarily = specific surface free energy, especially if segregation occurs*

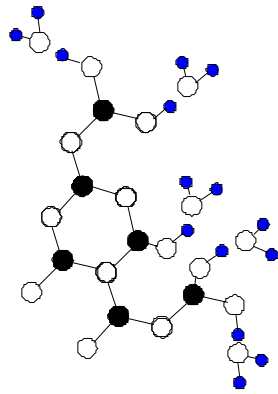
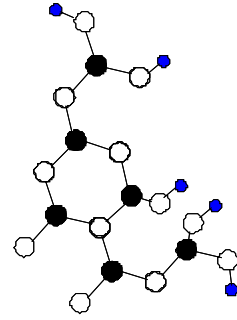
*It seems that  $\frac{d\gamma}{dT} < 0$  from experimental measurements, although not a lot of data exist.*

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

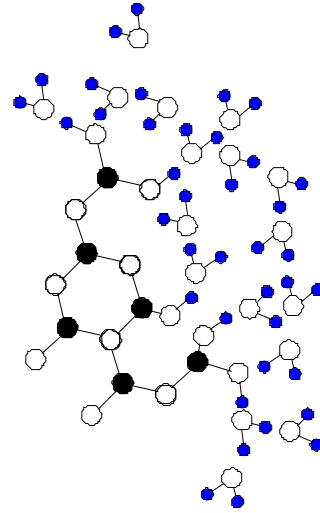
I. Fresh Fracture



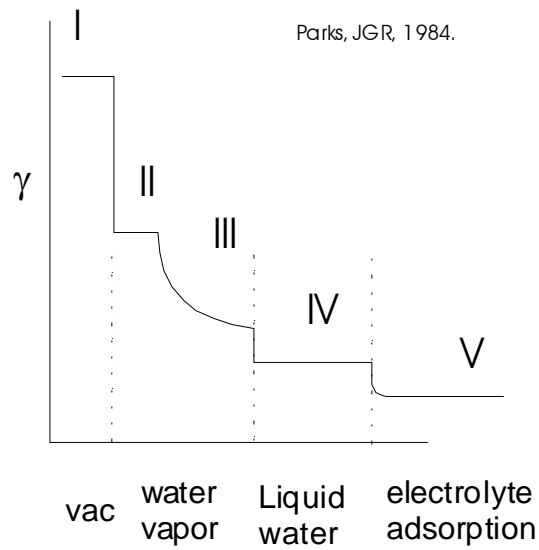
II. Hydroxylated



III. Adsorbed water

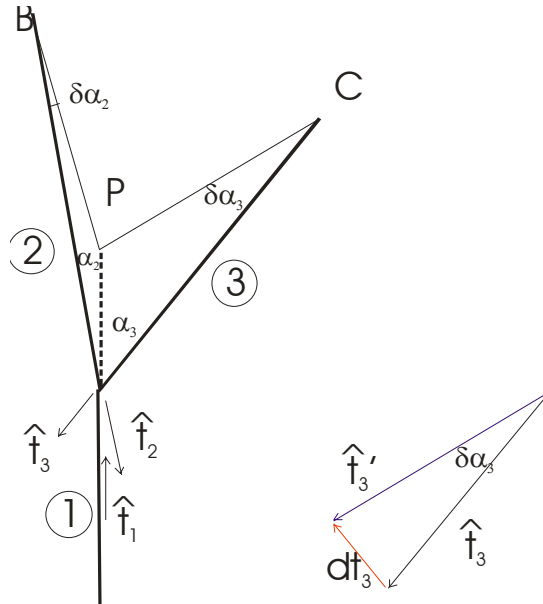


IV. Wet Surface



# 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  $dF = \gamma dA + Ad\gamma$

$$dF^{surface} = \gamma_1(OP) + \gamma_2(BP - BO) + \gamma_3(CP - CO) + \frac{\partial \gamma_2}{\partial \alpha_2} \delta \alpha_2 (BP) + \frac{\partial \gamma_3}{\partial \alpha_3} \delta \alpha_3 (CP)$$

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

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

**Conclusions: Two forces arise:**

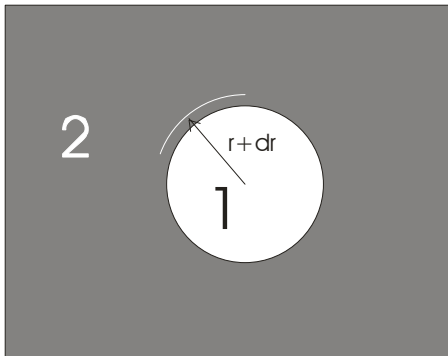
*First, capillarity forces that are tangent to the surface at each point and are proportional to the magnitude of the surface tension.*

*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.

$$V_{total} = V_1 + V_2 \text{ and } dV_2 = -dV_1$$



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

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

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

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