Theory of condensed matter

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The *structure* of a liquid or an amorphous material is governed by the statistical distribution of the centers of gravity of the atoms or molecules. In the liquid, of course the molecules keep moving, but we can ask about the atomic distributions if one could perform a snapshot of the atomic arrangements. This is what we call the (static) *structure* of the liquid. The structure of an amorphous material very often looks like that of a frozen liquid.

We now pose the question of how a collection of $N \approx 10^{23}$ atoms or molecules (or much less in a computer simulation) are distributed inside a certain volume V. We call the probability for these particles to occupy volume elements $d^3\mathbf{r}_1, d^3\mathbf{r}_2, \ldots d^3\mathbf{r}_N$ around positions $\mathbf{r}_1, \mathbf{r}_2, \ldots \mathbf{r}_N$

$$P(\mathbf{r}_1, \mathbf{r}_2, \ldots \mathbf{r}_N) d^3\mathbf{r}_1, d^3\mathbf{r}_2, \ldots d^3\mathbf{r}_N \,. \tag{2.1}$$

$P(\mathbf{r}_1, \mathbf{r}_2, \ldots \mathbf{r}_N)$ is the *probability density* of the configuration $\{\mathbf{r}_1, \mathbf{r}_2, \ldots \mathbf{r}_N\}$ and is normalized to 1:

$$\int_V \prod_{\alpha=1}^N d^3\mathbf{r}_\alpha P(\mathbf{r}_1, \mathbf{r}_2, \ldots \mathbf{r}_N) = 1 \,. \tag{2.2}$$

If a physical quantity A depends on the position of the particles the *configurational average* can be calculated as

$$\langle A \rangle = \int_V \prod_{\alpha=1}^N d^3\mathbf{r}_\alpha A(\mathbf{r}_1, \mathbf{r}_2, \ldots \mathbf{r}_N) P(\mathbf{r}_1, \mathbf{r}_2, \ldots \mathbf{r}_N) \,. \tag{2.3}$$

One can select $n < N$ particles in order to define the *reduced n-particle densities*

$$\rho^{(n)}(\mathbf{r}_1, \mathbf{r}_2, \ldots \mathbf{r}_n) = \frac{N!}{(N-n)!} \int_V \prod_{i=n+1}^{N} \mathrm{d}^3\mathbf{r}_\alpha P(\mathbf{r}_1, \mathbf{r}_2, \ldots \mathbf{r}_N) , \tag{2.4}$$

In the case of a *complete random arrangement*, which is only realized in an ideal gas we have

$$\rho^{(n)}(\mathbf{r}_1, \mathbf{r}_2, \ldots \mathbf{r}_n) = \left(\frac{N}{V}\right)^n \equiv \rho_0^n . \tag{2.5}$$

where ρ_0 is called the *homogeneous density* of the liquid. The deviation from this random distribution is given by the *n-particle correlation functions* $g^{(n)}$, which are defined as follows

$$\rho^{(n)}(\mathbf{r}_1, \mathbf{r}_2, \ldots \mathbf{r}_n) = \rho_0^n g^{(n)}(\mathbf{r}_1, \mathbf{r}_2, \ldots \mathbf{r}_n) . \tag{2.6}$$

In *homogeneous* systems we have

$$\rho^{(1)}(\mathbf{r}_1) = \rho_0 \tag{2.7}$$

$$g^{(1)}(\mathbf{r}_1) = 1 . \tag{2.8}$$

In a *homogeneous* and *isotropic* material we have

$$g^{(2)}(\mathbf{r}_1, \mathbf{r}_2) = g(|\mathbf{r}_1 - \mathbf{r}_2|) \tag{2.9}$$

$g(r)$ is called *radial pair correlation function* or *radial pair distribution function* and can, as we shall see, be determined by neutron or x-ray diffraction.

Let us consider again the X-ray or neutron scattering cross-section. Inserting (1.5) into (1.3) and averaging over an ensemble of different configurations of a liquid or non-crystalline material we obtain

$$\frac{\mathrm{d}\sigma}{\mathrm{d}\Omega} = |f(q)|^2 \left\langle \sum_{\alpha,\beta=1}^{N} e^{i\mathbf{q}\cdot[\mathbf{r}_\alpha - \mathbf{r}_\beta]} \right\rangle \equiv |f(q)|^2 N S(q) , \tag{2.10}$$
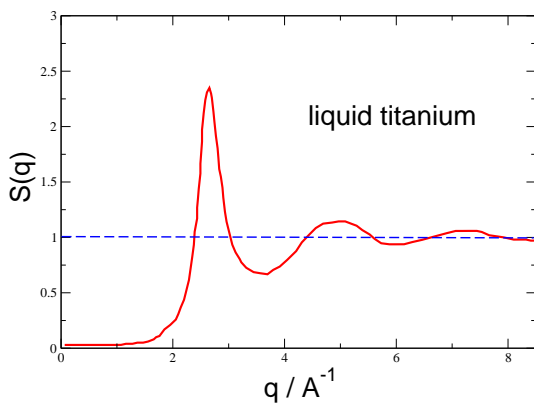
where $S(q)$ is the *static structure factor*

$$S(q) = \frac{1}{N} \left\langle \sum_{\alpha,\beta=1}^{N} e^{i\mathbf{q}\cdot[\mathbf{r}_\alpha - \mathbf{r}_\beta]} \right\rangle \tag{2.11}$$

It can be shown that $S(q)$ is related to the pair correlation function by a simple Fourier transform

$$S(q) = 1 + \rho_0 \int \mathrm{d}^3\mathbf{r} e^{i\mathbf{q}\mathbf{r}}[g(r) - 1] \tag{2.12}$$

which can - because g and S depend only on the moduli of their arguments - be simplified as

$$S(q) = 1 + \frac{4\pi\rho_0}{q} \int_0^\infty \mathrm{d}r\ r \sin(qr)[g(r) - 1] \tag{2.13}$$

Structure factor of liquid titanium, measured by *Lee et al*
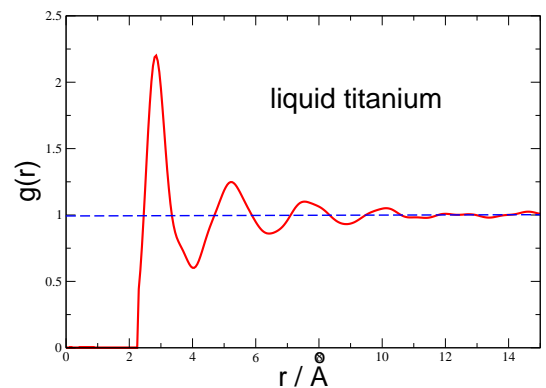
Corresponding pair distribution function calculated via Fourier-back transform from (2.13) with $\rho_0 = 0.05$

2.1.2 Thermodynamic relations

We are now assuming that the liquid under consideration can be described by a classical Hamiltonian

$$\mathcal{H} = \sum_{\alpha=1}^{N} \frac{1}{2} m \dot{\mathbf{r}}_{\alpha}^2 + \frac{1}{2} \sum_{\alpha \neq \beta} \phi(|\mathbf{r}_\alpha - \mathbf{r}_\beta|) \,. \tag{2.14}$$

There are the following thermodynamic relationships (*equations of state*):
Potential Energy

$$\frac{1}{N} \langle E_{\text{pot}} \rangle = 2\pi\rho_0 \int_0^\infty \mathrm{d}r \; r^2 \phi(r) g(r) \tag{2.15}$$

Pressure

$$\langle P \rangle \frac{V}{N k_B T} = \langle P \rangle \frac{1}{\rho_0 k_B T} = 1 - \frac{2\pi\rho_0}{3 k_B T} \int_0^\infty \mathrm{d}r \; r^3 \phi'(r) g(r) \tag{2.16}$$

