



Phase Transitions: Equilibrium

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Lecture 2/11
Jones: 3.1-3.2, 3.4

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Outline

What is a phase transition?

- Boiling and condensation (usually not interesting in SMP).
- Liquid-liquid mixing/unmixing.
- Melting and freezing.

The *glass* transition is a bit special and will be dealt with in other lectures...

We will first look at phase transitions from an equilibrium perspective: What is the change in free energy of the system? Can a phase transition occur or not?

In the next lecture we will look at the kinetics of phase transitions.

As usual we will derive generic laws and principles. We will not go into details on the chemistry (e.g. intermolecular bonds).

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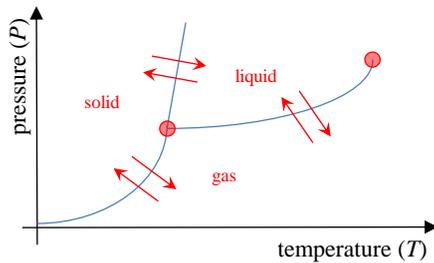
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Phase Transitions in General

A phase transition is characterized by a *discontinuous* and *qualitative* change in properties in response to a *continuous* and *quantitative* change in an external parameter.

The most common representation is a *phase diagram* with T and P . This tells us the phase with the lowest energy for a pure compound!



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Wikipedia: Sky



Wikipedia: Dew

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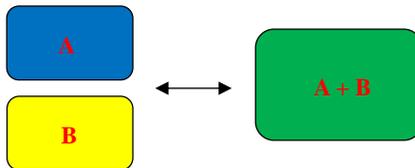


Liquid-Liquid Mixing

Consider a system that consists of two *incompressible* liquids. They can form different phases, mixed or separated. How can we know if and to what extent they mix?



Wikipedia: Miscibility

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

Oil and water forms two phases that are essentially fully separated. Water and ethanol practically always form a single mixed phase. But for some liquid combinations we will end up somewhere in between.

We need to look at Helmholtz free energy of mixing: $\Delta F_{\text{mix}} = \Delta U_{\text{mix}} - T\Delta S_{\text{mix}}$

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Entropy of Mixing

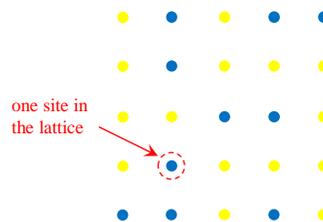
Assume the volume fraction of A molecules among B molecules in the mixture is Φ_A . We have $\Phi_A + \Phi_B = 1$

The initial state is two pure phases and the final state is the mixture. What is ΔF_{mix} ?

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 Boltzmann's formula:

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

Sidenote: One could claim there are more microstates because there are many molecules that we do not distinguish from each other. However, the entropy associated with this effect exists already in the pure phases!



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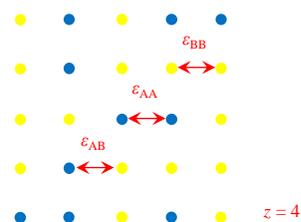


Energy of Mixing

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 as $U_i = z/2[\epsilon_{AA} + \epsilon_{BB}]$. Note that we divide by two to avoid counting each connection twice! (Per site and averaged.)

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).

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

interaction parameter

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

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The Free Energy of Mixing

We now have the Helmholtz free energy of mixing:

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

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

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

Note that all we need to calculate $\Delta F_{\text{mix}}(\Phi)$ 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 ΔF_{mix}).

Important: Things can be much more complicated in reality because ϵ_{AA} , ϵ_{BB} and ϵ_{AB} can depend on temperature! They have entropic contributions and are not purely energetic. (We will get back to this in relation to self assembly and polymers in solution.)

