



Wetting of Interfaces and Adhesion

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Lecture: 5/6

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Outline

We will look mainly at the following concepts:

- Wetting and contact angles.
- Liquid-liquid phase separation.
- Adhesion and friction.

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Liquid-Gas Equilibrium

What makes surfaces wet? If we do not pour liquid on them...

Condensation occurs when partial pressure is above equilibrium pressure.

Langmuir equation determines flux J at partial pressure p at equilibrium.

$$J = [p^*(T) - p] \left[\frac{m}{2\pi k_B T} \right]^{1/2}$$

Here p^* is the equilibrium pressure of vapor at the given temperature.



Wikipedia: Sky



Wikipedia: Dew

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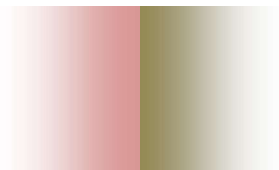


Terminology

Interfacial energy (γ) is work (per area) required to increase the area of the interface of two adjacent phases that do not mix. Relates to solids, liquids and gases.

- Liquid/gas: surface tension
- Solid/gas: surface energy
- Liquid/liquid: interfacial tension

Can also be viewed as a force per distance or “spring constant” ($\text{J/m}^2 = \text{Nm/m}^2 = \text{N/m}$).



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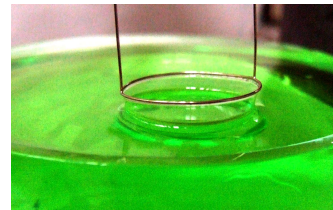
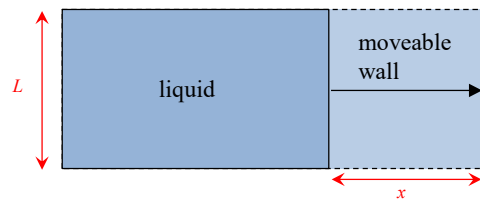


Measuring Surface Tension

Measurements of surface tension can be done directly.

Assume a liquid is placed in a frame with one moveable wall and pulled out. The force required to pull is γL if L is the width. Energy cost of pulling a distance x is $Lx\gamma$.

One common device type is the Du Noüy ring which measures the force required to pull up a ring.



Wikipedia: Tensiometer

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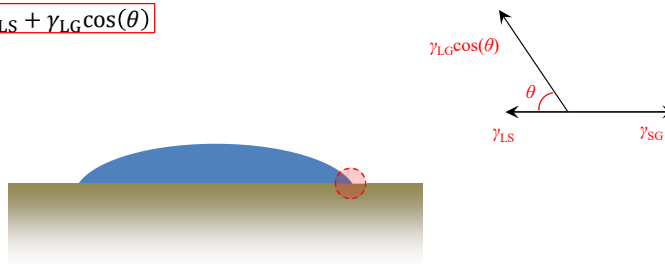
Young's Equation

The static contact angle is defined for a *sessile droplet* resting on the surface.

Assumes gravity can be ignored (small droplet) and no reactions occurring.

Force balance along the surface at the edge:

$$\gamma_{SG} = \gamma_{LS} + \gamma_{LG} \cos(\theta)$$



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Measuring Contact Angle

Simply measured optically by a camera.

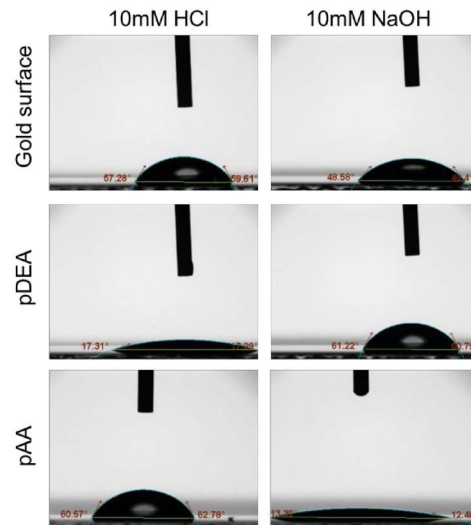
Droplet volume: a few μL

Size on surface: a few mm

Note that the surface appears perfectly smooth compared with the droplet dimensions.

Still the droplet cannot be too large because we want to avoid gravity effects.

Ferrand-Drake et al.
Journal of Physical Chemistry C **2018**, 122 (48), 27516-27527.