Number fluctuations and isothermal compressibility κ_T

$$\frac{\langle N^2 \rangle - \langle N \rangle^2}{N} = \rho_0 k_B T \left(-\frac{1}{V} \frac{\partial V}{\partial P} \right)_T = \rho_0 k_B T \kappa_T \tag{2.17}$$

$$= S(q=0) = 1 + 4\pi\rho_0 \int_0^\infty \mathrm{d}r \; r^2 [g(r) - 1] \tag{2.18}$$

2.1.3 Direct correlation function

The static structure factor can be split in an obvious way into a *self* and *distinct* part by separating the $\alpha \neq \beta$ term in the summation over the particles:

$$S(q) = \frac{1}{N} \left\langle \sum_{\alpha,\beta=1}^{N} e^{i\mathbf{q}\cdot[\mathbf{r}_\alpha - \mathbf{r}_\beta]} \right\rangle = 1 + \frac{1}{N} \left\langle \sum_{\alpha \neq \beta}^{N} e^{i\mathbf{q}\cdot[\mathbf{r}_\alpha - \mathbf{r}_\beta]} \right\rangle \equiv 1 + \rho_0 h(q) \tag{2.19}$$

The self part is just equal to unity, and the distinct part is ρ_0 times the Fourier transform of the *deviation of $g(r)$ from unity*, i.e.

$$h(r) = g(r) - 1 \,. \tag{2.20}$$

We now sub-divide the correlation function $h(r)$ into a part which involves only a particular pair of atoms, say $\mathbf{r}_1$ and $\mathbf{r}_2$ and a part which involves more than two atoms. Following Ornstein and Zernike, the first term is called *direct correlation function*. The second part can be generated by combining several direct functions in the following way:

$$h(r_{12}) = c(r_{12}) + \rho_0 \int \mathrm{d}^3\mathbf{r}_3 c(r_{13}) c(r_{32}) + \rho_0^2 \int \mathrm{d}^3\mathbf{r}_3 \int \mathrm{d}^3\mathbf{r}_4 c(r_{13}) c(r_{34}) c(r_{42}) + \ldots \tag{2.21}$$

The terms under the $\mathbf{r}_3$ integral can be summed again to give the function $h(r_{32})$:

$$h(r_{12}) = c(r_{12}) + \rho_0 \int \mathrm{d}^3\mathbf{r}_3 c(r_{13}) h(r_{32}) \tag{2.22}$$

This is the so-called *Ornstein-Zernike equation*. It is the starting point for some *integral equation theories* for $g(r)$ (See section 2.7).
If we introduce the Fourier transform $c(q)$ of $c(r)$ and use the convolution theorem we obtain

$$h(q) = \frac{c(q)}{1 - \rho_0 c(q)} \tag{2.23}$$

which finally leads to

$$S(q) = \frac{1}{1 - \rho_0 c(q)} \tag{2.24}$$

2.1.4 Density response function

We can be interested in the density change due to the presence of an external potential

$$\mathcal{V}_{\text{ext}}(\mathbf{r}) = \sum_{\alpha} \phi_{\text{ext}}(\mathbf{r} - \mathbf{r}_\alpha). \tag{2.25}$$

The average density in the presence of $\mathcal{V}_{\text{ext}}(\mathbf{r})$ is given by[1]

$$\langle \rho(\mathbf{r}) \rangle_{\mathcal{V}_{\text{ext}}} = \frac{1}{Z_{\mathcal{V}_{\text{ext}}}} \int \frac{\mathrm{d}^3 r'}{V} \prod_\alpha \mathrm{d}^3 r_\alpha \underbrace{\sum_\alpha \delta(\mathbf{r} - \mathbf{r}_\alpha)}_{\rho(\mathbf{r})} e^{-\beta V\{\mathbf{r}_\alpha\}} e^{-\beta \mathcal{V}_{\text{ext}}(\mathbf{r}')} \tag{2.26}$$

with

$$Z_{\mathcal{V}_{\text{ext}}} = \int \frac{\mathrm{d}^3 r'}{V} \prod_\alpha \mathrm{d}^3 r_\alpha e^{-\beta V\{\mathbf{r}_\alpha\}} e^{-\beta \mathcal{V}_{\text{ext}}(\mathbf{r}')} \tag{2.27}$$

and

$$V\{\mathbf{r}_\alpha\} = \frac{1}{2} \sum_{\alpha \neq \alpha'} \phi(|\mathbf{r}_\alpha - \mathbf{r}_{\alpha'}|) \tag{2.28}$$

Defining $\langle \rho \rangle_0$ to be the density average with $\mathcal{V}_{\text{ext}} = 0$ and going over to Fourier Transforms we obtain to lowest order in $\mathcal{V}_{\text{ext}} = 0$ (*linear response*)

$$\delta \rho(\mathbf{q}) = \langle \rho(\mathbf{q}) \rangle_{\mathcal{V}_{\text{ext}}} - \langle \rho \rangle_0 = -\frac{\beta}{V} \langle \rho^*(\mathbf{q})\rho(\mathbf{q}) \rangle \, \phi_{\text{ext}}(\mathbf{q}) \equiv \chi(q)\phi_{\text{ext}}(\mathbf{q}) \tag{2.29}$$

the (static) *response function* or *susceptibility* is therefore given by

$$\chi(q) = -\beta \rho_0 S(q) \tag{2.30}$$

This is a version of the famous *fluctuation-dissipation theorem*.

2.1.5 Mean field potential and random phase approximation

In order to to formulate an approximate theory for $S(q)$ it is useful to represent the interatomic interactions in terms of a *mean field potential* $U(q)$ which acts on the individual atoms as an *effective external polarization potential*

$$\phi_{\text{pol}}(\mathbf{q}) \equiv U(q)\delta \rho(\mathbf{q}). \tag{2.31}$$

One then can use the *non-interacting Curie response function* $\chi_0 = -\beta \rho_0$ to write down the density change in terms of the real and the effective external potential:

$$\begin{aligned} \delta \rho(q) &= \chi_0 \left[\phi_{\text{pol}}(\mathbf{q}) + \phi_{\text{ext}}(\mathbf{q}) \right] \\ &= \chi_0 \left[U(q)\delta \rho(\mathbf{q}) + \phi_{\text{ext}}(\mathbf{q}) \right] \\ &= \chi(\mathbf{q})\phi_{\text{ext}}(\mathbf{q}) \end{aligned} \tag{2.32}$$

from which follows

$$\chi(q) = \frac{\chi_0}{1 - \chi_0 U(q)} \tag{2.33}$$

If we compare this with (2.24) we find

$$c(q) = -\beta U(q) \tag{2.34}$$

We conclude that $-k_B T c(r)$ has the meaning of a *mean-field* potential. Identifying $U(r)$ with the true pairwise potential $\phi(r)$ is called the *Random-Phase approximation*. It gained its name from the theory of interacting electrons (or nucleons). There the RPA involves the decoupling of electronic correlation functions, which is only possible if the wave functions are assumed to have "random phases".

In many cases it is useful to sub-divide a potential into a "hard-core" repulsive part and a perturbative part, which extends to larger distances:

$$\phi(r) = \phi_0(r) + \phi_1(r) \tag{2.35}$$

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[1] $\beta = 1/k_B T$.

Correspondingly one writes for the direct correlation function

$$c(r) = c_0(r) + c_1(r) \tag{2.36}$$

The *perturbative random-phase approximation*, which consists in setting

$$c_1(r) \approx -\frac{1}{k_B T}\phi_1(r) \tag{2.37}$$

This approximation can be shown to hold in many cases, in paricular for the function $c(q)$ in the long-wavelength limit $q \to 0$.

