Part I
Intermolecular forces

Abstract

In the study of matter, one defines several different states. In this course, we will focus on the study of the properties of condensed matter. Crystals and liquids are examples of such condensed matter - the interaction between molecules of the latter is of the order of $E_{int} >> k_B T$ whereas the former presents an interaction energy $E_{int} \geq k_B T$ which can be put in contrast to a gas' $E_{int} << k_B T$. Let us note that thermal energy is much larger than the interactions between particules in the gaseous states.

1   Microscopic interaction potential

Let us consider the interaction between two different molecules. The total energy in the system can be written as

$$E_{tot}(r) = E_A + E_B + w(r) \tag{1.1}$$

where r is the distance between the molecules A and B and $w(r)$ is the *potential of interaction*, defined as

$$w(r) = E_{tot}(r) - E_{tot}(\infty) \tag{1.2}$$

$$w(r) = - \int_r^\infty F(r) dr \quad \Leftrightarrow \quad F(r) = -\frac{dw}{dr} \tag{1.3}$$

Beware to the minus sign between the two: the interaction is *attractive* when the potential is negative, and *repulsive* when the potential

2   Molecular interactions via electrostatic potentials

We will perform a review of the electrostatic potential interaction, with an increasing level of complexity. In particular, we will consider the interaction between...

- Two single point charges (approximation for two ions), dipole moments (approximation for two molecules)

- A single point charge and a non-rotating dipole moment

- Two non rotating dipole moments

- A single point charge and a rotating dipole moment

- Two rotating dipole moments

2.1   Electrostatic interaction between two point charges

Let us consider two single points charges Q_1 and Q_2 separated by a distance r. As a reminder, let us note that the electric field of a charge Q at a distance r is given by $E = \frac{Q}{4\pi\epsilon_r\epsilon_0 r^2}$. Therefore, the electric force of charge Q_1 on charge Q_2 is given by $F = E_1 Q_2 = \frac{Q_1 Q_2}{4\pi\epsilon_r\epsilon_0 r^2} = \frac{z_1 z_2 e^2}{4\pi\epsilon_r\epsilon_0 r^2}$ by introducing the valence numbers z_i. We deduce the macroscopic electrostatic potential

$$w(r) = -\frac{z_1 z_2 e^2}{4\pi\epsilon_r\epsilon_0 r} \tag{2.1}$$

2.1.1   Electrostatic interaction: application to $NaCl$

In a vaccum, one finds that $w_{NaCl} = -8.4 \times 10^{-19} J$. However, at room temperature one has that $U_T = k_B T \approx 1.38 \times 10^{-23} J/K \cdot 291 J = 4 \times 10^{-21} J$. Given that $w_{NaCl} > 200 k_B T$[1], NaCl is stable at room temperature in a vaccum. However, put it in a medium with high dielectric constant such as water and $w_{NaCl}^{H_2O}(r) \approx 2.5 k_B T$.

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[1]Why do we ignore the negative sign?

2.2 Dipole moments

Asymetric molecules bounded by covalent bounds often contains dipole moments. One defines the units of *Debye* for this purpose: take two charges e and $-e$ separated by a distance of one *Angstrum*:

$$\mu = 4.8D$$

2.2.1 Dipole moment of water

Example 2.1. *The molecule of water can be seen as two OH molecules separated by an angle of* 104.5ř*. Given that* $\mu_{OH} = 1.51D$*, we deduce that the dipole moment of water is given by*

$$\mu_{H_2O} = 2\cos\left(\frac{H\hat{O}H}{2}\right)\mu_{HO} = 1.85D \tag{2.2}$$

2.3 Ion-dipole interaction

Instead of looking a two single point charges and a dipole seperately, let us put them together and see what happens as shown in figure 1. The resulting macroscopic electrostatic potential is

$$w(r) = -\frac{qQ}{4\pi\epsilon_0 r_A} + \frac{qQ}{4\pi\epsilon_0 r_B} = \frac{qQ}{4\pi\epsilon_0}\left(\frac{1}{r_B} - \frac{1}{r_A}\right) \tag{2.3}$$