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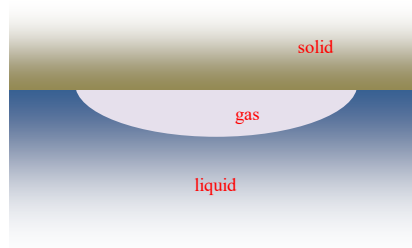
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Bubble Method

Look at a bubble on the top surface in a solid container filled with the liquid.

Young's equation is the same!



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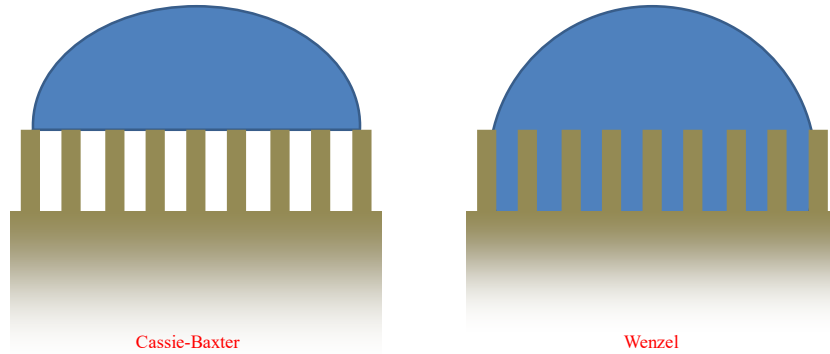


Structured Surfaces

The microstructure also contributes to wetting behavior.

Cassie-Baxter state: drop rests on top, gas trapped underneath.

Wenzel state: wetting the whole surface.



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Sliding Angle

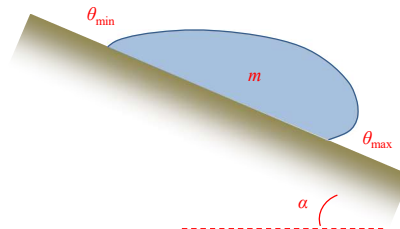
The plane where the sessile drop is resting is tilted. When does the droplet start to move?

Relevant for some applications like keeping outdoor surfaces free from rain or keeping sprayed paint from falling down.

If α is the angle where the droplet starts to move, the gravity pull is equal to the force derived from the different contact angles:

$$mg \sin(\alpha) \propto L \gamma_{LG} [\cos(\theta_{\min}) - \cos(\theta_{\max})]$$

Here L is the width of the drop!



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Dynamic Contact Angles

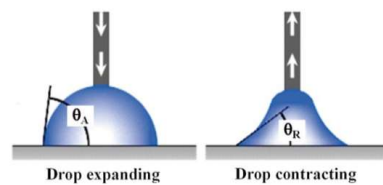
The contact angle will be different when the liquid is moving.

The *advancing* contact angle is “the highest contact angle that can be measured”.

The *receding* contact angle is “the lowest contact angle that can be measured”.

Can be captured by video of sessile droplet spreading.

The dynamic contact angle does not only depend on surface tension, but also viscosity!



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Wilhelmy Plate

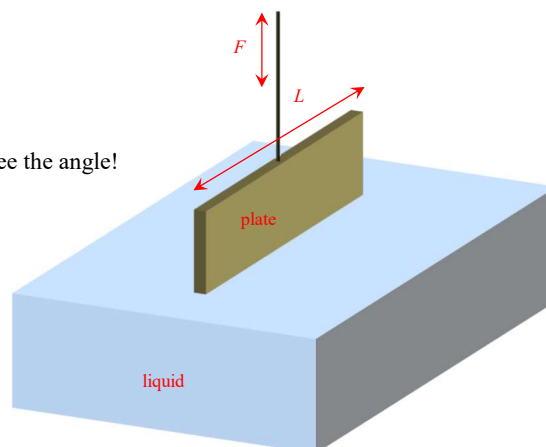
Measure advancing and receding contact angles fairly easily from force when dipping and pulling out:

$$F_a = L\gamma_{LG}\cos(\theta_a)$$

$$F_r = L\gamma_{LG}\cos(\theta_r)$$

But this is indirect, you cannot see the angle!

Also requires γ_{LG} first!



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Surface Energy

The surface energy cannot be measured directly!

Using Young's equation does not help as there is also the interfacial solid-liquid energy (γ_{SL}), which is not known either...



Advanced methods involve using different liquids and looking at sets of contact angles.