2.2 Binary solutions

2.2.1 Thermodynamics and partial quantities

As we now start dealing with mixtures (solutions) of liquids we gradually cross the borderline between physics and chemistry, so we must introduce the concept of *moles* which are lumps of $\mathcal{N}_{\mathrm{Avo}} = 6.022 \cdot 10^{23}$ particles (atoms or molecules). The number of moles is just $n = N/\mathcal{N}_{\mathrm{Avo}}$. We consider a mixture of two liquid phases A and B ("species") which are assumed to be in equilibrium with each other and consist of $N_A = n_A \mathcal{N}_{\mathrm{Avo}}$ and $N_B = n_B \mathcal{N}_{\mathrm{Avo}}$ particles, resp. If one is working at a given temperature T and pressure p (as we shall do) the appropriate thermodynamic potential is the Gibbs free enthalpy

$$G = H - TS = E - TS + pV \,. \tag{2.38}$$

where $H = E + pV$ is the enthalpy. The fundamental thermodynamic equation for G reads

$$dG = -S dT + V dp + \sum_{i=A,B} \mu_i dn_i \tag{2.39}$$

from which follows

$$S = -\frac{\partial G}{\partial T} \qquad \text{entropy} \tag{2.40a}$$

$$V = \frac{\partial G}{\partial p} \qquad \text{volume} \tag{2.40b}$$

$$\mu_i = \frac{\partial G}{\partial n_i} \qquad \text{chemical potentials} \tag{2.40c}$$

For any physical variable X (like G, E, T, S, p, and V) that characterizes the total mixture one can introduce so-called *partial* quantities which are defined as

$$x_i = \frac{\partial X}{\partial n_i} \qquad i = A, B \tag{2.41}$$

from which follows (this is an exercise to be done!)

$$X = n_A x_A + n_B x_B \tag{2.42}$$

X is also called an *extensive* quantity, and the x_i are the corresponding *intensive* quantities. We indentify immediately the chemical potentials μ_i as the partial free enthalpies of the mixture. We now introduce the so-called *concentrations* or *mole fractions* $c_i = N_i/N = n_i/n$. Since $c_A + c_B = 1$ only one of these variables is independent, and we define $c_A \equiv c$ to be the independent variable, so that $c_B = 1 - c$. For any extensive quantity X we have (exercises!)

$$\frac{\partial X}{\partial c} = x_A - x_B \tag{2.43}$$

and

$$x_A \frac{\partial x_A}{\partial c} + x_B \frac{\partial x_B}{\partial c} = 0 \,. \tag{2.44}$$

In particular, we have

$$x_A \frac{\partial \mu_A}{\partial c} + x_B \frac{\partial \mu_B}{\partial c} = 0 \,, \tag{2.45}$$

which is the famous *Gibbs-Duhem* relation.

2.2.2 Cross-sections and partial correlation functions

Let us recall the scattering cross-section for energy unresolved neutron or X-ray scattering from a liquid

$$\frac{\mathrm{d}\sigma}{\mathrm{d}\Omega} = \left\langle \sum_{\alpha,\beta=1}^{N} f_\alpha^*(q) f_\beta(q) e^{i\mathbf{q}\cdot[\mathbf{r}_\alpha - \mathbf{r}_\beta]} \right\rangle, \tag{2.46}$$

where we now have labelled the form factors with atomic indices α, β. Let us assume, that the atoms now belong to either species A or species B. We would like to factorize (2.46) into a form and structure factor as done with the expression (14) for the mono-atomic liquid. However, due to the heterogeneous character of a mixture such a factorization is no more possible. All we can do is to come up with a *linear combination* of form and structure factors. In order to derive such an expression we again separate the terms into self and distinct parts. Let us keep in mind that the distinct correlation function $h(q)$ was defined as

$$h(q) = \frac{1}{\rho_0}\left[S(q) - 1\right] = \frac{V}{N^2} \left\langle \sum_{\alpha \neq \beta} e^{i\mathbf{q}\cdot[\mathbf{r}_\alpha - \mathbf{r}_\beta]} \right\rangle. \tag{2.47}$$

We now define the corresponding quantities in which the α, β sums are only over A- or B-type atoms:

$$h_{ij}(q) = \frac{V}{N_i N_j} \left\langle \underbrace{\sum_{\alpha=1}^{N_i} \sum_{\beta=1}^{N_j}}_{\alpha \neq \beta} e^{i\mathbf{q}\cdot[\mathbf{r}_\alpha^{(i)} - \mathbf{r}_\beta^{(j)}]} \right\rangle \qquad i,j = \text{A or B} \tag{2.48}$$

and obtain, since the incoherent $\alpha = \beta$ terms occur only linearly in the concentrations c_i

$$\frac{\mathrm{d}\sigma}{\mathrm{d}\Omega} = N \left(c_A |f_A(q)|^2 + c_B |f_B(q)|^2 + \rho_0 \sum_{i=A,B} \sum_{j=A,B} c_i c_j f_i^*(q) f_j(q) h_{ij}(q) \right) \tag{2.49}$$

One defines the so-called *partial structure factors* as

$$S_{ij}(q) = 1 + \rho_0 h_{ij}(q) \qquad i,j = \text{A or B}, \tag{2.50}$$

but, as we see from (2.49) and (**??**), this definition is not of much use, as the functions $h_{ij}(q)$ and not $S_{ij}(q)$ enter into the expressions. On the other hand, the Fourier transforms of $h_{ij}(q)$ are related to the *partial radial distribution functions* $g_{ij}(r)$

$$h_{ij}(r) = \frac{1}{2\pi^2 r} \int_0^\infty \mathrm{d}q\, q\, \sin(q) h(q) = g_{ij}(r) - 1 \tag{2.51}$$

$\rho_0 4\pi r^2 g_{ij}(r)\mathrm{d}r$ gives the probability for the presence of a j particle inside a spherical shell of thickness $\mathrm{d}r$, if there is an i particle at the origin.

2.2.3 Number and Concentration fluctuations

Instead of working with the partial structure factors $S_{ij}(q)$ or the functions $h_{ij}(q)$ one can define linear combinations of these functions which are the correlation functions of the density fluctuations $\delta\rho$ and the concentration fluctuations δc (Bhatia, Thornton, 1970):

$$\begin{align}
S_{\rho\rho}(q) &= c_A^2 S_{AA}(q) + c_B^2 S_{BB}(q) + 2c_A c_B S_{AB}(q) \tag{2.52a}\\
S_{\rho c}(q) &= c_A c_B \left\{ c_A \left[S_{AA}(q) - S_{AB}(q)\right] - c_B \left[S_{BB}(q) - S_{AB}(q)\right] \right\} \tag{2.52b}\\
S_{cc}(q) &= c_A c_B \left\{ 1 + c_A c_B \left[S_{AA}(q) + S_{BB}(q) - 2S_{AB}(q)\right] \right\} \tag{2.52c}
\end{align}$$

In terms of these quantities (2.49) and (**??**) take the form

$$\frac{\mathrm{d}\sigma}{\mathrm{d}\Omega} = N \left(\left|\overline{f}\right|^2 S_{\rho\rho}(q) + |f_A - f_B|^2 S_{cc}(q) + 2\overline{f^*}(f_A - f_B) S_{\rho c}(q) \right) \tag{2.53}$$

with $\overline{X} \equiv c_A X_A + c_B X_B$.