Let us note that $r_A \approx r - \frac{l}{2}\cos\theta$ whereas $r_B \approx r + \frac{l}{2}\cos\theta$. Applying the approximation $\frac{r_A - r_B}{r_A r_B} \approx -\frac{l\cos\theta}{r^2}$, one finds that (2.3) can be rewritten as

$$w(r) \approx -\frac{qQ}{4\pi\epsilon_0}\frac{l\cos\theta}{r^2} = -\mu\frac{Q\cos\theta}{4\pi\epsilon_0 r^2} \quad w(r) = -\mu E(r)\cos\theta \tag{2.4}$$

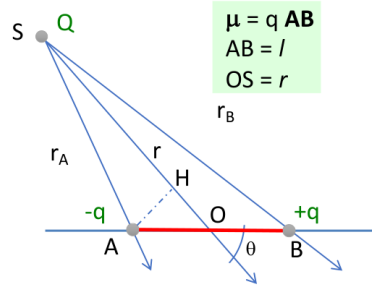The potential is either attractive or repulsive, depending on the orientation of the molecule.

Figure 1: Ion-dipole interaction

2.4 Dipole-dipole interaction

Assuming the two dipoles can freely move in the xyz space, one would need to replace the angle θ used previously by three different angles - θ_1, θ_2 and φ as shown in figure 2a. The interaction potential can then be written as

$$w(r, \theta_1, \theta_2, \varphi) = -\frac{\mu_1\mu_2}{4\pi\epsilon_o\epsilon_r r^3}\left(2\cos\theta_1\cos\theta_2 - \sin\theta_1\sin\theta_2\cos\varphi\right) \tag{2.5}$$

To simplify the problem, let us assume the angles θ_1 is equal to 0, meaning that the only allowed variation is in θ_2 and in the rotation angle φ. Then,

- $\theta_2 = 0 \iff w(r, 0, 0, \varphi) = -\frac{2\mu_1\mu_2}{4\pi\epsilon_r\epsilon_0 r^3}$. The two dipoles are attracted to each other.

- $\theta_2 = 90$. The dipoles are neither attracted nor repulsed by each other - they are said to be neutral.

- $\theta_2 = 180$. The dipoles are repelled by each other.

- $\theta_2 = 270$. The dipoles are neither attracted nor repulsed by each other - they are said to be neutral.

Let us note that in all situations, if the dipoles are free to rotate, then they tend to align themselves (situation with the lowest potential). This is shown in figure 2b.
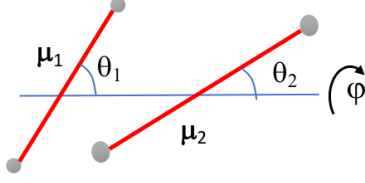
(a) Dipole-Dipole interaction
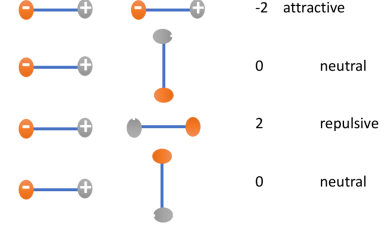
(b) Summary of the different possible states with $\theta_1 = 0$.

2.5 Interactions involving freely rotating molecules

To take into account all different orientations, one would need to average the potential over the solid angle. Unfortunately, that is difficult to obtain analytically. How can we appropriately approximate the consequences of all the angles? Let us average all the possible orientations over the solid angle Ω.

$$e^{-\frac{w(r)}{kT}} = \frac{\int e^{-\frac{w(r,\Omega)}{kT}} d\Omega}{\int d\Omega} = \left\langle e^{-\frac{w(r,\Omega)}{kT}} \right\rangle \tag{2.6}$$

When $kT >> w(r,\Omega)$, one finds

$$\left\langle \exp\left[-\frac{w(r,\Omega)}{kT}\right] \right\rangle = \left\langle 1 - \frac{w(r,\Omega)}{kT} + \frac{1}{2}\left[\frac{w(r,\Omega)}{kT}\right]^2 + (...) \right\rangle \tag{2.7}$$