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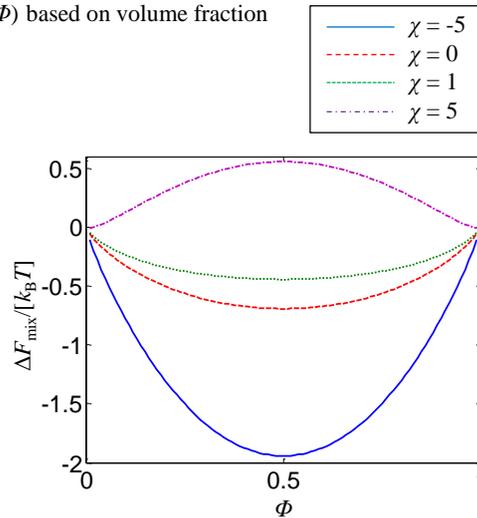
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Liquid-Liquid Mixing

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

- $\Delta F_{\text{mix}}(\Phi)$ 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.



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Coexisting Compositions

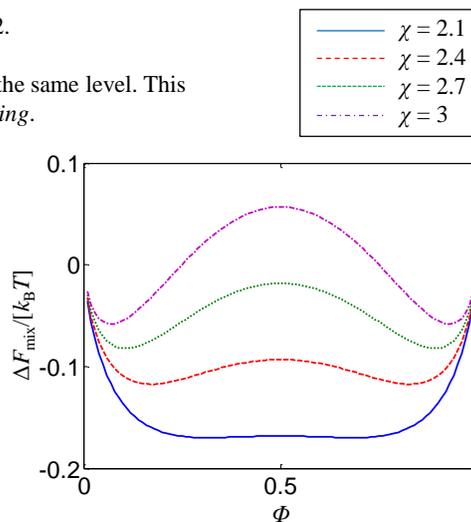
The interesting region occurs when $\chi > 2$.

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 .

Remember that one can change χ , for instance by temperature!
Phase separation of a mixture can thus be induced!

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

The new free energy is then:

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

We are still working with the free energy of mixing so ΔF_{new} represents the free energy change in comparison with fully separated compounds. (Very unclear in Jones!) To get the free energy change of the phase separation we subtract the initial state:

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

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Graphical Treatment of Phase Separation

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

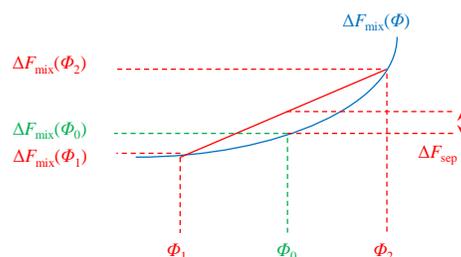
It is possible to read ΔF_{sep} directly from the $\Delta F_{\text{mix}}(\Phi)$ graph. This follows from the equation for ΔF_{sep} (and a straight line in xy coordinates).

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

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

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

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



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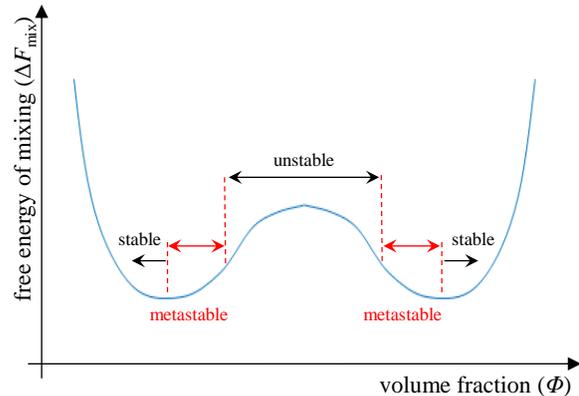
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Metastable Mixtures

Mixtures where ΔF_{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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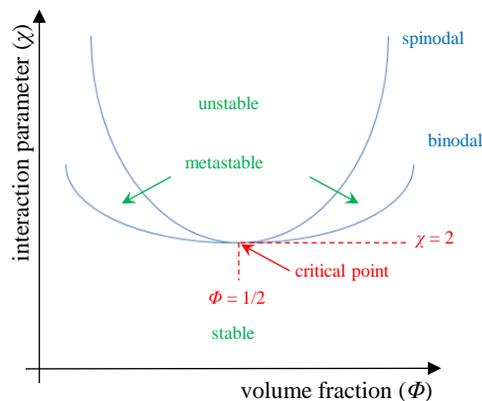


Liquid-Liquid Phase Diagram

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:

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



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Exercise 2.1

Two liquids mix according to the regular solution model with $\chi = A/T$ where A is a constant.