At $q = 0$ the following relations hold:

$$S_{\rho\rho}(0) = \frac{1}{N}\langle(\Delta N)^2\rangle = \theta + \delta^2 S_{cc}(0) \tag{2.54a}$$

$$S_{\rho c}(0) = \langle\Delta N \Delta c\rangle = -\delta S_{cc}(0) \tag{2.54b}$$

$$S_{cc}(0) = N\langle(\Delta c)^2\rangle = k_B T / g_{cc} \tag{2.54c}$$

with the three thermondynamic quantities

$$\theta = \rho_0 k_B T \kappa_T \tag{2.55a}$$

$$\delta = \frac{1}{V}\left(\frac{\partial V}{\partial c}\right)_{P,T,N} = \frac{v_A - v_B}{n_A v_A + n_B v_B} \tag{2.55b}$$

$$g_{cc} = \frac{1}{N}\left(\frac{\partial^2 G}{\partial c^2}\right)_{P,T,N} = \frac{1}{N}\left(\frac{\partial^2 \Delta G}{\partial c^2}\right)_{P,T,N} \tag{2.55c}$$

Here θ is again related to the isothermal compressibility κ_T, v_i are the partial molar volumina and g_{cc} is the *stability function*. ΔG is the *free enthalpy of mixing*, which is defined to be

$$\Delta G = G - N_A G_A^{(0)} - N_B G_B^{(0)} \tag{2.56}$$

where $G_i^{(0)}$ are the free enthalpies of the pure systems. As these quantities do not depend on concentration we only need to know ΔG for calculating g_{cc}.
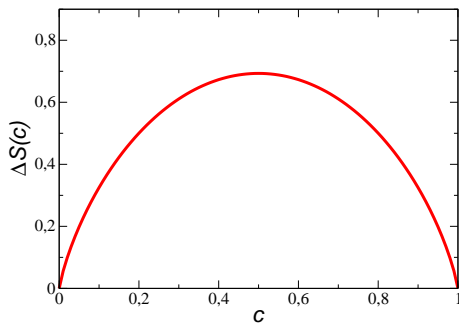
2.2.4 Entropy of mixing
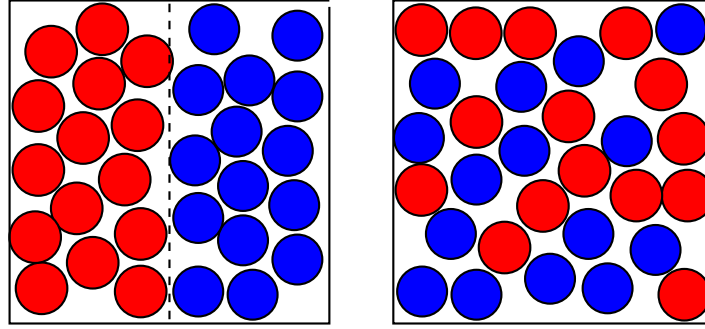
$$S_A = k_B \ln N_A! = k_B N_A \ln N_A$$
$$S_B = k_B \ln N_B! = k_B N_B \ln N_B$$

$$S = k_B \ln N! = k_B N \ln N$$

Red and blue particles in the demixed and mixed state

Entropy as a function of concentration

Let us perform the classical gedanken experiment for defining the entropy and showing that the entropy increases with mixing. For a system of N particles the entropy is defined to be k_B times the logarithm of the number of possible configurations. We imagine that the particles can be distributed into N volume "cells" in $N!$ different ways. Then the entropy is just

$$S = k_B \ln N! \overset{N \to \infty}{=} k_B N \ln N \tag{2.57}$$

We now start the gedanken experiment at the left side of our figure. The Entropy is initially the sum of the red and blue terms. If we achieve a complete random mixture the entropy is given by the black expression. The increase in entropy is

$$\Delta S^{(0)} = k_B[(N_A + N_B)\ln N - N_A \ln N_A - N_B \ln N_B]$$
$$= -k_B N[c_A \ln c_A + c_B \ln c_B] \tag{2.58}$$

For non-interacting particles (for which $\Delta H = 0$) the stability function obviously is given by

$$
\begin{aligned}
g_{cc} = \frac{1}{N}\frac{\partial^2}{\partial c^2}\left[-T\Delta S\right] &= k_B T \frac{\partial^2}{\partial c^2}\left[c\ln c + (1-c)\ln(1-c)\right] \\
&= k_B T \left[\frac{1}{c} + \frac{1}{(1-c)}\right] = k_B T \left[\frac{1}{c(1-c)}\right] \qquad \text{(2.59a)}
\end{aligned}
$$

$$
\Rightarrow \qquad S_{cc}(0) = c(1-c) \qquad \text{(2.59b)}
$$

2.2.5 Partial structure factors of ideal solutions

Ideal solutions are defined to be systems in which there are either no interactions or all interactions are equal so that there are no *excess* interactions:

$$
\phi_{AA}(r) = \phi_{BB}(r) = \phi_{AB}(r) \qquad \text{(2.60)}
$$

In such a system the partial structure factors S_{ij} are all equal and we have

$$
S_{\rho\rho}^{(0)}(q) \equiv S(q) \qquad S_{\rho c}^{(0)}(q) = 0 \qquad S_{cc}^{(0)}(q) = c(1-c) \qquad \text{(2.61)}
$$

Inserting this into (2.53) we obtain

$$
\frac{\mathrm{d}\sigma}{\mathrm{d}\Omega} = \left|\overline{f}\right|^2 S(q) + |f_A - f_B|^2 c(1-c) \qquad \text{(2.62)}
$$

One obtains the same expression from (2.49) if all h_{ij} are set equal to $\frac{1}{\rho_0}\left[S(q) - 1\right]$. In the case of X-ray diffraction on weakly interacting alloys the second term is just a *background* which is q independent and is called *Laue background*. Such a background is also observed in randomly mixed crystals.

2.2.6 Direct correlation functions

As in the single-component case one can define *direct correlation functions* by the equations

$$
h_{ij}(r) = c_{ij}(r) + \rho_0 \sum_{\ell=A,B} c_\ell \int \mathrm{d}^3\mathbf{r}' h_{i\ell}(r')c_{\ell j}(|\mathbf{r} - \mathbf{r}'|) \qquad \text{(2.63)}
$$

By applying the convolution theorem and a 2×2 matrix inversion one can derive the following relations between their Fourier transforms $C_{ij}(q) \equiv \rho_0\mathrm{d}^3\mathbf{r}e^{i\mathbf{qr}}c_{ij}(r)$ and the number and concentration structure factors:

$$
S_{\rho\rho}(q) = \Theta(q) + \Delta^2(q)S_{cc}(q) \qquad \text{(2.64a)}
$$

$$
S_{\rho c}(q) = -\Delta(q)S_{cc}(q) \qquad \text{(2.64b)}
$$

$$
S_{cc}(q) = \left[\frac{1}{c_A c_B} - \frac{\Delta(q)^2}{\Theta(q)} - C_{AA}(q) - C_{BB}(q) + 2C_{AB}(q)\right]^{-1} \qquad \text{(2.64c)}
$$

$$
\Theta(q) = \left[1 - c_A^2 C_{AA}(q) - c_B^2 C_{BB}(q) - 2c_A c_B C_{AB}(q)\right]^{-1} \qquad \text{(2.64d)}
$$

$$
\Delta(q) = \Theta(q)\left[c_A\left(C_{AA}(q) - C_{AB}(q)\right) - c_B\left(C_{BB}(q) - C_{AB}(q)\right)\right] \qquad \text{(2.64e)}
$$

Here the quantities $\Theta(q)$ and $\Delta(q)$ are the generalizations of $\theta = \Theta(q=0)$ and $\delta = \Delta(q=0)$ of (2.55).

2.2.7 Perturbative RPA for $q = 0$ and regular solution model

As in the single-component case we now generalize the perturbative RPA as follows

$$
C_{ij}(q = 0) = C_{ij}^{(0)} - \frac{1}{k_B T}U_{ij}^{(1)} \qquad \text{(2.65)}
$$

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with

$$
U_{ij}^{(1)} =
\begin{cases}
\rho \int \mathrm{d}^3 \mathbf{r} \phi_{ij}(r) & RPA \\
\\
\rho \int \mathrm{d}^3 \mathbf{r} g_{ij}(r) \phi_{ij}(r) & ERPA
\end{cases}
\tag{2.66}
$$

We now define a *Flory-Huggins interaction parameter* by

$$
\omega = k_B T \chi = U_{AB}^{(1)} - \frac{1}{2} \left[U_{AA}^{(1)} + U_{BB}^{(1)} \right]
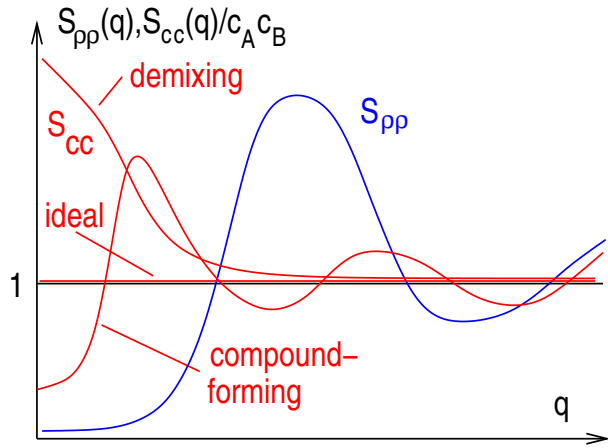\tag{2.67}
$$

and obtain for $S_{cc}(0)$

$$
S_{cc}(0) = \left[\frac{1}{S_{cc}^{(0)}} - \frac{\delta_0^2}{\theta_0} + \frac{\delta_1^2}{\theta_1} - \frac{1}{k_B T} 2\omega \right]^{-1},
\tag{2.68}
$$

where the index 0 refers to the hard-core system, and the index 1 refers to the combination of the direct correlation functions $C_{ij}^{(1)}(q=0) \equiv -U_{ij}^{(1)}(q=0)/k_B T$ given by (95d) and (95e).