As the potential is expanded over a Taylor series, it looses its angular contribution and acquires a temperature dependance which leads to

$$\overline{w}(r,T) \approx \left\langle w(r,\Omega) - \frac{w(r,\Omega)^2}{2kT} + (...) \right\rangle \tag{2.8}$$

2.5.1 Interaction between a charge and a flexible dipole

Reminding ourselves that $\left\langle \sin\theta \right\rangle = 0 = \left\langle \cos\theta \right\rangle$, and noting that

$$\int d\Omega = \int_0^{2\pi} d\phi \int_0^\pi \sin\theta d\theta = 4\pi, \tag{2.9}$$

$$\left\langle \cos^2\theta \right\rangle = \frac{1}{4\pi} \int_0^\pi \cos^2\theta \sin\theta d\theta \int_0^{2\pi} d\phi = \frac{1}{3}, \tag{2.10}$$

one shows that

$$\overline{w}(r,T) \approx \left\langle -\frac{Q\mu}{4\pi\epsilon_0\epsilon_r r^2}\cos\theta - \left(\frac{Q\mu}{4\pi\epsilon_0\epsilon_r r^2}\right)^2 \frac{\cos^2\theta}{2kT} + (...) \right\rangle = -\frac{Q\mu}{4\pi\epsilon_0\epsilon_r r^2}\left\langle \cos\theta \right\rangle - \frac{1}{2kT}\left(\frac{Q\mu}{4\pi\epsilon_0\epsilon_r r^2}\right)^2 \left\langle \cos^2\theta \right\rangle + (...) \tag{2.11}$$

meaning that in the limit $kT >> w(r,\Omega)$,

$$\overline{w}(r,T) \approx -\frac{1}{6kT}\frac{(Q\mu)^2}{(4\pi\epsilon_0\epsilon_r)^2 r^4}. \tag{2.12}$$

2.5.2 Interaction between two freely rotating molecules

Using the results of 2.4, one finds at the high temperature limit $kT > \frac{\mu_1\mu_2}{4\pi\epsilon_0\epsilon_r r^3}$ the expression of the *Keesom forces* (1921)

$$\overline{w}(r,T) \approx -\frac{1}{3kT}\frac{\mu_1^2\mu_2^2}{(4\pi\epsilon_r\epsilon_0)^2}\frac{1}{r^6} \tag{2.13}$$

3

2.5.3 Interactions between a charge and a nonpolar molecule

The proximity of an ion induces a dipole moment in the nonpolar molecule to appear. If ΔE is the difference in the electric field induced within the molecule, the magnitude of the dipole acting on the nonpolar molecule is

$$E = \mu \frac{\sqrt{1 + 3\cos^2\theta}}{4\pi\epsilon_0\epsilon_r r^3} \tag{2.14}$$

The interaction potential can then be written as

$$w(r,\theta) = -\int f\,dr = -\int \alpha_0 E\,dE = -\frac{1}{2}\alpha_0 E^2 \tag{2.15}$$

where we introduced the polarizability constant $\alpha_0 = \frac{\mu}{E}$. Merging (2.14) and (2.15), one finds

$$w(r,\theta) = -\frac{\alpha_0\mu^2}{2}\frac{1 + 3\cos^2\theta}{(4\pi\epsilon_0\epsilon_r)^2\,r^6} \tag{2.16}$$

which can be averaged over θ. The interaction between the different molecules is then given by

$$w(r) = -\frac{\alpha_{01}\mu_1^2 + \alpha_{02}\mu_2^2}{(4\pi\epsilon_0\epsilon_r)^2\,r^6} \tag{2.17}$$

This is the expression of the *Debye forces* (1920's).

