

Dec. 11 2002: Lecture 35:

## Introduction to Surface Thermodynamics

Last Time

**Electrochemical Potential**

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**Nernst Equation**

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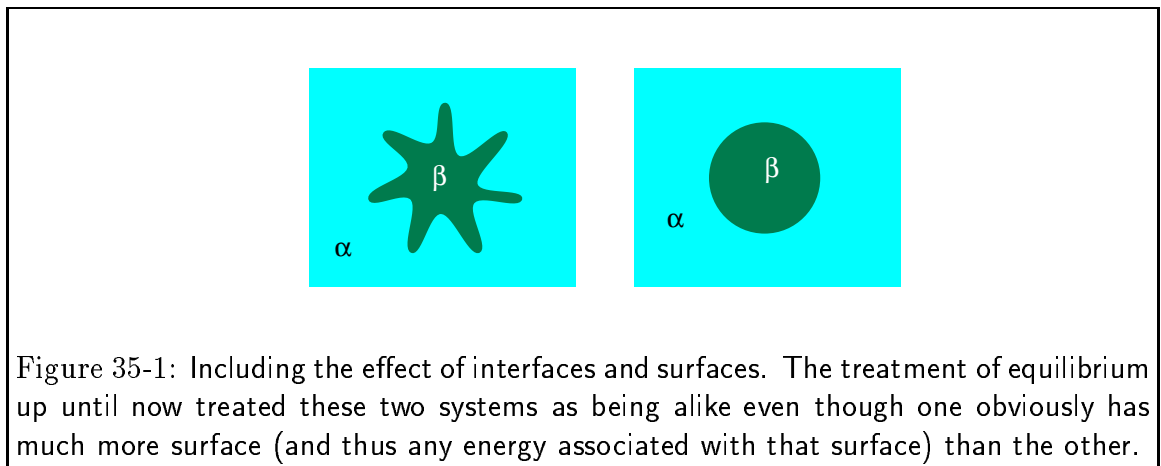
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### Estimate of the Excess Energy Associated with Surfaces

In the treatment of the equilibrium of phases the effect of the surface that separates the various phases was neglected.

In other words, no distinction was made between systems that had an abundance of surface and those that do not—there was no distinction made between:



Consider, as an example, that an atom on a surface as having a 50% higher energy than those in the bulk, then there will be an extra energy associated with the surface of a sphere.

To estimate how much energy is associated with the surface let:

$$\text{surface area} \equiv \text{surface area of } \alpha\text{-phase} = 4\pi R_s^2$$

$$\text{volume} \equiv \text{volume of } \alpha\text{-phase} = \frac{4}{3}\pi R_s^3$$

The energy of the system is:

$$\bar{U}^{xs} = \frac{N^{\text{surf}}U^{\text{surf}} + N^{\text{bulk}}U^{\text{bulk}}}{N^{\text{total}}} \quad (35-1)$$

Letting the energy of an atom on the surface be half again that of the bulk:

$$U^{\text{surf}} \approx \frac{3}{2}U^{\text{bulk}} \quad (\text{assumption}) \quad (35-2)$$

$$\bar{U}^{xs} = \left( 1 + \frac{1}{2} \frac{N^{\text{surf}}}{N^{\text{total}}} \right) \quad (35-3)$$

If  $\Omega$  is the volume per atom and  $R_A$  is the radius of an atom, then

$$\begin{aligned} N^{\text{surf}} &= \frac{(\text{Surface Area})R_A}{\Omega} \\ N^{\text{bulk}} &= \frac{(\text{Volume})}{\Omega} \end{aligned} \quad (35-4)$$

Letting  $R_s$  be the radius of the sphere:

$$\bar{U}^{xs} = \left( 1 + \frac{3R_A}{2R_s} \right) \quad (35-5)$$

How small does the sphere need to be in order that the excess is about 1%?

$$R_s \approx 150R_A \quad (\text{for excess of about 1 percent}) \quad (35-6)$$

This is pretty small, but important important in many systems.