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Work of Adhesion

The *work of adhesion* W_{ad} between a solid and a liquid is defined from the interfacial/surface tension/energy terms:

$$\frac{W_{ad}}{A} = \gamma_{LS} - \gamma_{LG} - \gamma_{SG}$$

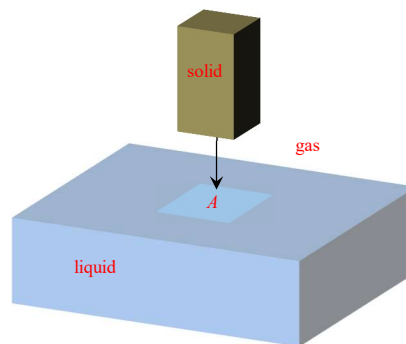
But hey, what if we use Young's equation?

$$\frac{W_{ad}}{A} = -\gamma_{LG}[1 + \cos(\theta)]$$

Exactly those quantities we can measure!

W_{ad} is always attractive!

For two solid surfaces, W_{ad} does not have a defined value because it depends on distance between them (Lecture 1).



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Liquid-Liquid Interfaces

Systems consisting of multiple liquids may either mix or phase separate.

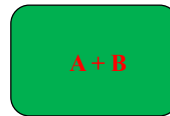
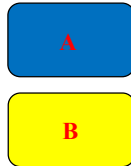
Not exactly relevant for solid surface engineering, but for “interface engineering”.

The regular solution model is explained in additional slides at the end (extra material).

oil and water



Wikipedia: Miscibility



ethanol and water



The Absolut Company:
<http://www.absolut.com/>

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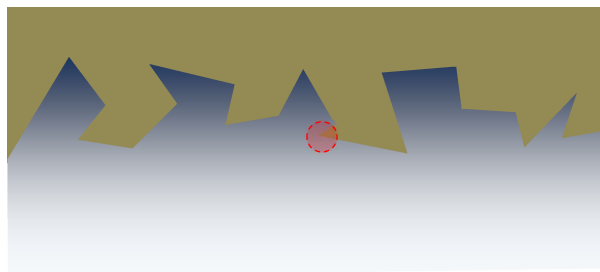


Mechanical Adhesion

Attachment by cavities in the surface structure.

Can be achieved by a glue that solidifies, great on rough surfaces like wood. (But not all glues work like this!)

We are more interested in the physics and chemistry of adhesion.



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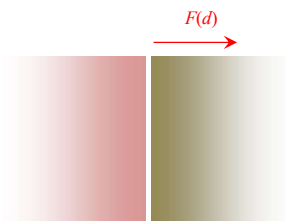


Adhesion Tests

Adhesion is in the end a measure of energy per area.

Measure by integrating force-distance curve when pulling things apart from each other.

Can also be measured with shear stress for coatings like paints etc.



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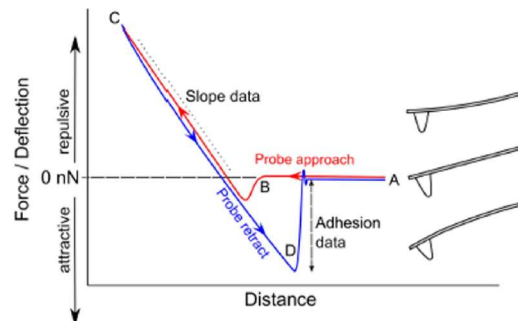
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AFM Measurements

Operation by indentation mode gives the adhesion strength on a small scale.



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Tribology

Tribology is the study of friction and surface wear.

Extremely important for industry to increase lifetime of mechanical components.

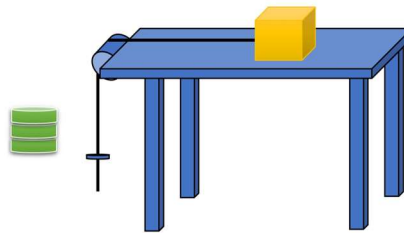
Lubrication is generally the way to reduce friction.

The *breakaway force* is when the object starts to move.

The friction coefficient μ is given by:

$$F_f = \mu F_n$$

Determined by surface properties,
in particular *roughness*.



Roughness

Surface roughness is characterized by two parameters: a spatial frequency and a magnitude.

Sometimes only a magnitude is reported!

