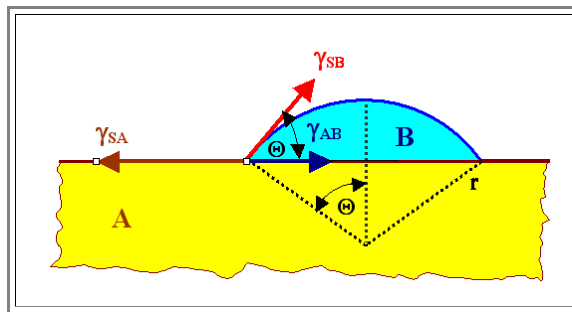


Nucleation Theory

Advanced

- ▶ We want to minimize the free enthalpy G_{nuc} of some nuclei - a cluster of atoms (or molecules) of kind **B** on a substrate **A**.
 - One thing to do, just to make life easier, is to minimize the surface area of the cluster of **B** atoms. We can do this by assuming that the cluster is a little sphere since the surface of a sphere has the smallest surface per volume ratio.
 - But that would defy the purpose so we just assume that the cluster can take any shape, and if it can do that it would behave like a liquid. What we would get then is the shape of some liquid more or less "wetting" some substrate - water on glass or something like that.
 - So we consider a situation like the one shown in the picture below:



- ▶ Next we have to discuss a bit the meaning of the surface or interface energies γ . The basic definition is that it is simply the (differential) work dW needed to increase the surface or interface area by dA . So we have

$$\gamma = \frac{dW}{dA} = \frac{dW}{dx \cdot dy}$$

- ▶ In other words, the surface energy has the dimension of a stress or tension, and we may simply interpret it as the *force* pulling back when you try to increase the surface in one dimension.
 - This is symbolized by the arrows in the picture above.
- ▶ Obviously, in equilibrium, we need the forces to cancel and this gives us immediately a rather important equation:

$$\gamma_{SA} = \gamma_{AB} + \gamma_{SB} \cdot \cos \theta$$

- ▶ Obviously, if we know the three surface or interface energies involved, we can easily calculate the contact angle or **wetting angle** θ of the cluster. However, before we discuss this relation in more detail, let's first write down the free enthalpy G_{nuc} of the situation. We have

$$G_{\text{nuc}} = a_3 \cdot r^3 \cdot G_V + a_1 \cdot r^2 \cdot \gamma_{SB} + a_2 \cdot r^2 \cdot \gamma_{AB} - a_2 \cdot r^2 \cdot \gamma_{SA}$$

- The meaning is clear. G_{nuc} is the energy (OK, free enthalpy change) of the system containing a **B**-cluster with a size given by the radius r (without the cluster we put it at zero), G_V is the free enthalpy of the cluster, and the a_i are the coefficients that relate the volume of the cluster (the "cap"), the surface area of the cluster and the interface area to the radius r (that describes completely the geometry of the arrangement). From (boring, but necessary) spherical geometry we find:

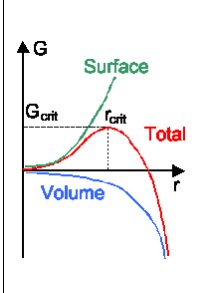
$$a_1 = 2\pi \cdot (1 - \cos \theta)$$

$$a_2 = \pi \cdot \sin^2 \theta$$

$$a_3 = \pi/3 \cdot (2 - 3\cos \theta + \cos^3 \theta)$$

The first thing to note is that the equation for ΔG_{nuc} has cubic and quadratic terms in r and thus will give the general behavior shown in the [backbone](#) and in the [Introduction to Materials Science I](#).

- Thermal equilibrium is achieved if $dG_{\text{nuc}}/dr=0$; and this will give us the critical radius r_{crit} because it is just the radius at the minimum of $G_{\text{nuc}}(r)$ and the critical free enthalpy $G_{\text{crit}}(r_{\text{crit}})$. Going through the differentiation gives

$r_{\text{crit}} = -2 \cdot \frac{(a_1 \cdot \gamma_{\text{SB}} + a_2 \cdot \gamma_{\text{AB}} - a_2 \cdot \gamma_{\text{SA}})}{3a_3 \cdot G_V}$ $G_{\text{crit}} = 4 \cdot \frac{16 \pi \cdot (\gamma_{\text{SB}})^3}{3 \cdot (G_V)^2} \cdot \frac{2 - 3 \cos\theta + \cos^3\theta}{4}$	
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- Looking at the denominators of the equation above we see that we have a small critical radius r_V or a small G_{crit} if a lot of volume energy is gained, i.e. if G_V is large, as it should be.
- Looking at the nominator, we see for r_{crit} the same kind of reckoning up surface and interface energies as we had for the forces in the equation [on top](#). Just multiply with the respective areas expressed in the a_i 's, and you get energies. We have thus a direct relation between the contact angle θ and the critical radius r_{crit} or the critical free enthalpy G_{crit} ; the second equation for G_{crit} already expresses this fact.
- The contact angle θ is obviously a quantity of major concern. It is a kind of direct account balance for the three competing interface energies, giving the energetically best mix of interface areas for a given cluster size.
 - θ can vary between $\theta=0^\circ$, meaning that the cluster would spread into a thin layer, and $\theta=180^\circ$, meaning that the cluster would form a perfect little ball touching the substrate just at one point.
 - The second term in the equation for G_{crit} is only a function of the wetting angle and looks like this (You can generate curves like that yourself in [this module](#)).
 - Note that for $\theta=0^\circ$ (or 0π) the second fraction in the equation for G_{crit} is zero, giving $G_{\text{crit}}=0$. For $\theta=180^\circ$, (or π) the second fraction is =1 and G_{crit} then increases with the third power of the surface energy of the material to be deposited.

Enough of basic nucleation theory at this point. We simply note two major points:

- The formalism shown here is easily expanded to more complex situations (e.g. where stress and strain comes in) and, if carried out, allows to obtain valuable information about what you must expect to happen when you try to deposit **B** on **A**.
- A lot of relevant information can already be obtained by just considering the wetting angle θ