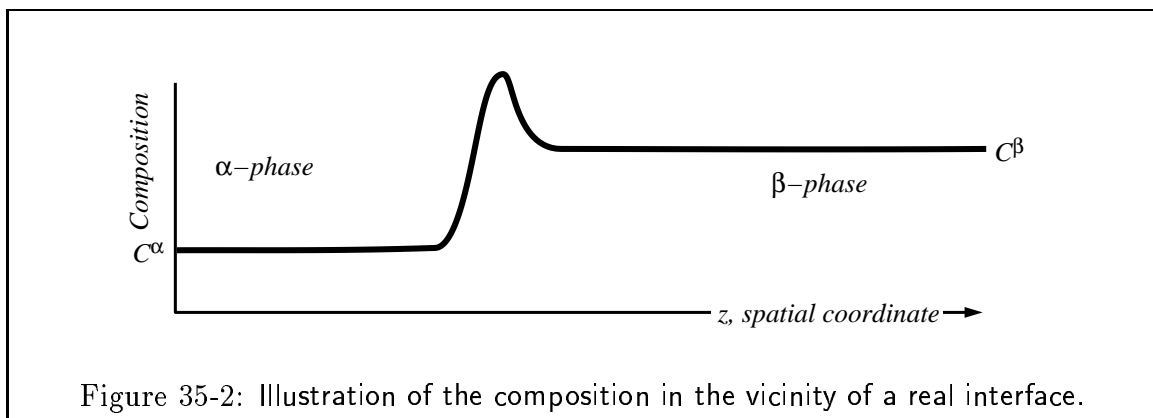
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## Gibbs Treatment of the Interfacial Energy

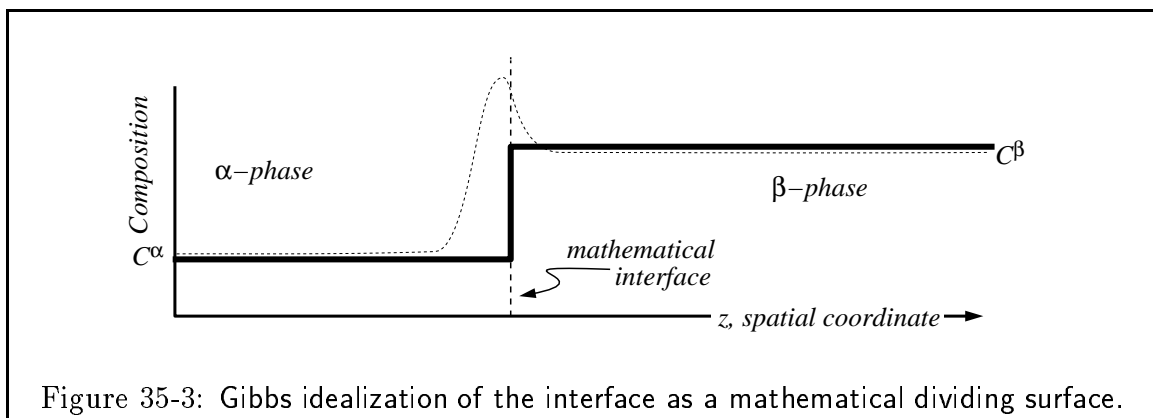
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Note the atoms at the surface were treated as being somehow different than those of the bulk. This idea can be extended rigorously to treat the interface as a relatively thin layer. This thin layer will be treated as a separate “quasi-two-dimensional phase.”

The original Gibbs idea was as follows: Suppose the composition is different between to phases (but dictated by  $\mu_i^\alpha = \mu_i^\beta$ , of course). There is no requirement that the concentration should be uniform in the vicinity of the interface:

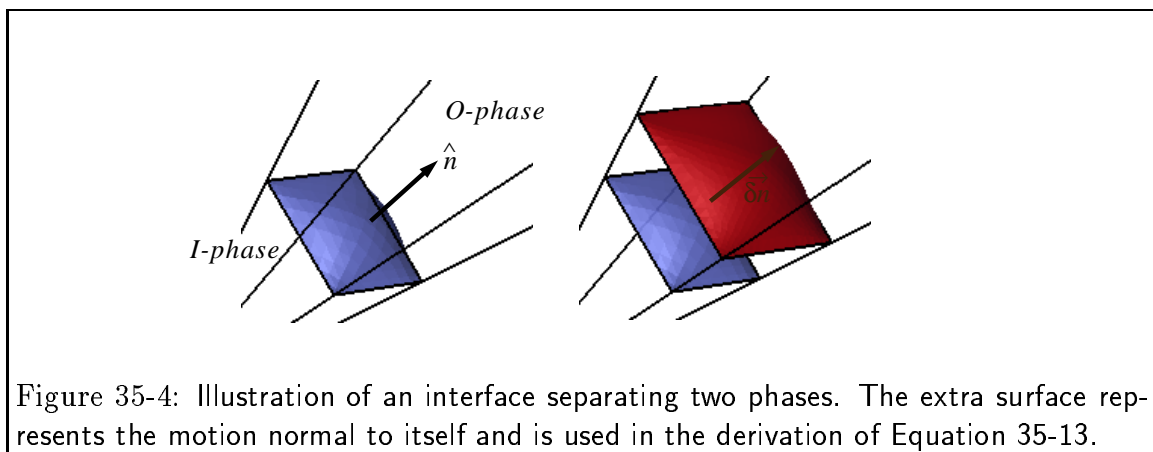


The Gibbs treatment extends each of the homogeneous phases up to a mathematical surface:



Subtract the real system in Figure 35-2 from its idealization in Figure 35-3 to define an excess quantity associated with the mathematical surface “The Gibbs Surface” which has no volume associated with it, but excess extensive quantities.

If the following illustration represents a thermodynamic system:



For the surface phase:

$$dU^{\text{surf}} = TdS^{\text{surf}} + \gamma dA + \sum_{i=1}^c \mu_i dN_i^{\text{surf}} \quad (35-7)$$

where  $A$  is the surface area of the interface.

What is  $\gamma$ ?

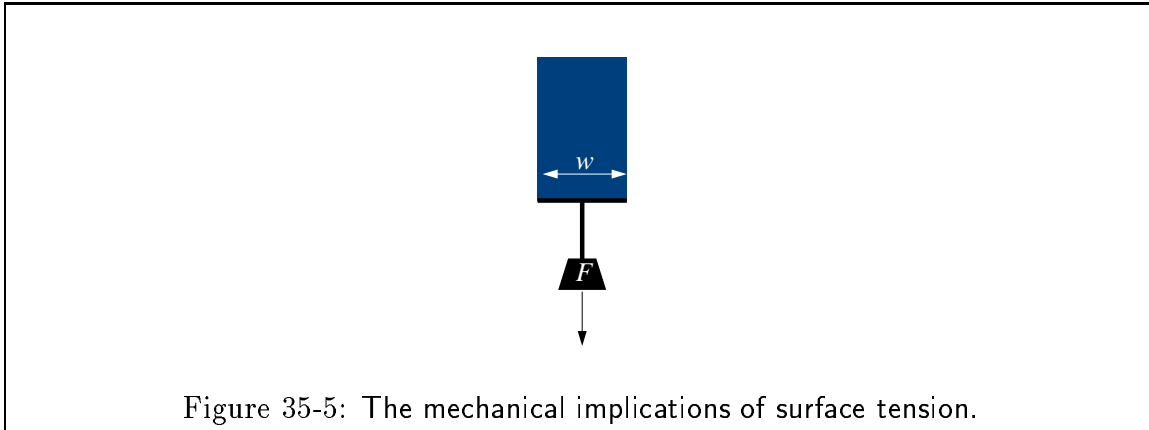
Obviously,

$$\gamma = \left( \frac{\partial U^{\text{surf}}}{\partial A} \right)_{\text{const } S, \text{const } N_i^{\text{surf}}} \quad (35-8)$$

But, it also represents the work done to increase the surface area

$$\begin{aligned} d(\gamma A) &= F dl = \\ \gamma w dl &= F dl \\ \implies \gamma &= \frac{F}{w} \end{aligned} \quad (35-9)$$

where a force  $F$  is applied to a surface of width  $w$  to extend its length  $l$ .