In the case $\delta = 0$, $S_{cc}^{(0)}(0) = c_A c_B$ we have

$$
S_{cc}(0) = \left[\frac{1}{c_A c_B} - \frac{1}{k_B T} 2\omega \right]^{-1}
\tag{2.69}
$$

$S_{\rho\rho}(q)$ and the different possible forms of $S_{cc}(q)/c_A c_B$ for different types of chemical order

The quantity $S_{cc}(0)$ can be taken as a parameter which describes the *degree of chemical ordering*. In the non-interacting case, which is equivalent to the case in which all three pair potentials are equal, there is no chemical ordering and we have $S_{cc}(0) = c_A c_B$. If the $A-B$ potential is more *attractive* than the average of the $A-A$ and $B-B$ potentials we have a tendency towards forming an $A-B$ compound, and there will be a *chemical ordering* as in an antiferromagnet. This establishes a *superstructure* (Überstruktur) and is accompanied by a *prepeak* in $S_{cc}(q)$, which is situated half-way between the principle peak of $S_{\rho\rho}(q)$ and $q=0$. On the other hand, if the $A-B$ potential is *less attractive* than the average of the $A-A$ and $B-B$ potentials we have a tendency towards de-mixing, which can result in a demixing phase transition if the quantity $\chi = \omega/k_B T$ becomes too large.

A tendency towards demixing is accompanied by an enhanced *small-angle scattering*, i.e. an increase in the low-q part of $S_{cc}(q)$.

We now call a model substance in which $\delta = 0$, $S_{cc}^{(0)} = c_A c_B$ holds, a *regular solution*. Inserting (2.68) into (2.54c) and (2.55c) we obtain (with $c \equiv c_A$) for the stability function

$$
g_{cc} = \frac{1}{N} \left(\frac{\partial^2 \Delta G}{\partial c^2} \right)_{P,T,N} = -2\omega + k_B T \frac{1}{c(1-c)}
\tag{2.70}
$$

If we integrate (2.70) twice with the boundary condition $\Delta G(c=0) = \Delta G(c=1) = 0$ we obtain the *free enthalpy of mixing for a regular solution*

$$
\frac{1}{N} \Delta G = c(1-c)\omega + k_B T \left[c \ln c + (1-c) \ln(1-c) \right]
\tag{2.71}
$$

2.2.8   Phase separation in regular solutions
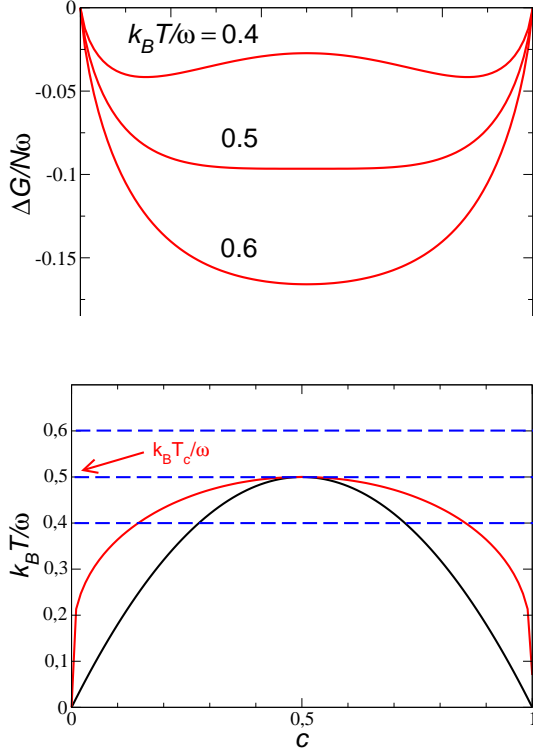
Top figure: Enthalpy of mixing for the three temperatures $k_B T/\omega = 0.4, 0.5(T_C)$, and 0.6.
Bottom figure: The phase diagram with spinodal lines and equilibrium concentrations. The dashed lines give the temperatures of the top figure.

We now consider a regular solution with a free enthalpy of mixing

$$\frac{1}{N}\Delta G = c(1-c)\omega + k_B T\left[c\ln c + (1-c)\ln(1-c)\right] \quad (2.72)$$

and a corresponding stability function

$$g_{cc} = \frac{1}{N}\left(\frac{\partial^2 \Delta G}{\partial c^2}\right)_{P,T,N} = -2\omega + k_B T\frac{1}{c(1-c)} \quad (2.73)$$

We immediately notice that there occurs an instability, once $k_B T/2\omega \leq c(1-c)$. Because $c(1-c)$ does not exceed 0.25, the critical temperature for separation into a B-rich and an A-rich phase is given by $k_B T_c/\omega = 0.5$. Below this temperature the line of instability, given by

$$\frac{k_B T}{\omega} = \frac{1}{\chi} = 2c(1-c) \quad (2.74)$$

is called *spinodal line*. The equilibrium concentrations of the A-rich and B-rich phases are obtained by the condition that the chemical potentials of both species must coincide:

$$\mu_{A,\text{rich}} = \mu_{A,\text{poor}} \qquad \mu_{B,\text{rich}} = \mu_{B,\text{poor}} \quad (2.75)$$

If these equations hold, we must also have

$$\mu_{A,\text{rich}} - \mu_{B,\text{rich}} = \mu_{A,\text{poor}} - \mu_{B,\text{poor}} \quad (2.76)$$

Because the chemical potential difference is just proportional to the *slope* of the curve $\Delta G(c)$, the two equilibrium concentrations are given by the *double-tangent construction*: in the instable region, where $\Delta G(c)$ varies non-monotonically with concentration one seeks a line which touches the curve at two points (double tangent). In our case these concentrations co-incide with the positions of the minima of $\Delta G(c)$ and are given by

$$k_B T/\omega = \frac{2c-1}{\ln c - \ln(1-c)} \quad (2.77)$$

2.3 Structure of polymer materials

2.3.1 Solutions of polymers as macromolecules
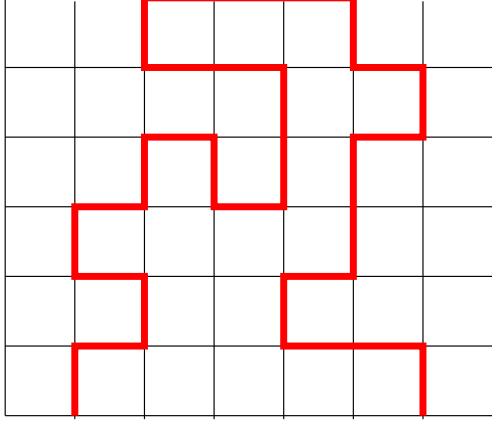
Flory-Huggins model of a polymer as a random walk on a lattice