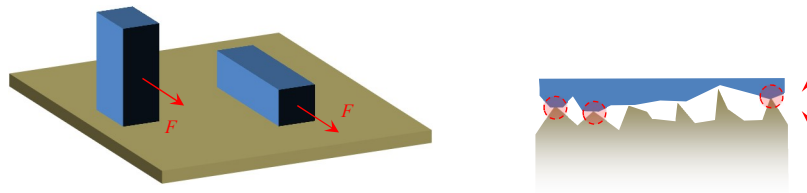




Why no Area Dependence?

The friction force is not influenced by the contact area, only the normal force. Why?

Actually the “real” contact area (atomic contact points) is the same for the same load!



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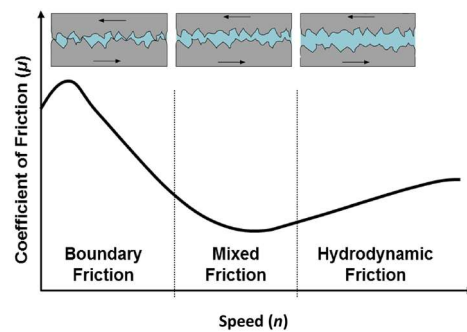


Stribeck Curves

Different friction regimes for lubricated systems.

At sufficiently high speed there is no more surface contact.

Can be done by slow or fast acceleration, which changes many things...



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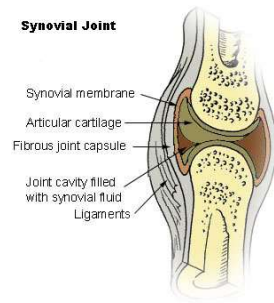
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Biological Friction

Joints are lubricated with *synovial fluid* to reduce wear on bones.

Problems lead to *arthritis*: swollen and stiff joints (many different types).



Wikipedia: Synovial fluid

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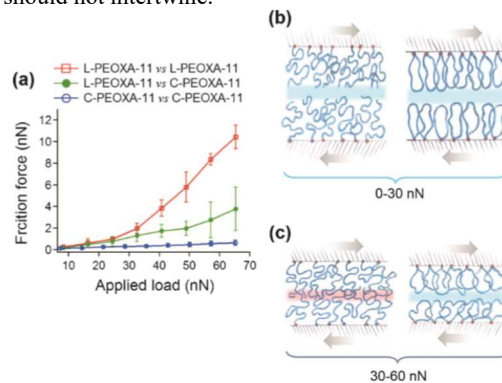
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Polymer Brushes Reduce Friction

Since the self-repulsion is so strong, the brushes strongly reduce friction in liquid.

Ideally the chains should not intertwine.



Morgese et al.
Angewandte Chemie International Edition **2016**, 55 (50), 1-7.

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Reflections & Questions



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Entropy of Mixing

Assume the volume fraction of A molecules among B molecules in the mixture is Φ_A . We have $\Phi_A + \Phi_B = 1$

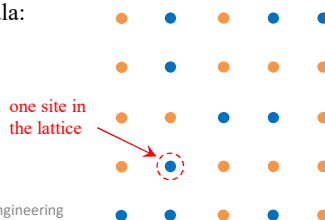
The initial state is two pure phases and the final state is the mixture. What is the free energy change?

Assume the molecules are in a lattice. The probability that a site is occupied by A (or B) is equal to Φ_A (or Φ_B). Entropy per site is given by:

$$\Delta S_{\text{mix}} = -k_B \Phi_A \log(\Phi_A) - k_B \Phi_B \log(\Phi_B) = -k_B [\Phi_A \log(\Phi_A) + \Phi_B \log(\Phi_B)]$$

This comes from Boltzmann's general formula:

$$S = -k_B \sum_{i=1}^n p_i \log(p_i)$$



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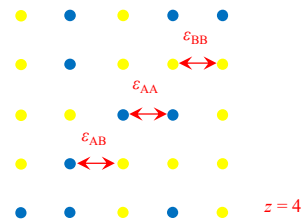


Energy of Mixing

Assume that:

- Each molecule (A or B) is in contact with z neighbors.
- The probability that one finds A or B as neighbor does not depend on whether the site contains A or B (mean field assumption).
- The molecules interact only with their nearest neighbors.

Now we can derive an expression for the energy of mixing (again per “site”) by denoting the three different interaction energies as ϵ_{AA} , ϵ_{BB} and ϵ_{AB} .