This is the surface tension, it has units of force per unit length or, equivalently, surface energy per area. It is the energy associated with creating surface.<sup>36</sup>

Consider the entire system:

$$\begin{aligned} \delta U^{\text{total}} &= \delta U^{\text{inside}} + \delta U^{\text{surf}} + \delta U^{\text{outside}} \\ &= T \delta S^{\text{inside}} - P \delta V^{\text{inside}} + \sum_{i=1}^C \mu_i \delta N_i^{\text{inside}} \\ &\quad + T \delta S^{\text{surf}} + \gamma \delta A + \sum_{i=1}^C \mu_i \delta N_i^{\text{surf}} \\ &\quad + T \delta S^{\text{outside}} - P \delta V^{\text{outside}} + \sum_{i=1}^C \mu_i \delta N_i^{\text{outside}} \end{aligned} \quad (35-10)$$

<sup>36</sup>Note: in solids, another term can arise which is associated with stretching the existing surface—this is called the surface stress.

Because the surface represents an object that can resist pressure, it can no longer assumed that the pressures on the inside and the outside phase are equal.

For equilibrium  $dU = 0$ , along with the temperature and chemical potentials being uniform:

$$\gamma\delta A - P\delta V^{\text{inside}} - P\delta V^{\text{outside}} \quad (35-11)$$

Imagine that the surface moves normal to itself (such as in Figure 35-4) Then the following relations hold:

$$\delta V^{\text{inside}} = A\delta\hat{n} \quad \text{and} \quad \delta V^{\text{outside}} = -A\delta\hat{n} \quad (35-12)$$

$$\begin{aligned} \delta A &= (\kappa_1 + \kappa_2)A\delta\hat{n} \\ &= (\kappa_1 + \kappa_2)\delta V^{\text{inside}} \\ &= \left(\frac{1}{R_1} + \frac{1}{R_2}\right)\delta V^{\text{inside}} \end{aligned} \quad (35-13)$$

where  $K_1$  and  $K_2$  are the “curvatures” of the surface in each of two perpendicular planes, where the axis of intersection is normal to the surface.

$$\kappa_{\text{mean}} \equiv \kappa_1 + \kappa_2 \quad (35-14)$$

is called the “mean curvature” of the surface  $1/R_1 = K_1$ , and  $1/R_2 = K_2$  where  $R_1$  and  $R_2$  are the radii of curvature.

Putting equations 35-12, 35-13, and 35-14 together, the following important relation holds:

$$\gamma\kappa_{\text{mean}} = P^{\text{inside}} - P^{\text{outside}} \quad (35-15)$$

which is known as the **Gibbs-Thompson** equation. It relates the difference in pressure at an interface to its surface tension and curvature.

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## Curvatures of Simple Surfaces

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The relation:

$$\delta A = \kappa_{\text{mean}}\delta V = \left(\frac{1}{R_1} + \frac{1}{R_2}\right)\delta V \quad (35-16)$$

was used above to relate the pressure difference across an interface. If the pressure is to be the same within each phase, then at equilibrium a surface must have constant curvature.

Consider how curvature relates to some geometrical objects that have “constant mean curvature.”

For the sphere:

$$\frac{\partial A}{\partial V} = \frac{\partial A}{\partial R_S} \frac{\partial R_S}{\partial V} = \frac{8\pi R_S}{4\pi R_S^2} = \frac{2}{R_S} = \kappa_{mean} \quad (35-17)$$

There is one radius of curvature for each perpendicular plane with an axis normal to the surface at each point.

For the cylinder:

$$\frac{\partial A}{\partial V} = \frac{\partial A}{\partial R_C} \frac{\partial R_C}{\partial V} = \frac{2\pi L}{2\pi R_C L} = \frac{1}{R_C} = \kappa_{mean} \quad (35-18)$$

### Fundamental relations for surfaces

In this section it will be shown that there are additional solubility effects associated with interfaces.