We now consider N_p polymer molecules consisting of N segments immersed in a solvent consisting of N_s molecules. The total number of molecules[2] is $N_m = N_s + N_p$. Following Flory and Huggins (1942) we imagine that we arrange the monomers and the solvent molecules on a simple cubic lattice (volume V, lattice constant a), which provides $N_V = V/a^3 = NN_p + N_s$ sites. With respect to the concentrations $c_p = c = N_p/N_m$, $c_s = 1 - c = N_s/N_m$ the Entropy of mixing takes the form

$$\Delta S(c) = -N_m k_B [c \ln c + (1 - c) \ln(1 - c)]. \qquad (2.78)$$

Instead of working with the polymer concentration we want to work with the *volume fraction* ϕ occupied by the polymer. This number is given by

$$\phi = N \frac{N_p}{N_V} = N c_p \frac{N_m}{N_v}. \qquad (2.79)$$

Consequently we have for c and $1 - c$

$$c = \frac{\phi}{N} \frac{N_V}{N_m} \qquad 1 - c = (1 - \phi) \frac{N_V}{N_m} \qquad (2.80)$$

So that we obtain

$$
\begin{aligned}
\Delta S_c &= -N_V k_B \left[\frac{\phi}{N} \ln \frac{\phi N_V}{N N_m} + (1 - \phi) \ln(1 - \phi) \frac{N_V}{N_m} \right] \\
&= -N_V k_B \left[\frac{\phi}{N} \ln \phi + (1 - \phi) \ln(1 - \phi) + \frac{\phi}{N} \ln \frac{N_V}{N N_m} + (1 - \phi) \ln \frac{N_V}{N_m} \right]. \qquad (2.81)
\end{aligned}
$$

With respect to the variable ϕ we obtain the following entropy of mixing per lattice site

$$
\begin{aligned}
\Delta S &= \frac{1}{N_V} [\Delta S_c(\phi) - \phi \Delta S_c(\phi = 1) - (1 - \phi) \Delta S_c(\phi = 0)] \\
&= -k_B \left[\frac{\phi}{N} \ln \phi + (1 - \phi) \ln(1 - \phi) \right]. \qquad (2.82)
\end{aligned}
$$

Now we add an enthalpy term of the same form as that in the theory of regular solution, except that we now work with the variable ϕ:
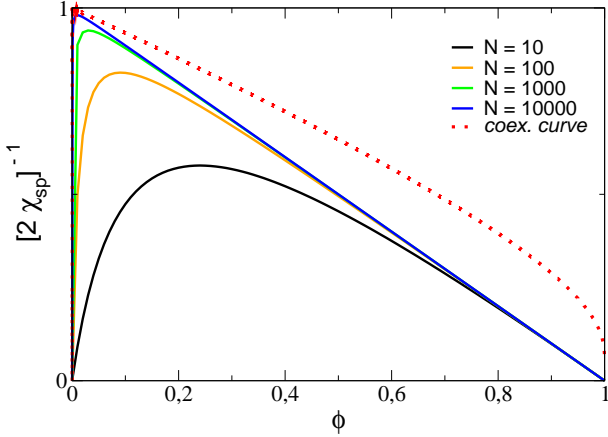
$$\Delta H = \phi(1 - \phi)\epsilon = \phi(1 - \phi)\chi k_B T \qquad (2.83)$$

Here ϵ is the energy difference

$$\epsilon = z \left[\epsilon_{ps} - \frac{1}{2} (\epsilon_{pp} + \epsilon_{ss}) \right] \qquad (2.84)$$

between p–s nearest-neighbors and the averaged p–p and s–s nearest-neighbors. z is the lattice coordination number (i.e. $z = 6$). So we obtain the *Flory-Huggins expression* for the free enthalpy per site and $k_B T$

$$\Delta g = \frac{1}{k_B T} \Delta G = \phi(1 - \phi)\chi + \frac{\phi}{N} \ln \phi + (1 - \phi) \ln(1 - \phi) \qquad (2.85)$$

Phase diagram for the Flory-Huggins model. Straight lines are the spinodals, Eq. (2.86), the dotted curve is the coexistence curve, Eq. (2.92), for $N \to \infty$.

Of course this model embodies a very crude approximation to the reality, as the different possible polymer chain conformations are completely neglected. However, it has turned out that despite the model is more than 50 years old it still serves as a starting point for discussing the thermodynamics of polymer solutions. For the spinodal value of χ we obtain

$$2\chi_{sp} = \frac{1}{N\phi} + \frac{1}{1-\phi} \tag{2.86}$$

If we seek the minimum of this curve we obtain for the critical concentration

$$\phi_c = \frac{\sqrt{N}-1}{N-1} \approx \frac{1}{\sqrt{N}} \tag{2.87}$$

We see that for large N the critical point becomes situated at very dilute volume fractions, and the critical temperature approaches the so-called Θ limit:

$$\lim_{N\to\infty} \chi_c = \lim_{N\to\infty} \frac{\epsilon}{k_B T_c} = \frac{\epsilon}{k_B \Theta} = 2 \tag{2.88}$$

From the equality of the chemical potentials of the concentrated and the dilute phase we have for the equilibrium volume fractions $\phi_{1,2}$: (double-tangent construction)

$$\frac{\Delta g_1 - \Delta g_2}{\phi_1 - \phi_2} = \left.\frac{\partial \Delta g}{\partial \phi}\right|_{\phi_1} = \left.\frac{\partial \Delta g}{\partial \phi}\right|_{\phi_2} \tag{2.89}$$

We know that the equilibrium volume fractions for the concentrated and the and dilute phase must be situated outside the spinodal curve. As for large N there is not much of an inteval left for the concentrated volume fraction, we conclude that

$$\lim_{N\to\infty} \phi_1 = 0 \,, \tag{2.90}$$

from which follows in the limit $N \to \infty$:

$$0 = \phi_2 \left.\frac{\partial \Delta g}{\partial \phi}\right|_{\phi_2} - \Delta g_2 = -\phi_2^2 \chi + \phi_2 \left(\frac{1}{N}-1\right) + \ln\frac{1}{1-\phi_2} \approx -\phi_2^2 \chi + \ln\frac{1}{1-\phi_2} - \phi_2 \,. \tag{2.91}$$

This leads to a coexistence curve of the form

$$\frac{1}{2\chi} = \frac{\phi_2^2}{2}\frac{1}{\ln\frac{1}{1-\phi_2} - \phi_2} = \frac{\phi_2^2}{2}\frac{1}{\frac{1}{2}\phi_2^2 + \frac{1}{3}\phi_2^3 + \frac{1}{4}\phi_2^4 + \cdots} \tag{2.92}$$

We see that - according to the Flory-Huggins RPA theory - in the phase-separated state the concentrated phase contains still a lot of solvent molecules, whereas the dilute phase is entirely made up of polymer solute molecules.

2.3.2 Diblock Copolymers
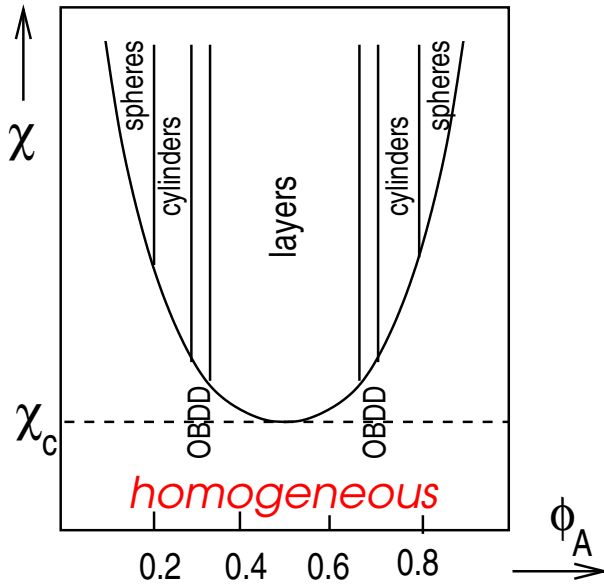
Phase diagram for equilibrium diblock-copolymer phases as a function of the χ parameter and the volume fraction ϕ_A.