- (A) Above which temperature are all volume fractions stable mixtures?
- (B) Determine the unstable volume fraction interval at $T = A/3$!

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Exercise 2.1

(A) For the regular solution model all mixtures are stable for $\chi < 2$. Thus $A/T < 2$ so:
 $T > A/2$

(B) We have $\chi = 3$. The unstable volume fraction interval is within the region of positive curvature:

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

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

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

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

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Demonstration: Ethanol and Water

Alcohol by volume?



Brouwerij van Steenberge: Gulden Draak
<http://www.vansteenberge.com/>

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In Reality

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

- Gibbs instead of Helmholtz. (We usually have constant pressure but not necessarily volume.) Use mole fractions and preserve total number of molecules instead!
- 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.

Jones does not discuss these things!

I.W. Hamley
Introduction to Soft Matter Wiley 2007

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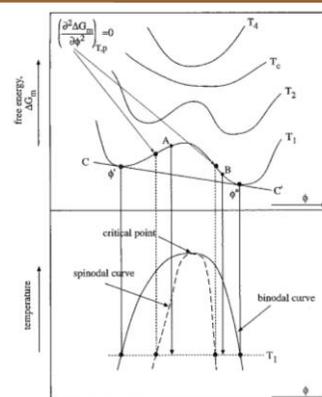
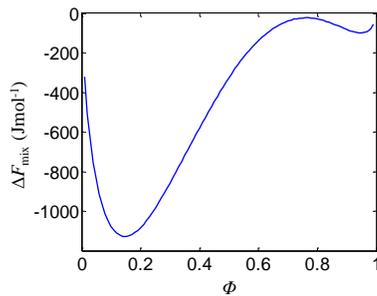


Figure 2.16 Analysis of phase behaviour of a binary blend of polymer and solvent or two polymers exhibiting an upper critical solution temperature, T_c . Top: variation of Gibbs free energy with composition, ϕ ($\phi = \phi_1$ or ϕ_2) at four temperatures. The tie line CC' defines the compositions on 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_1' and ϕ_2') 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.



Exercise 2.2

The free energy per mole for a two component mixture is given by $\Delta F_{\text{mix}} = N_A k_B T [4\Phi \log(\Phi) + [1 - \Phi] \log(1 - \Phi) + 4\Phi[1 - \Phi]\chi]$ with $\chi = 1.6$ as plotted in the figure. The total volume fraction of component one is $\Phi = 0.6$.



- (A) Estimate the relative volumes of the compositions representing coexisting phases!
 (B) Estimate the free energy change of the phase separation process!

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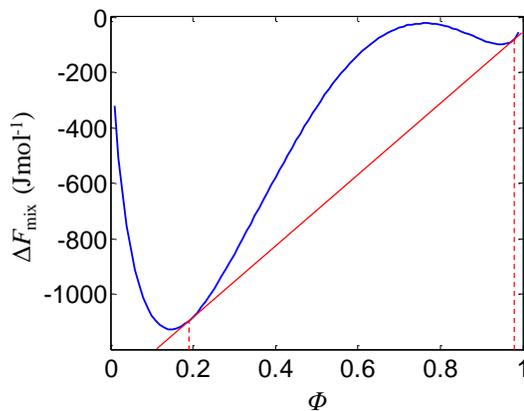
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Exercise 2.2

(A) This is not the regular solution model. ($\chi < 2$ does not mean the mixture is stable.) A tangent must be used to find the coexisting compositions. This gives approximately $\Phi_1 = 0.19$ and $\Phi_2 = 0.97$. (Note that $\Phi_1 + \Phi_2 > 1$.)



$$\frac{V_1}{V_0} = \frac{\Phi_2 - \Phi_0}{\Phi_2 - \Phi_1} = \frac{0.97 - 0.6}{0.97 - 0.19} \approx 47\%$$

$$\frac{V_2}{V_0} = \frac{\Phi_0 - \Phi_1}{\Phi_2 - \Phi_1} = \frac{0.6 - 0.19}{0.97 - 0.19} \approx 53\%$$

A more exact solution requires setting the derivative of ΔF_{mix} equal to the tangent slope and match function values...