Consider:

$$dU^{\text{surf}} = TdS^{\text{surf}} + \gamma dA + \sum_{i=1}^c \mu_i dN_i^{\text{surf}} \quad (35-19)$$

since the dependent variables are all extensive, we can integrate (i.e. homogeneous degree 1 in all of its variables), therefore

$$U^{\text{surf}} = TS^{\text{surf}} + \gamma A + \sum_{i=1}^c \mu_i N_i^{\text{surf}} \quad (35-20)$$

Taking the derivative (as was done when deriving the Gibbs-Duhem equation);

$$dU^{\text{surf}} = TdS^{\text{surf}} + S^{\text{surf}}dT + \gamma dA + Ad\gamma + \sum_{i=1}^c \mu_i dN_i^{\text{surf}} + \sum_{i=1}^c N_i^{\text{surf}} d\mu_i \quad (35-21)$$

comparing to Equation 35-19,

$$0 = S^{\text{surf}}dT + Ad\gamma + \sum_{i=1}^c N_i^{\text{surf}} d\mu_i \quad (35-22)$$

which expresses a relation between variations of the intensive degrees of freedom for a surface to remain in equilibrium.

Dividing through by the total surface area (so as to normalize by the area, creating derived intensive variables) and defining

$$\widetilde{S}^{\text{surf}} = \frac{S^{\text{surf}}}{A} \quad (35-23)$$

as the entropy of the surface per area, then,

$$\begin{aligned} 0 &= d\gamma + \widetilde{S}^{\text{surf}} dT + \Gamma_1 d\mu_1 + \Gamma_2 d\mu_2 + \dots + \Gamma_C d\mu_C \\ &= d\gamma + \widetilde{S}^{\text{surf}} dT + \sum_{i=1}^C \Gamma_i d\mu_i \end{aligned} \quad (35-24)$$

where

$$\Gamma_i \equiv N_i^{\text{surf}} \quad (35-25)$$

is the standard notation for the excess surface concentration.

Holding everything (temperature, *et cetera*) constant except  $\mu_1$ , we get a relation that expresses the relation between the change in surface tension to the change in chemical potential of an absorbing species:

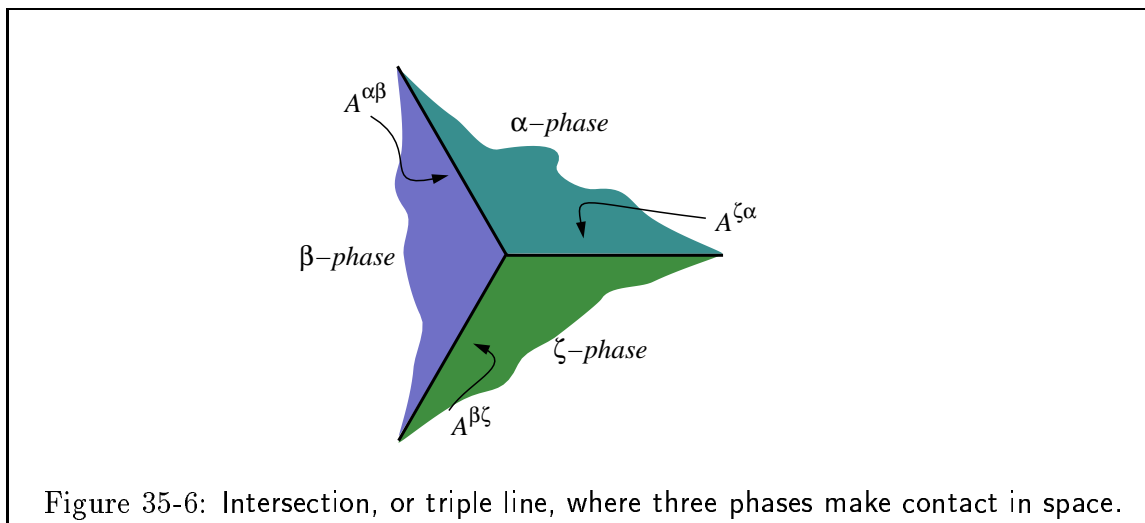
$$\left( \frac{\partial \gamma}{\partial \mu_i} \right)_{\text{constant } T, \mu_j \neq \mu_i} = -\Gamma_i \quad (35-26)$$

This is the ‘‘Gibbs Adsorption Isotherm.’’