If n polymer species are linked together chemically one speaks of *block copolymers* The molecules in the special case of $n = 2$ are called *diblock copolymers*. As any A molecule is tied to a B molecule, the volume fraction of the A species is just given by

$$\phi_A = \frac{N_A}{N_A + N_B} \qquad (2.93)$$

and can only be changed by the chemist, not by the physicist. As the van-der-Waals interactions of different polymers will still be different in the case of linking two species together, equation (**??**) for the monomer-monomer interaction will hold and one expects a segregation tendency as in the case of polymer mixtures. The overall thermodynamics for $\chi < \chi_c$ including the critical small-angle scattering law (**??**) will be the same. However for $\chi > \chi_c$ the molecules cannot segregate, because they are tied together. Instead they can form *regular structures*.

These structures differ for different volume fractions. So one obtains a rich phase diagram (see figure). For small concentrations $\phi_A \ll 1$ or $\phi_B \ll 1$ spheres are formed with the minority species inside. This situation is quite comparable to solutions of polymers with large χ parameter but with a hydrophilic end group (lipids) in water. The spherical structures form a *bcc* lattice. For larger fractions *cylinders* are formed, which are arranged in a hexagonal $2 - d$ lattice. For $N_A \approx N_B$ layered structures are formed. In the concentration range $\phi \approx 0.3$ two interpenetrating diamond-type filament structures (*ordered bicontinuous double diamond, OBDD*) are formed. As the thermodynamic and interaction parameters are A_B symmetric, so is the phase diagram.

From (**??**) one would estimate for $\phi_A = 0.5$, i.e. $N_A = N_B = N$ a critical χ parameter of $\chi_c = 2/N$. However empirically it was found that the transition is at $\chi \approx 5/N$.

2.3.3 Random walks and diffusion
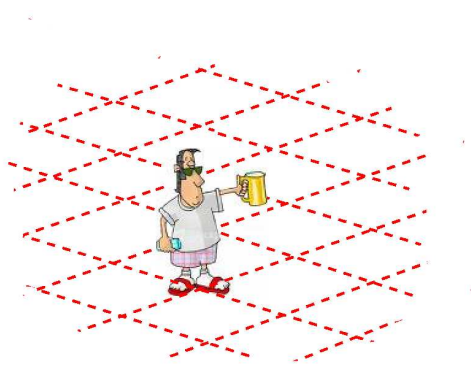
A random walker on a two-dimensional lattice

The motion of a Brownian particle can be visualized by that of a "random walker", e.g. by a drunken person, who changes its direction at random after every step. The statistics of such a motion can be easily worked out on a lattice. We start with this on a one-dimensional array of points with lattice constant a. the time steps are called τ. The propabilities $P(x = a, t = \tau)$ and $P(x = -a, t = \tau)$ are $1/2$, those for one time step for $|x| > a$ are zero. The non-zero probabilities for the νth time step are $(1/2)^\nu$ times the number of ways one can reach the site $x_n = na$ on the triangle.

This number increases from 1 at the maximum distance $|x|_{\max} = \nu a$ with $k = (|x|_{\max} - |x|)/a$ as $\binom{n}{k}$, which can be represented as
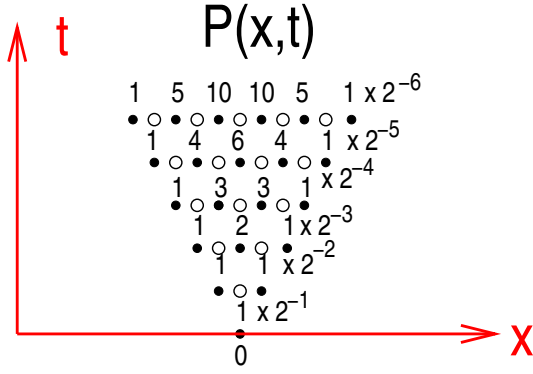
Pascal's triangle for a 1d random walk. The number of ways a time-space point can be reached from the bottom is given by Pascal's algorithm, i.e. each number is the sum of the two numbers underneath.

$$P(x_n, \nu\tau) = \left(\frac{1}{2}\right)^\nu \binom{\nu}{k} \qquad k = \left[\frac{1}{2}(n+\nu)\right], \tag{2.94}$$

where $[\nu]$ is the smallest integer κ with $\kappa \geq \nu$. It is worth wile to note that at an even/odd time step ν only even/odd random walk sites x_n can be reached.

We consider now the recursion formula for the binomial coefficients

$$\binom{n+1}{k} = \binom{n}{k} + \binom{n}{k-1} \tag{2.95}$$

We re-write this recursion formula with the help of the probabilities $P(nx, \nu\tau)$:

$$P(x_n, t+\tau) = \left(\frac{1}{2}\right)^{\nu+1} \binom{\nu+1}{k_{n,\nu+1}} = \frac{1}{2}P(x_{n+1}, t) + \frac{1}{2}P(x_{n-1}, t) \tag{2.96}$$

This can be re-written as

$$\frac{P(x_n, t+\tau) - P(x, t)}{\tau} = D\left[\frac{P(x_n+a) + P(x_n-a, t) - 2P(x, t)}{a^2}\right] \tag{2.97}$$

with

$$D = \frac{a^2}{2\tau} \tag{2.98}$$

We take now the double limit $\tau \to 0$ and $a \to 0$ keeping the ratio $D = a^2/2\tau$ fixed. This leads to

$$\frac{\partial P(x, t)}{\partial t} = D\frac{\partial^2}{\partial x^2}P(x, t) \tag{2.99}$$

This is the famous *diffuson equation*, which was first derived by Charles Fourier. We want to solve now this equation. Going over to a spatial Fourier transform

$$P(k, t) = \int_{-\infty}^{\infty} dx\, e^{ikx} P(x, t) \tag{2.100}$$

and a temporal Laplace transform

$$P(k, p) = \int_0^{\infty} dt\, e^{-pt} P(k, t) \tag{2.101}$$

we obtain from (2.99)

$$pP(k, p) - P(k, t{=}0) + Dk^2 P(k, p) = 0 \tag{2.102}$$

with the solution

$$P(k, p) = \frac{P(k, t{=}0)}{p + Dk^2} = P(k, t{=}0)G(k, p) \tag{2.103}$$

where we have introduced the special solution G(k,t), (Greens function) which has the initial condition

$$G(k, t{=}0) = 1 \tag{2.104}$$

corresponding to

$$G(x, t{=}0) = \delta(x) \tag{2.105}$$

$G(x, t)$ can be interpreted as the probability density of a Brownian particle which started his journey at $t = 0$ at the origin $x = 0$ (see next subsection). The back transforms of $G(k, p)$ are

$$G(k, t) = e^{-Dk^2 t} \tag{2.106}$$

21

and

$$G(x,t) = \frac{1}{\sqrt{4\pi Dt}} e^{-x^2/4Dt} \tag{2.107}$$

An important quantity is the *mean square distance* walked by the Brownian particle at a certain time t. It can be calculated from the function $G(x,t)$ as

$$
\begin{align}
\langle x^2(t) \rangle &= \int_{-\infty}^{\infty} \mathrm{d}x\, x^2\, G(x,t) \tag{2.108a} \\
&= -\frac{\partial^2}{\partial k^2} \int_{-\infty}^{\infty} \mathrm{d}x\, e^{ikx}\, G(x,t) \bigg|_{k=0} \tag{2.108b} \\
&= -\frac{\partial^2}{\partial k^2} e^{-Dk^2 t} \bigg|_{k=0} \tag{2.108c} \\
&= 2Dt \tag{2.108d}
\end{align}
$$

This equation states that the mean distance a Brownian particle moves away on the average from its starting point grows with the square-root of time.