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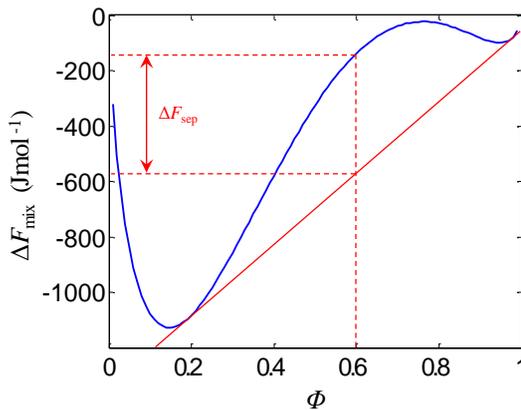
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Exercise 2.2

(B) Initially we have $\Delta F_{\text{mix}}(\Phi_0)$ per site for the whole system. After we have a new free energy per site given by the relative volumes and the ΔF_{mix} value of each phase. We can thus read ΔF_{sep} from the graph as -440 Jmol^{-1} .



An exact solution requires inserting all Φ values into ΔF_{mix} and calculate...

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Regarding Incompressibility

- Recall that $\Phi_A + \Phi_B = 1$ in a binary mixture, but we are now looking at only one component Φ (the other is always $1 - \Phi$).
- In the regular solution model, if phase separation occurs to the coexisting phases we have $\Phi_1 + \Phi_2 = 1$ simply because they are symmetric around $1/2$. But we do not break any physical law by having $\Phi_1 + \Phi_2 \neq 1$.
- The volumes of the new phases are free to vary, but not the total volume in the regular solution model.
- One must, however, always have $\Phi_1 < \Phi_0$ and $\Phi_2 > \Phi_0$. (One new phase has higher and one has lower concentration.)
- Note that the incompressibility is necessary to derive the model. Even if it is not true (ethanol and water) we must make this assumption...
- The final mixtures are still normally quite incompressible (liquids tend to be). It is just that the total volume might not be preserved in the mixing process.

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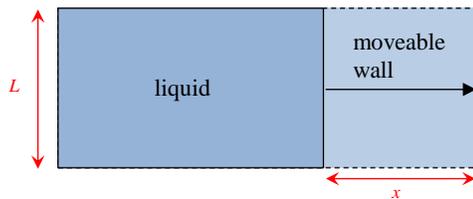
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Interfacial Tension

There must be an additional energy γ associated with creating the *interface* between the liquids if they phase separate. (Just like surface tension of any liquid.)



Wikipedia: Gerridae

Force view: 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, so γ has dimension Nm^{-1} .

Energy view: Interfacial tension is the (free) energy needed to create one unit area of the interface (Jm^{-2}). The energy required to pull a distance x is γLx .

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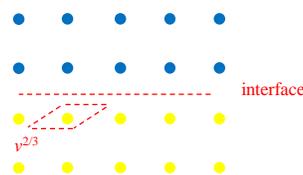


Interaction Parameter and Interfacial Tension

Using the regular solution model as a basis we can derive a relation between χ and γ :

$$\gamma = \frac{1}{v^{2/3}} \left[\epsilon_{AB} - \frac{\epsilon_{AA} + \epsilon_{BB}}{2} \right] = \frac{\chi k_B T}{z v^{2/3}}$$

after interface formed before interface formed



Here v is a characteristic molecular volume. If each molecule is a cube, $v^{2/3}$ is the interfacial area exposed per molecule.

The relation is not very useful in practice since z and v are hard to know, but it shows how χ and γ are related in principle.