Note that if a species adsorbs to the surface  $\Gamma_i > 0$  and the surface tension decreases as the chemical potential of that species is increased.

## — The Conditions of Equilibrium where Several Surfaces Intersect

Consider the case where three different phases make contact:



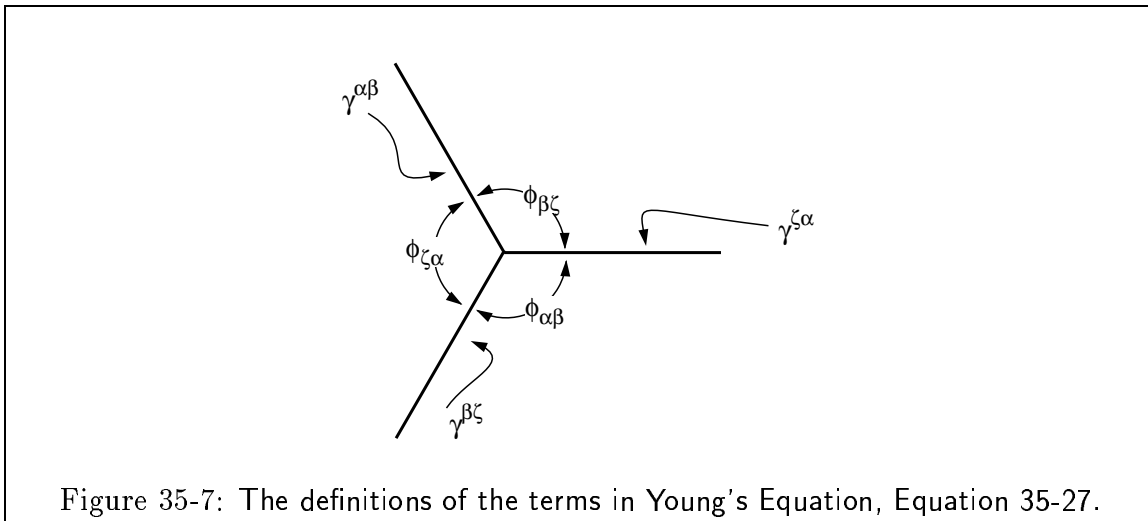
Considering

$$dU^{\text{surf}} = \gamma^{\alpha\beta} dA^{\alpha\beta} + \gamma^{\beta\zeta} dA^{\beta\zeta} + \gamma^{\zeta\alpha} dA^{\zeta\alpha}$$

must be a minimum, one may derive two relations for the angles of contact:

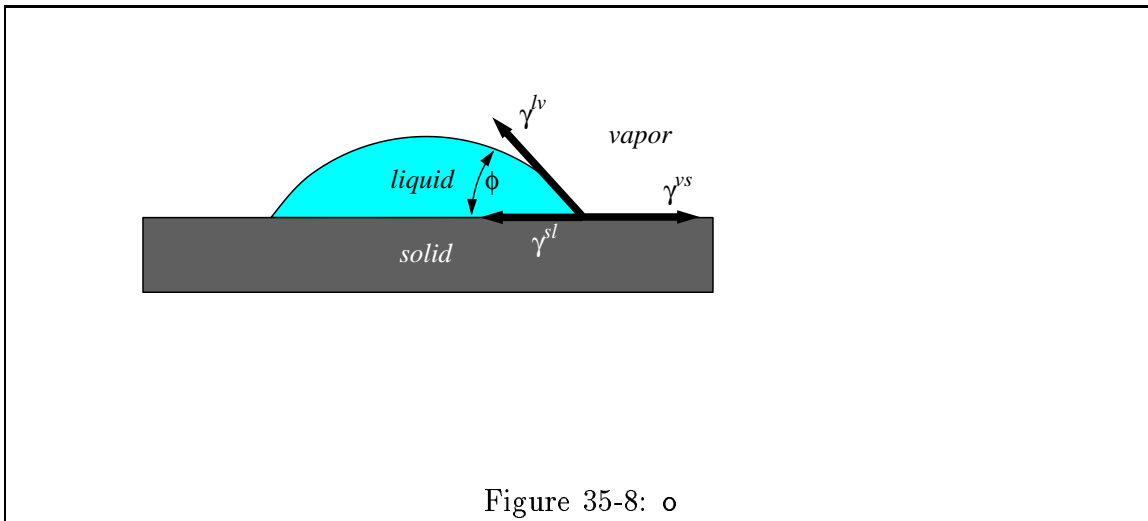
$$\frac{\sin \phi_{\alpha\beta}}{\gamma_{\alpha\beta}} = \frac{\sin \phi_{\beta\zeta}}{\gamma_{\beta\zeta}} = \frac{\sin \phi_{\zeta\alpha}}{\gamma_{\zeta\alpha}} \quad (35-27)$$