2.5.4 Interactions between neutral particules

Quantum fluctuations of the charge density inside a nonpolar molecule can induce the formation of an instantaneous dipole moment. This permits interactions with other nonpolar molecules - it is an induced dipole moment. London derived the interaction between $s-electrons$ of two neighboring atoms and solved the problem considering quantum oscillator of frequency ν and thus of ionization potential $I = h\nu$. The *London (dissipative) forces* (1937) can be written as

$$w(r) \approx -\frac{1}{2(4\pi\epsilon_0\epsilon_r)^2}\frac{\alpha_1\alpha_2}{r^6}\frac{I_1 I_2}{I_1 + I_2} \tag{2.18}$$

2.5.5 Van der Waals interactions

The Van der Waals forces are comprised of three terms, corresponding to (2.13) (dipole-dipole),(2.17) (dipole-induced dipole) and (2.18) (induced dipole-induced dipole). The largest contribution is given by London (20-99%) and Keesom forces.

Part II
Phase transitions I : Thermodynamics

Abstract

We will describe the stability of a material phase through the use of thermodynamics. In particular, we will review general notions of thermodynamics and study the classification of phase transitions, as well as the study of phases.

A phase transition occurs when a phase becomes unstable. Let us now derive the parameters determining the stability of a phase.

3 Thermodynamics of phase transitions

Let $X(P,V,T,N)$ be a thermodynamic function of state, such as *Helmholtz free energy* $F(T,V) = U - TS$ and *Gibbs free energy* $G(T,P) = H - TS = U + PV - TS = F + PV$. At the phase transition, one has that

$$G_{\Phi_i}(T_T) = G_{\Phi_j}(T_T) \tag{3.1}$$

where Φ_i and Φ_j are two different phases and T_T is the transition temperature.

3.1 Classification of phase transitions

Definition 3.1. *The transition is said to be of the (n)-th order if:*

- *(n)-th derivative of G vs. T or P is continuous;*

- *$(n+1)$-th derivative of G vs. T or P is infinite.*

3.1.1 Derivatives of the energy functions

Computing the first-derivative of the internal energy, the enthalpy, the Helmholtz free energy and the Gibbs free energy one finds the following *total differentials*

$$\begin{cases} dU & = TdS - PdV = \delta Q - PdV \\ dH & = TdS + VdP = \delta Q + VdP \\ dF & = -SdT + -PdV \\ dG & = -SdT + VdP \end{cases} \tag{3.2}$$

Because they are total differentials, one has the following equalities.

$$\left.\frac{\partial U}{\partial V}\right|_S = -P = \left.\frac{\partial F}{\partial V}\right|_T, \quad \left.\frac{\partial F}{\partial T}\right|_V = -S = \left.\frac{\partial G}{\partial T}\right|_P, \quad \left.\frac{\partial H}{\partial P}\right|_S = V = \left.\frac{\partial G}{\partial P}\right|_T \tag{3.3}$$

3.1.2 Maxwell relations

Another property of total differentals is that we can commute their derivatives. Applied to thermodynamics, one finds truly astonishing equalities between the second-derivatives of seemingly different functions of state. Here is an example.

$$\frac{\partial^2 U}{\partial V \partial S} \quad \Rightarrow \quad \left.\frac{\partial T}{\partial V}\right|_S = -\left.\frac{\partial P}{\partial S}\right|_V \tag{3.4}$$

Definition 3.2. *The heat capacity is a physical property of matter defined as the amount of heat to be supplied to an object to produce a unit of change in its temperature. It is defined as*

$$C = \lim_{dT \to 0} \frac{\Delta Q}{\Delta T} = \frac{\delta Q}{\delta T} \tag{3.5}$$

As often in thermodynamics, one needs to specify the constants taken in the derivative. If the variable X is contant, we denote it as C_X. We will consider C_V and C_P in this course.

Proposition 3.3. *For the heat capacity at constant volume C_V, one has the following equalities.*

$$C_V = \left.\frac{dQ}{dT}\right|_V = T\left.\frac{\partial S}{\partial T}\right|_V = \left.\frac{\partial U}{\partial T}\right|_V = -T\left.\frac{\partial^2 F}{\partial T^2}\right|_V \tag{3.6}$$

Similarly,

Proposition 3.4. *For the heat capacity at constant pressure C_P, one has the following equalities*

$$C_P = \left.\frac{dQ}{dT}\right|_P = T\left.\frac{\partial S}{\partial T}\right|_P = \left.\frac{\partial H}{\partial T}\right|_P = -T\left.\frac{\partial^2 G}{\partial T^2}\right|_P \tag{3.7}$$

We now define the next two quantities.