The diffusion equation and its solution are easily generalized to the three-dimensional case. The diffusion equation reads

$$\frac{\partial \rho(\mathbf{r},t)}{\partial t} - D\nabla^2 \rho(\mathbf{r},t) = 0\,. \tag{2.109}$$

with solution

$$G(\mathbf{k},t) = \int_{-\infty}^{\infty} \mathrm{d}^3\mathbf{r}\, e^{i\mathbf{k}\cdot\mathbf{r}} G(\mathbf{r},t) = e^{-Dk^2 t}\,, \tag{2.110}$$

subject to the initial condition $G(\mathbf{k},t{=}0) = 1 \Leftrightarrow G(\mathbf{k},t{=}0) = \delta(\mathbf{r})$. We now have $k^2 = |\mathbf{k}|^2 = k_x^2 + k_y^2 + k_z^2$. The solution in $\mathbf{r}$ space has the form

$$G(\mathbf{r},t) = \left[\frac{1}{\sqrt{4\pi Dt}}\right]^3 e^{-r^2/4Dt} \tag{2.111}$$

with $r^2 = |\mathbf{r}|^2 = x^2 + y^2 + z^2$. For the three-dimensional mean-square distance we obtain the Einstein relation
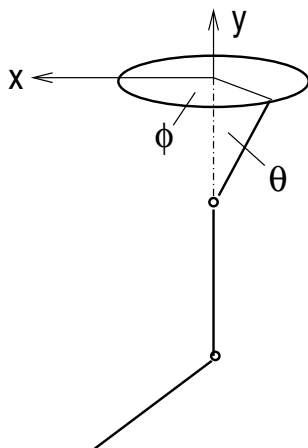
$$
\begin{align}
\langle r^2(t) \rangle &= \int_{-\infty}^{\infty} \mathrm{d}^3\mathbf{r}\, \left(x^2 + y^2 + z^2\right) G(\mathbf{r},t) \tag{2.112a} \\
&= -\left(\frac{\partial^2}{\partial k_x^2} + \frac{\partial^2}{\partial k_y^2} + \frac{\partial^2}{\partial k_z^2}\right) \int_{-\infty}^{\infty} \mathrm{d}^3\mathbf{r}\, e^{i\mathbf{k}\cdot\mathbf{r}} G(\mathbf{r},t) \bigg|_{k_x=k_y=k_z=0} \tag{2.112b} \\
&= -\left(\frac{\partial^2}{\partial k_x^2} + \frac{\partial^2}{\partial k_y^2} + \frac{\partial^2}{\partial k_z^2}\right) e^{-Dk^2 t} \bigg|_{k_x=k_y=k_z=0} \tag{2.112c} \\
&= 6Dt \tag{2.112d}
\end{align}
$$

2.3.4   Polymer chain as a random walk

A *real* polymer molecule has a rather rigid bond structure, which allows only certain bond angles θ and ϕ (see figure). the same length a. On the other hand, these molecules are so huge, that one can choose the unit "beads" much larger than a single molecular segment. The angles between these beads ("Kuhn segment") can then be assumed to be random, and the itinerary of the chain in 3-dimensional space can be considered to be described by a random walk.

Thre segments of a polymer chain with bond angles θ and azimuthal angle ϕ by which the bond can be directed into the *trans* and the *gauche* direction

The probability density for the end of the chain of length N to be a distance R from the other end (origin) is, using (189) with $2Dt = a^2 t/\tau = a^2 N$:

$$P(R, N) = [2\pi a^2 N]^{-3/2} e^{-R^2/2a^2 N} \tag{2.113}$$

The number of random walks with N steps leading from the origin to any point inside a sphere of radius R^* is then given by

$$\zeta(R^*, N) = 4\pi \int_0^{R^*} R^2 P(R, N) \tag{2.114}$$

From this we can calculate the number of random walks having exactly the distance R from the origin as

$$Z(R, N) = \left.\frac{\mathrm{d}\zeta}{\mathrm{d}R^*}\right|_{R^*=R} = 4\pi R^2 P(R, N) \tag{2.115}$$

The corresponding entropy is

$$S(R, N) = k_B \ln[Z(R, N)] = -k_B \frac{R^2}{2a^2 N} + k_B \ln[4\pi R^2] - (3/2)k_B \ln[2\pi a^2 N] \tag{2.116}$$

and the free energy

$$F_{\mathrm{id}} = -T S_{\mathrm{id}} = k_B T \frac{R^2}{2R_0^2} - k_B T \ln[4\pi R^2] - (3/2)k_B \ln[2\pi R_0^2] = F_0 + k_B T \frac{R^2}{2R_0^2} \tag{2.117}$$

From this we can, for example, calculate the distance x the chain will be elongated if an external force f in x direction is applied. The corresponding potential is $\phi_f = -fx$ so that the free energy is

$$F_f = -fx + F_0 + k_B T \frac{x^2 + y^2 + z^2}{2R_0^2} \tag{2.118}$$

Minimizing F_f with respect to x yields

$$x = f \frac{R_0^2}{k_B T} = f \frac{N a^2}{k_B T} \tag{2.119}$$

2.3.5   Swollen polymer chains

However, we made a serious mistake in the previous section: A polymer chain cannot occupy more than once the same portion of space. A random walk which never uses the same site is has already used is

called a *self-avoiding random walk*. In a real polymer the excluded-volume property is, of course, due to a repulsive potential $\phi(|\mathbf{r} - \mathbf{r}'|)$ between two monomer units at locations $\mathbf{r}$ and $\mathbf{r}'$. Flory has calculated the relation between the length N and the extension R of a self-avoiding random chain by a thermodynamic argument. We now estimate the mean repulsive energy as follows:

$$E = \rho_0^2 \int_V d^3\mathbf{r} \int_V d^3\mathbf{r}' g(|\mathbf{r} - \mathbf{r}'|)\phi(|\mathbf{r} - \mathbf{r}'|) \tag{2.120}$$

Here $V = R^3$, $g(r)$ is the radial pair distribution function of the monomers and $\rho_0 = N/V = NR^{-3}$ is their density. As $g(r)$ is 0 for $|\mathbf{r} - \mathbf{r}'| < d$ (where $d \approx a$ is the distance of nearest approach) and $\phi(r)$ is supposed to drop quickly to 0 beyond d we can make the approximation

$$g(r)\phi(r) \approx \epsilon\delta(r - d)\,, \tag{2.121}$$

where ϵ has the dimension of an energy times a volume. We obtain

$$E = \rho_0^2 V\epsilon = \epsilon N^2/R^3 \tag{2.122}$$

We can now write down the free energy

$$
\begin{aligned}
F &= E - TS \\
&= \epsilon N^2/R^3 + k_B T \ln[Z(R, N)] \\
&= \epsilon N^2/R^3 + k_B T \frac{R^2}{2a^2 N} - k_B T \ln[4\pi R^2] - (3/2)k_B \ln[2\pi a^2 N]
\end{aligned}
\tag{2.123}
$$

We now seek the equilibrium value of R for a self-avoiding random walk of N steps, which, is obtained by that value of R which minimizes F, i.e.

$$0 = \frac{\partial F(R, N)}{\partial R} = -3\frac{\epsilon N^2}{R^4} + \frac{k_B TR}{a^2 N} - \frac{2k_B T}{R}\,, \tag{2.124}$$

from which follows

$$\frac{R^2}{Na^2} = 3\frac{N^2\epsilon}{R^3 k_B T} + 2 \tag{2.125}$$

In the limit of large N and R (and for temperatures equal or smaller than $\epsilon N^2/R^3$) the constant term 2 is negligible, and we obtain

$$N(R) = \left[\frac{k_B T}{3\epsilon a^2}\right]^{1/3} R^{5/3}\,, \tag{2.126}$$

which can be inverted to yield

$$R(N) = \left[\frac{k_B T}{3\epsilon a^2}\right]^{1/5} N^{3/5}\,, \tag{2.127}$$

The exponent 3/5=0.6 is considerably larger than the "free-chain" exponent 0.5. One therefore speaks of chains which are "swollen" through the excluded-volume interaction. Interestingly enough the excluded-volume interaction, which leads to the Flory exponent, acts only, if the polymer molecule is free to expand, wich is the case in *dilute* polymer solutions. In concentrated solutions the