which is the general equation the angles at a triple line, called *Young's equation*, where



which is equivalent to the “force balance” where each of the  $\gamma$  are considered the forces applied to the vertex.

For the special case in which one interface is constrained to be flat, as in



we can derive (by force balance most simply)

$$\begin{aligned}\gamma_{lv} \cos \phi + \gamma_{sl} &= \gamma_{vs} \\ \cos \phi &= \frac{\gamma_{vs} - \gamma_{sl}}{\gamma_{lv}}\end{aligned}\quad (35-28)$$

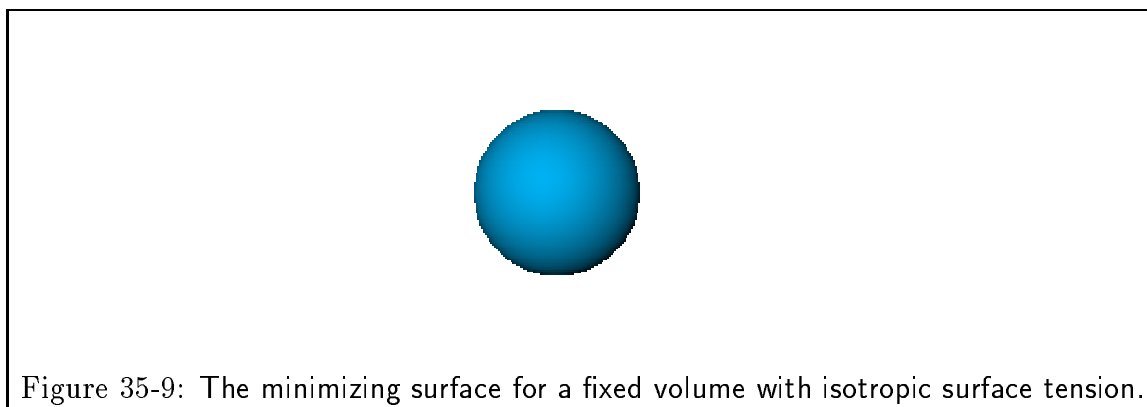
which is Young's equation for flat surfaces.