Definition 3.5. *The isobaric (thermal) expansity*

$$\alpha_P = \frac{1}{V}\left.\frac{\partial V}{\partial T}\right|_P \tag{3.8}$$

Definition 3.6. *The isothermal compressibility*

$$\kappa_T = -\frac{1}{V}\left.\frac{\partial V}{\partial P}\right|_T \tag{3.9}$$

3.1.3 Phase transitions according to Ehrenfest

Applying definition 3.1, one has the following equalities

3.1.4 Case study: Absorption/desorption transition

Molecules absorb (what do they absord?) in proximity of an attractive wall if the energy gain upon aborption is positive ($\Delta G < 0$). Let us note that the absorbed state is a characteristic of low temperatures - molecules tend to desorb at high tempertures. How does the internal energy, volume and entropy change upon absorption? What is the order of the transition? Let us build a T vs. time diagram to indicate the stability of the absorbed phase.

Definition 3.7 (Boltzmann definition). *Let Ω be the number of possible microstates of a system. Then, entropy is $S = k_B \log \Omega$*

Example 3.8 (Mixing of two liquids). *Our aim is to predict the free energy of mixing $F_{mix} = F_{A+B} - (F_A + F_B)$. To treat this problem, we will introduce the notion of* mean field theory.

- *Calculation of $\Delta F_{mix} = -T\Delta S_{mix} + \Delta U_{mix}$ in the case of an idealised gas.*

  To compute the entropy of mixing in the approximation of idealised gases, let us assume the two gases lie in different compartiments of a closed box. Upon removing the boundary between them, the gases will spontaneously mix together. For idealised gases, the internal energy is given by $U = C_V T$. The variation of internal energy being 0 for a closed system, one finds that the temperature of the system is constant. Therefore, using the first principle of themodynamics one has

$$dU = 0 = -PdV + TdS \quad \Rightarrow \quad dS = \frac{P}{T}dV \tag{3.10}$$

  Using the ideal gas law $PV = nRT$,

$$dS = nR\frac{dV}{V} \quad \Rightarrow \quad \Delta S_{mix} = nR\log\frac{V_2}{V_1} \tag{3.11}$$

  Therefore,

$$\Delta S_{mix} = n_A R\log\frac{V_A + V_B}{V_A} + n_B R\log\frac{V_A + V_B}{V_B} = -k_B\left[N_A\log\frac{V_A}{V_A + V_B} + N_B\log\frac{V_B}{V_A + V_B}\right] \tag{3.12}$$

  Note that $\frac{V_i}{V_i+V_j} = \frac{N_i}{N_i+N_j} = x_i$ for a gas i such that

$$\overline{\Delta S_{mix}} = -k_B\left[x_A\log x_A + x_B\log x_B\right] \tag{3.13}$$

  This is the expression of the mean change of entropy of mixing, computed based on the thermodynamics of idealised gases.

  In an ideal mixture, $u_{AA} = u_{AB} = u_{BB}$. Then, the mean change in free energy is given by

$$\Delta\overline{F}_{mix} = -T\Delta\overline{S}_{mix} = kT\left[\phi\log\phi + (1-\phi)\log(1-\phi)\right] \tag{3.14}$$

  Noting that since $\phi_i < 1$, the free energy is stricly negative : Entropy (free energy?)always favors mixing.

- *Calculation of $\Delta F_{mix} = -T\Delta S_{mix} + \Delta U_{mix}$ in the (general?) case.*

  *Let us compute the change in entropy on mixing, and the change of internal energy on mixing. The **mean field theory** approach consists on:*

  − *Arranged on a lattice, with each lattice location having z direct neighbors,*

– *Composed of a mixture expressed in volume fractions* $\phi_1, (...), \phi_n$

Note it is not required to know whether a site is occupied by an A or B molecule, because $\phi_A + \phi_B = 1 = V_A + V_B$.