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The Interaction Parameter

We get the energy before separation as $U_i = z/2[\epsilon_{AA} + \epsilon_{BB}]$. Note that we divide by two to avoid counting each connection twice!

In the mixture, the number of A neighbors is $z\phi_A$ and the number of B neighbors is $z\phi_B$. We must also take into account the probabilities that we actually have A or B at the site given site (again ϕ_A and ϕ_B).

$$\begin{aligned}\Delta U_{\text{mix}} &= U_f - U_i = \phi_A \left[\frac{z\phi_A\epsilon_{AA}}{2} + \frac{z\phi_B\epsilon_{AB}}{2} \right] + \phi_B \left[\frac{z\phi_B\epsilon_{BB}}{2} + \frac{z\phi_A\epsilon_{AB}}{2} \right] - \frac{z[\epsilon_{AA} + \epsilon_{BB}]}{2} \\ &= \frac{z}{2} [\phi_A^2 \epsilon_{AA} + \phi_B^2 \epsilon_{BB} + 2\phi_A\phi_B\epsilon_{AB} - \epsilon_{AA} - \epsilon_{BB}] \\ &= -\frac{z}{2} [\phi_A[1 - \phi_A]\epsilon_{AA} + \phi_B[1 - \phi_B]\epsilon_{BB} - 2\phi_A\phi_B\epsilon_{AB}] \\ &= -\frac{z}{2} \phi_A\phi_B [\epsilon_{AA} + \epsilon_{BB} - 2\epsilon_{AB}] = \chi k_B T \phi_A \phi_B\end{aligned}$$

$$\chi = -\frac{z}{2k_B T} [\epsilon_{AA} + \epsilon_{BB} - 2\epsilon_{AB}]$$

interaction parameter

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The Free Energy of Mixing

We now have the free energy of mixing:

$$\Delta G_{\text{mix}} = \Delta H_{\text{mix}} - T\Delta S_{\text{mix}} = k_B T [\phi_A \log(\phi_A) + \phi_B \log(\phi_B) + \phi_A \phi_B \chi]$$

Let us from now on use only ϕ to denote the volume fraction of A:

$$\Delta G_{\text{mix}} = k_B T [\phi \log(\phi) + [1 - \phi] \log(1 - \phi) + \phi [1 - \phi] \chi]$$

Note that all we need to calculate $\Delta G_{\text{mix}}(\phi)$ is the interaction parameter χ at the given temperature!

Low χ comes from high ε_{AA} and ε_{BB} or low ε_{AB} . Per definition χ is proportional to T^{-1} .

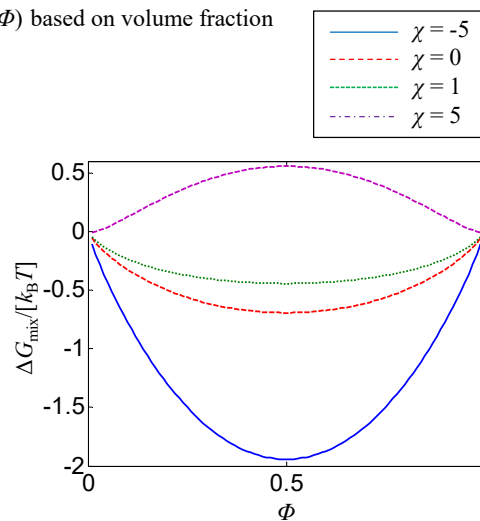
We see how high temperature promotes mixing in general (entropic terms in ΔG_{mix}).



Liquid-Liquid Mixing

We can now generate a graph of $\Delta G_{\text{mix}}(\phi)$ based on volume fraction of A in B and the value of χ .

- $\Delta G_{\text{mix}}(\phi)$ is always symmetric around $\phi = 1/2$.
- For $\chi = 0$ we have only entropic contributions and a simple minimum (at the microstate maximum).
- High enough χ means the mixing is impossible due to unfavorable interactions between A and B.





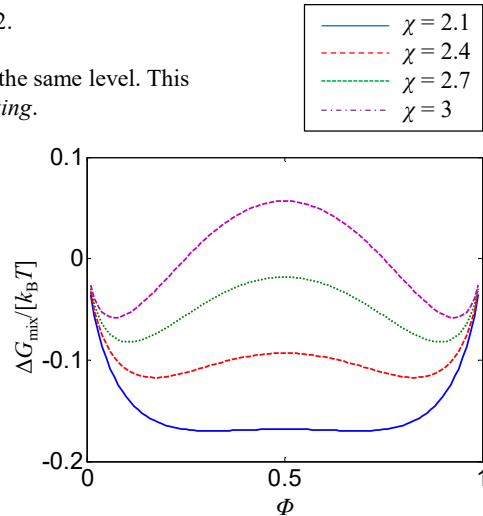
Coexisting Compositions

The interesting region occurs when $\chi > 2$.