Sidenote: In reality, molecules move around and the interface is rough and always changing. (Jones says this means γ is lower due to this entropy associated with the interface, to me it is a bit unclear because a rougher interface has a higher area...)

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Liquid-Solid Transitions

Melting and freezing processes are relevant for many types of soft matter. We will now work with Gibbs free energy (constant pressure).

- The main characteristic of the liquid-solid transition is the degree of order among the molecules. The liquid phase has little order while in the solid the molecules are positioned periodically over longer distances (until a grain boundary).
- At the phase transition temperature T_m we have $\Delta G = 0$ for melting/freezing per definition. The free energy is the same in both phases.
- For a “first order transition” the derivative of free energy with respect to temperature (entropy) changes discontinuously (continuously for second order transitions).

As we can expect, the change in free energy during the transition will depend on the difference between T and T_m , i.e. the *undercooling* or *overheating*.

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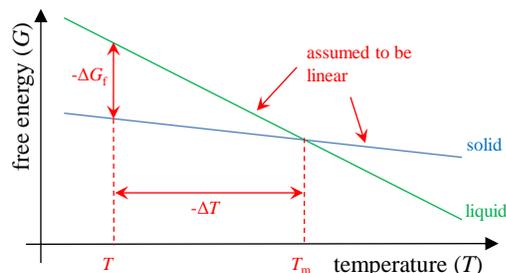
Gibbs Energy of Freezing and Melting

If $T = T_m$ then $\Delta G = 0$ for melting and thus:

$$\Delta S_m = \frac{\Delta H_m}{T_m}$$

Clearly, $\Delta S_m > 0$ (consider the ordering) and $\Delta H_m > 0$ (breaking interaction forces). We assume that ΔH_m and ΔS_m do not change so much with T . If $\Delta T = T - T_m$ then:

$$\begin{aligned} \Delta G_m &= \Delta H_m - T\Delta S_m = \\ \Delta H_m \left[1 - \frac{T}{T_m} \right] &= \\ -\Delta H_m \frac{T - T_m}{T_m} &= \\ -\frac{\Delta H_m \Delta T}{T_m} \end{aligned}$$



Thus the change in free energy is proportional to ΔT . Results are the same for melting and freezing since $\Delta H_m = -\Delta H_f$. (This is a bit confusing in Jones...)

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Reflections and Questions



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Exercise 2.3

Derive the two equations that define the exact values of Φ_1 and Φ_2 in Exercise 2.2A (they would have to be solved numerically).

→

$$\frac{\partial \Delta F_{\text{mix}}(\Phi)}{\partial \Phi} \Big|_{\Phi=\Phi_1} = \frac{\partial \Delta F_{\text{mix}}(\Phi)}{\partial \Phi} \Big|_{\Phi=\Phi_2}$$

$$\Delta F_{\text{mix}}(\Phi_1) - \Phi_1 \frac{\partial \Delta F_{\text{mix}}}{\partial \Phi} \Big|_{\Phi=\Phi_1} = \Delta F_{\text{mix}}(\Phi_2) - \Phi_2 \frac{\partial \Delta F_{\text{mix}}}{\partial \Phi} \Big|_{\Phi=\Phi_2}$$

$$4 \log(\Phi_1) - \log(1 - \Phi_1) - 12.8\Phi_1 = 4 \log(\Phi_2) - \log(1 - \Phi_2) - 12.8\Phi_2$$

$$4\Phi_1 \log(\Phi_1) + [1 - \Phi_1] \log(1 - \Phi_1) + 6.4\Phi_1 [1 - \Phi_1] - \Phi_1 [9.4 - 12.8\Phi_1 + 4 \log(\Phi_1) - \log(1 - \Phi_1)] =$$

$$4\Phi_2 \log(\Phi_2) + [1 - \Phi_2] \log(1 - \Phi_2) + 6.4\Phi_2 [1 - \Phi_2] - \Phi_2 [9.4 - 12.8\Phi_2 + 4 \log(\Phi_2) - \log(1 - \Phi_2)]$$

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