Let us use the (new) definition 3.7 of entropy. The number of microstates in the system is given by $\Omega = \frac{(N_A + N_B)!}{N_A! N_B}$. *Hence, using the approximation* $\log N! = N \log N - N$ *one finds the result using the following steps:*

$$\Delta S_{mix} = k_B \log \left[\frac{(N_A + N_B)!}{N_A! N_B!} \right] \tag{3.15}$$

$$= Something \tag{3.16}$$

$$= -k_B \left[N_A \log \left(\frac{N_A}{N_A + N_B} \right) + N_B \log \left(\frac{N_B}{N_A + N_B} \right) \right] \tag{3.17}$$

$$= -k_B \left(N_A + N_B \right) \left[x_A \log x_A + x_B \log x_B \right] \tag{3.18}$$

We then find that the expression of the mean change of entropy of mixing is exactly given by (3.13).

Let us now compute the energy of mixing U_{mix}, *using the following assumptions:*

– *Intermolecular interaction energies.*
– *Molecules only interact with their nearest neighbors.*

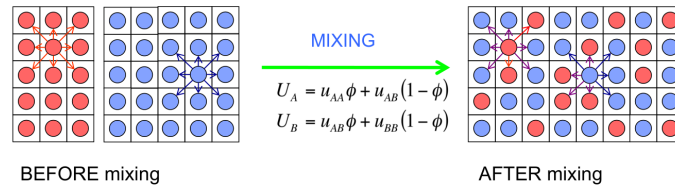*At each location of the lattice, figure 3 shows how the energy is distributed.*

$$U_A = u_{AA}\phi + u_{AB}(1-\phi)$$
$$U_B = u_{AB}\phi + u_{BB}(1-\phi)$$

BEFORE mixing   AFTER mixing

Figure 3: Representation of the situation - before and after mixing

where ϕ *is the volume fraction of the substance B, and* $(1 - \phi)$ *corresponds to the volume fraction of the substance A.*

Before mixing the molecules (ie, when the molecules are kept separated), the internal energy is given by

$$U_0 = \frac{zn}{2} \left[u_{AA}\phi + u_{BB} \left(1 - \phi \right) \right] \tag{3.19}$$

wheras after the process of mixing them, the total internal energy is

$$U = \frac{zn}{2} \left[U_A \phi + U_B \left(1 - \phi \right) \right] \tag{3.20}$$

such that

$$\Delta \overline{U}_{mix} = \frac{U - U_0}{n} = \frac{z}{2} \phi \left(1 - \phi \right) \left(2u_{AB} - u_{AA} - u_{BB} \right) \tag{3.21}$$

*One defines the **Flory interaction parameter** such that*

$$x = \frac{z}{n} \frac{2u_{AB} - u_{AA} - u_{BB}}{k_B T}. \tag{3.22}$$

It expresses the change in units of $k_B T$ *gained when a molecule of A is taken from an environment of pure A and put intp an environment of pure B. The change in energy can then be written as*

$$\Delta U_{mix} = x\phi \left(1 - \phi \right) k_B T \tag{3.23}$$

One can then express the change in free energy as

$$\Delta F_{mix} = -T\Delta S_{mix} + \Delta U_{mix} = k_B T \left[\phi \log \phi + \left(1 - \phi \right) \log \left(1 - \phi \right) + x\phi \left(1 - \phi \right) \right] \tag{3.24}$$

3.1.5 Flory-Huggins equation

Theorem 3.9 (Flory-Huggins equation). *Assuming that a mixture of two types of molecules can be expressed as in the mean field theory, ie it can be assumed that each individual molecule can be*

- *Arranged on a lattice, with each lattice location having z direct neighbors,*

- *Composed of a mixture expressed in volume fractions $\phi_1, (...), \phi_n$*

then the free energy of the mixture is expressed as (3.24).