The curve shows two energy minima at the same level. This means that two compositions are *coexisting*.

The conclusion is that two stable phases can exist, one with high Φ and one with low Φ .

Even for very high χ there are two minima! (They are just very close to 0 and 1.)



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Phase Separation

Assume we start with one phase with Φ_0 and volume V_0 that separates into two new phases with Φ_1 in V_1 and Φ_2 in V_2 .

We have from conservation of matter: $\Phi_0 V_0 = \Phi_1 V_1 + \Phi_2 V_2$

Also, if the volume is preserved: $V_0 = V_1 + V_2$

The free energy change is then:

$$\Delta G = \frac{V_1}{V_0} \Delta G_{\text{mix}}(\Phi_1) + \frac{V_2}{V_0} \Delta G_{\text{mix}}(\Phi_2) = \frac{\Phi_2 - \Phi_0}{\Phi_2 - \Phi_1} \Delta G_{\text{mix}}(\Phi_1) + \frac{\Phi_0 - \Phi_1}{\Phi_2 - \Phi_1} \Delta G_{\text{mix}}(\Phi_2)$$

We are still working with the free energy of mixing so this ΔG represents the free energy change in comparison with fully separated compounds. To get the free energy change of the phase separation we subtract the initial state:

$$\Delta G_{\text{sep}} = \frac{\Phi_2 - \Phi_0}{\Phi_2 - \Phi_1} \Delta G_{\text{mix}}(\Phi_1) + \frac{\Phi_0 - \Phi_1}{\Phi_2 - \Phi_1} \Delta G_{\text{mix}}(\Phi_2) - \Delta G_{\text{mix}}(\Phi_0)$$

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Graphical Treatment of Phase Separation

How do we know if ΔG_{sep} is negative?

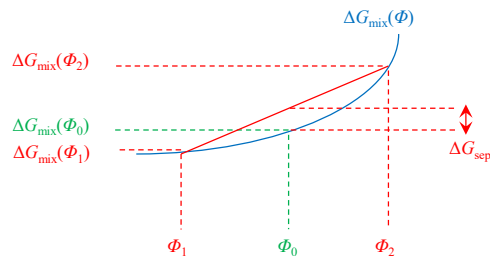
It is possible to read ΔG_{sep} directly from the $\Delta G_{\text{mix}}(\Phi)$ graph. This follows from the equation for ΔG_{sep} (and a straight line in χy coordinates).

- Connect $\Delta G_{\text{mix}}(\Phi_1)$ and $\Delta G_{\text{mix}}(\Phi_2)$ with a line.
- Go vertically from $\Delta G_{\text{mix}}(\Phi_0)$ to this line.
- The change represents ΔG_{sep} !

The curvature of $\Delta G_{\text{mix}}(\Phi)$ is critical!

$$\frac{\partial^2 \Delta G_{\text{mix}}}{\partial \Phi^2} > 0 \Rightarrow \Delta G_{\text{sep}} > 0$$

$$\frac{\partial^2 \Delta G_{\text{mix}}}{\partial \Phi^2} < 0 \Rightarrow \Delta G_{\text{sep}} < 0$$



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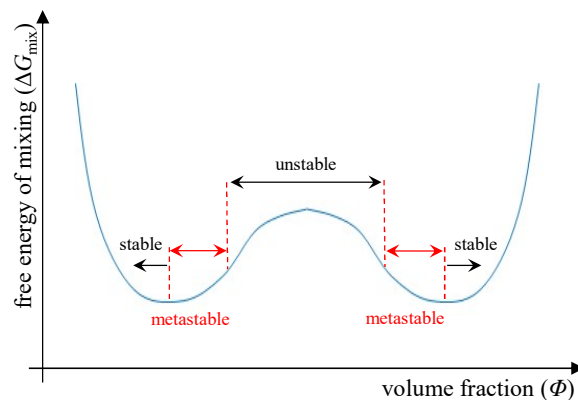
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Metastable Mixtures

Mixtures where ΔG_{sep} is positive for small changes but where the free energy is not at the global minima are *metastable*. They occur in between stable and unstable regions.