$$\phi \equiv \text{wetting angle } 0 < \phi < 180^\circ \quad (35-29)$$

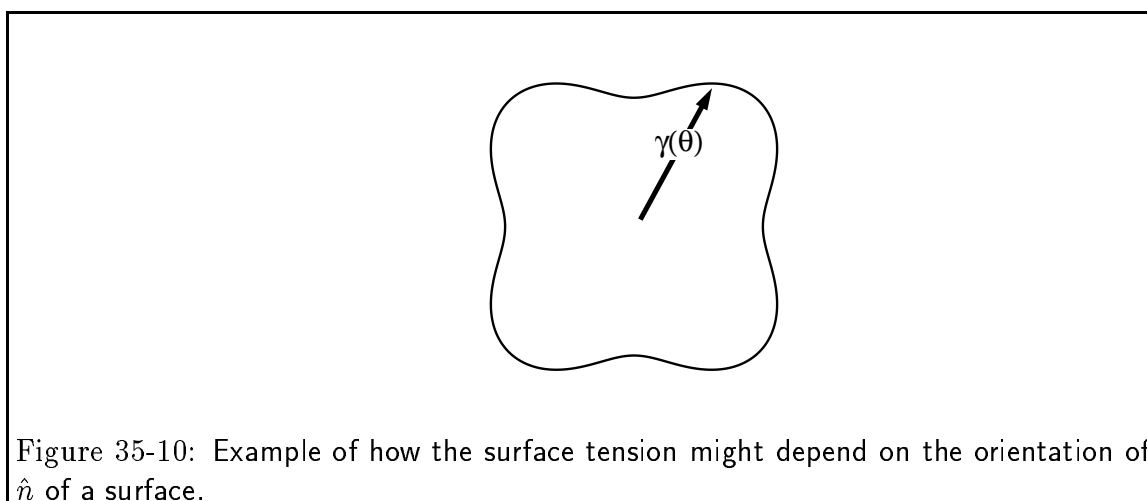
## The Shapes of Things

Above,  $\gamma$  has been assumed to be isotropic. Under this assumption, a finite (isolated) volume body will reduce its total surface energy to a minimum. The result for an isolated body for isotropic surface tension is a sphere.

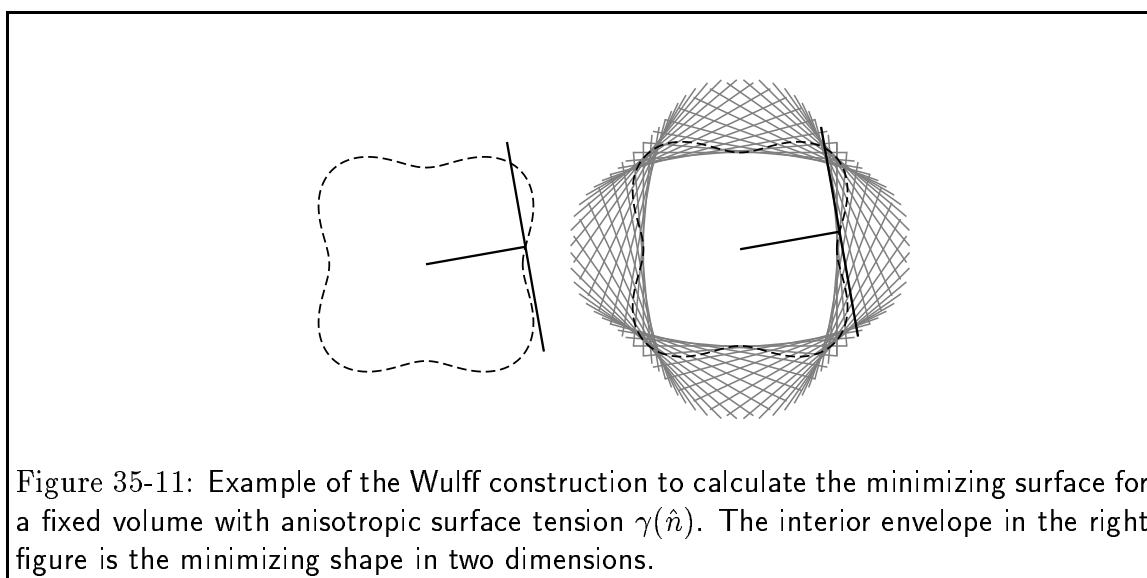




However, for crystals,  $\gamma$  is a function of the orientation of the surface  $\gamma(\hat{n})$ . For example, in 2-D



The shape is given by the *Wulff* construction:



The Wulff construction is performed as follows:<sup>37</sup>

<sup>37</sup>The Wulff theorem, which establishes the Wulff construction is the minimizing surface is surprisingly hard

For each orientation  $\hat{n}$ , draw a ray from the origin to the surface of  $\gamma(\hat{n})$ . At the end of each ray, construct the perpendicular half plane. The interior of the envelope that results from all such half planes is the minimizing shape for a finite isolated volume.

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to prove, but can be understood on the basis of what has been learned in thermodynamics course in a paper by J.W. Cahn and W.C. Carter, *Crystal shapes and phase equilibria: A common mathematical basis*, Met. Trans. A, pp 1431, (1996).