Proof. See the second part of example 3.8. ∎

Proposition 3.10. *For all negative Flory-Huggins interaction parameters, the mean free energy of the mixture is negative for all ϕ. In this case, mixing is favorable for all compositions.*

Proposition 3.11. *When the Flory-Huggins parameter is positive, the equilibrium does not depends on the sign of ΔF_{mix} - rather, it depends on the $\Delta F_{mix}(\phi)$.*

Remark 3.12. *In a real system, $x \approx A + \frac{B}{T}$.*

Concave curve scenario

To be completed

Convex curve scenario

To be completed

Stability of compositions

To be completed

From free energy to phase diagrams

To be completed

Part III
Phase transitions II : Spinodal decomposition and solidification

Abstract

In this part the mechanisms of equilibration of unstable and metastable systems is explained. For metastable systems, we study the process of nucleation and growth. For unstable systems, we study the spinodal decomposition.

4 Mechanisms of phase transition

Definition 4.1 (Spinodal decomposition). *Continuous phase separation taking place in all the regions of a thermodynamic unstable sample. There is no thermodynamic barrier associated, thus we can treat it as a purely diffusive problem.*

An example of such a situation is the demixing of liquids quenched together below/above the critical temperature (conversion of **unstable** phases).

Definition 4.2 (Homogeneous nucleation). *Transformation occuring via the formation of nuclei and the growth of domains. Nuclei are created after overcoming a thermodynamic barrier, related to the balance of surface and volume energies.*

An example of such a situation is the solidification from concentrated solutions (conversion of metastable phases, binodal decomposition).

Definition 4.3. *Nucleation is here assisted by the presence of catalysers, increasing the rate of formation of new species (but not the growth!). Typical catalysers are surfaces of contaminants, powder or preformed crystals of the same material.*

4.1 Liquid-liquid transition - Spinodal decomposition

The tension surface γ is defined as the ratio between the work necessary to build up a new surface, and the area of the surface itself.

The free energy necessary to build up a spherical surcace of radius R is

$$\Delta G_{surf} = \gamma 4\pi R^2 \tag{4.1}$$

If the radius were to increase by dR, the free energy would increase by a factor

$$d\Delta G_{surf} = \gamma 8\pi R dR \tag{4.2}$$

One deduces the expression of the Young-Laplace equation from this:

$$\Delta p 4\pi R^2 dR = \gamma 8\pi R dR \quad \Rightarrow \quad \Delta p = \gamma \left(\frac{1}{R_1} + \frac{1}{R_2} \right) \tag{4.3}$$

Discussion on wavelengths

4.1.1 Quantitative (phenomenological) picture

Phenomenologically, one has that the total free energy density must depend on:

- Local free energy;

- Gradient of composition (a term containing the square of concentration gradient).

Therefore, if F denotes the density of free energy then

$$F \propto \int \left[f_0(\phi) + \kappa \left(\frac{d\phi}{dx} \right)^2 \right] dx \tag{4.4}$$

where f_0 is the free energy per unit volume for a uniform mixture, and κ is the gradient energy coefficient, assumed constant in time.

Fick's laws and spinodal

In the following paragraph, J is the flux and n is the density number.

Proposition 4.4 (Diffusion equation - Fick's 1st law)**.**

$$\boldsymbol{J} = -D\boldsymbol{\nabla}n \tag{4.5}$$

where D is *what is it?* *a function of time with the final condition $D(t_f) = 0$.*

Proposition 4.5 (Continuity equation)**.**

$$\frac{dn}{dt} + \boldsymbol{\nabla} \cdot \boldsymbol{J} = 0 \tag{4.6}$$

Proposition 4.6 (Fick's 2nd law)**.**

$$\frac{dn}{dt} = D\boldsymbol{\nabla}^2 n \tag{4.7}$$

In this course, we will consider volume fraction and limit ourselves to the 1D-case. Hence, the properties can be rewritten as

$$J = -D\frac{d\phi}{dx} \tag{4.8}$$

$$\frac{d\phi}{dt} = -\frac{dJ}{dx} \tag{4.9}$$

$$\frac{d\phi}{dt} = D\frac{d^2\phi}{dx^2} \tag{4.10}$$

Proposition 4.7 (Modified diffusion equation)**.** *Let J_A be the flux of species A, M a positive transport coefficient (Onsager coefficient) and $\mu_A - \mu_B$ the exchange of chemical potential. It corresponds to the exchange of free energy by replacing an A-molecule by a B molecule. Then,*

$$J_A = -M\frac{d}{dx}(\mu_A - \mu_B) \tag{4.11}$$

One can express μ by taking a derivative of the free-energy density:

$$\mu = \frac{d}{d\phi}\int\left[f_0(\phi) + \kappa\left(\frac{d\phi}{dx}\right)^2\right]dx \tag{4.12}$$