The regions can be identified by the graphical method or by the derivatives.



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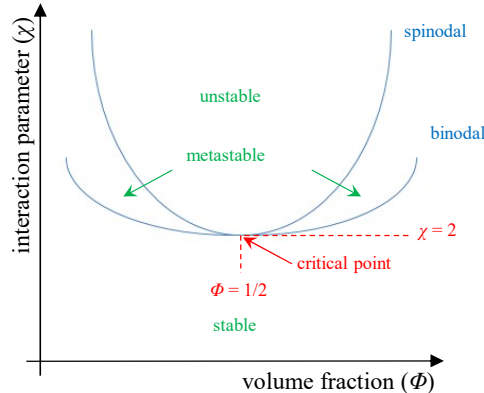


Liquid-Liquid Phase Diagram

We can now generate a phase diagram (with χ and Φ as parameters instead of T and P).

- All mixtures are fully stable when $\chi < 2$.
- The *spinodal* separates the unstable and the metastable regions (derived from curvature change).
- The *binodal* separates the fully stable and the metastable regions (derived from coexistence points).
- The *critical point* is where the spinodal and binodal meet and:

$$\frac{\partial^3 \Delta G_{\text{mix}}}{\partial \Phi^3} = 0$$



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In Reality

In reality, our model is often not good enough...

- Need to work with mole fractions instead (fixed lattice volume implies *Helmholtz* free energy).
- The curves are asymmetric because the molecules are not arranged independently on a lattice.
- The coexisting phases are not simply given by the minima: A tangent is used instead.

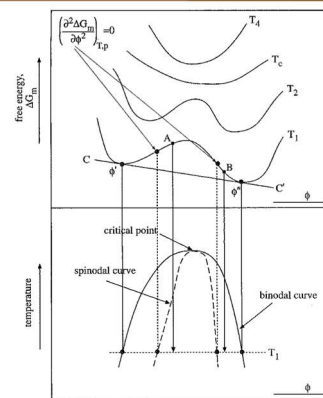


Figure 2.16 Analysis of phase behaviour of a binary blend of polymer and solvent or two polymers exhibiting an upper critical solution temperature, T_c . Top: variation of Gibbs free energy with composition, ϕ ($\phi = \phi_1$ or ϕ_2) at four temperatures. The line CC' defines the compositions on the binodal curve. The locus of points defined by the points of inflection $(\partial^2 G / \partial \phi^2)_{T,P} = 0$ define the spinodal curve. At point A (inside the spinodal curve), the mixture will spontaneously phase separate (into domains with compositions ϕ' and ϕ'') via spinodal decomposition. However, at point B (outside the spinodal curve) there is an energy barrier to phase separation, which then occurs by nucleation and growth

I.W. Hamley
Introduction to Soft Matter Wiley 2007

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Exercise 5.1

Two liquids mix according to the regular solution model with $\chi = 3$. Determine the unstable volume fraction interval!

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Exercise 5.1

The unstable volume fraction interval is within the region of positive curvature:

$$\begin{aligned}\frac{\partial \Delta G_{\text{mix}}}{\partial \Phi} &= k_B T \left[1 \times \log(\Phi) + \Phi \times \frac{1}{\Phi} - \log(1 - \Phi) - [1 - \Phi] \times \frac{1}{1 - \Phi} + 3 - 6\Phi \right] \\ &= k_B T [\log(\Phi) - \log(1 - \Phi) - 6\Phi + 3]\end{aligned}$$

$$\frac{\partial^2 \Delta G_{\text{mix}}}{\partial \Phi^2} = k_B T \left[\frac{1}{\Phi} + \frac{1}{1 - \Phi} - 6 \right]$$

$$\frac{\partial^2 \Delta G_{\text{mix}}}{\partial \Phi^2} = 0$$

$$\begin{aligned}\frac{1}{\Phi} + \frac{1}{1 - \Phi} - 6 &= 0 \Rightarrow \Phi^2 - \Phi + \frac{1}{6} = 0 \Rightarrow \Phi = \frac{1}{2} \pm \left[\frac{1}{4} - \frac{1}{6} \right]^{1/2} \\ &= \frac{1}{2} \pm \left[\frac{1}{12} \right]^{1/2}\end{aligned}$$

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