The integral over this expression yields to

$$\mu = \frac{df_0}{d\phi} + 2\kappa\frac{d^2\phi}{dx^2} \tag{4.13}$$

Substituting in (4.11) results in

$$-J_A = \left(M\frac{d^2f_0}{d\phi^2}\right)\frac{d\phi}{dx} + (2M\kappa)\frac{d^3\phi}{dx^3} \tag{4.14}$$

Combining this result and (4.9) yields to

$$\frac{\partial\phi(x,t)}{\partial t} = \underbrace{(Mf_0'')\frac{\partial^2\phi}{\partial x^2}}_{\text{Diffusion equation}} + \overbrace{(2M\kappa)\frac{\partial^4\phi}{\partial x^4}}^{\text{Gradient term}} \tag{4.15}$$

This is the **Cahn-Hillard equation**. It is often written as

$$\frac{\partial\phi(x,t)}{\partial t} = D_{eff}\frac{\partial^2\phi}{\partial x^2} + (2M\kappa)\frac{\partial^4\phi}{\partial x^4} \tag{4.16}$$

The solution to this equation can be written as

$$\phi(x,t) = \phi_0 + A\cos(qx)\exp\left[\underbrace{-D_{eff}q^2\left(1 + \frac{2\kappa q^2}{f_0''}\right)t}_{\text{Amplification factor } R(q)}\right] \tag{4.17}$$

Discussion on the solution

4.2 Liquid-solid transition - Homogeneous nucleation

The liquid-liquid transition could be described in terms of the change of one parameter (density) : this is not possible in the liquid-solid equivalent, as it would require the consideration of an infinite number of order parameters. Thus, the treatement is mostly phenomenological.

In the process of solidification, there is a reduction of free energy (gain) but also a non-negligeable loss in the formation of the interfaces. How can we form crystals at T_m ? Using the same approach as for the binodal decomposition and assuming the spontaneous appearance of a spherical crystal nucleus of radius r,

$$\Delta G(r) = \frac{4}{3}\pi r^3 \Delta G_r + 4\pi r^2 \gamma_{sl} \tag{4.18}$$

$$\Delta S_m = \left(\frac{\partial G_s}{\partial T}\right)_P - \left(\frac{\partial G_l}{\partial T}\right)_P = \frac{\Delta H_m}{T_m} \tag{4.19}$$

To initiate the process of crystalization, one has to undercool the melt by a small value ΔT - the free energy change upon freezing becomes (assuming constant derivative)

$$\Delta G_b = -\frac{\Delta H_m}{T_m}\Delta T \tag{4.20}$$

Analysis of the solution

The free energy change when the crystal nucleus of radius r appears is then

$$\Delta G(r) = -\frac{4}{3}\pi r^3 \frac{\Delta H_m}{T_m}\Delta T + 4\pi r^2 \gamma_{sl} \tag{4.21}$$

One shows that the maximum of $\Delta G(r)$ is at $r^* = \frac{2\gamma_{sl}T_m}{\Delta H_m \Delta T}$. The maximum is then

$$\Delta G^* = \frac{16\pi}{3}\gamma_{sl}^3 \left(\frac{T_m}{\Delta H_m}\right)^2 \frac{1}{\Delta T^2} \tag{4.22}$$

If the nuclei is bigger than r^*, it will continue to grow: it is said to be a stable nuclei. Conversely, if it is smaller than r^* is will shrink until it is gone. It is said to be an unstable nuclei.

4.3 Liquid-solid transition - Heteregeneous nucleation

To be completed