

Theory disordered systems

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— Script of the Lecture (under construction) —

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1 Disordered structures

1.1 Introduction

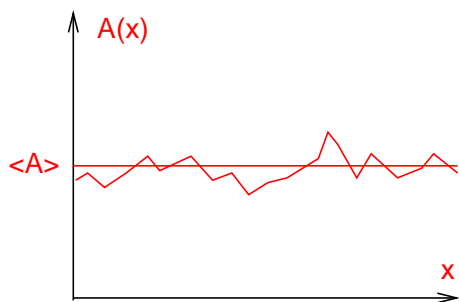


Fig. 1:
Spatially fluctuating physical quantity $A(x)$

By *disorder* we mean a *spacial* disorder, which is defined as a spatial fluctuation of some physical variable $A(x)$

$$A(x) = \langle A \rangle + \Delta A(x) \quad (1.1)$$

The most important characterization of the fluctuations $\Delta A(x)$ is the *correlation function*

$$C_{AA}(x) = \langle A(x + x_0) \rangle \quad (1.2)$$

$\langle \dots \rangle$ means an average with respect to some distribution in a Gibbsian ensemble (ensemble average).

One can also define a *spatial average*:

$$\bar{A}^{\Delta x}(x_0) = \frac{1}{\Delta x} \int_{x_0 - \frac{\Delta x}{2}}^{x_0 + \frac{\Delta x}{2}} dx A(x) \quad (1.3)$$

For not too large Δx the function $\bar{A}^{\Delta x}(x_0)$ is called *smoothed* or *coarse-grained* version of $A(x)$. If for $\Delta x \rightarrow \infty$ $\bar{A}^{\Delta x}$ approaches the ensemble average $\langle A \rangle$ we call A *self-averaging*. This property is the spatial variant of the ergodic property of dynamically fluctuating variables $A(t)$.

Another important concept is the distinction between *quenched* and *annealed* disorder. By *annealed* disorder we mean spatial fluctuations which arise as a result of thermal equilibrium e.g. in a liquid. It is characterized by the usual equilibrium distribution functions. By *quenched* disorder a “frozen” spatial variation is meant, which is characterized e.g. by its correlation functions (1.1) or by an equilibrium distribution function of an annealed system with the temperature given by that from which the system was quenched (annealing temperature).

1.2 Topological disorder and disorder in crystals

1.2.1 Molecular distribution functions

The *structure* of a liquid is governed by the statistical distribution of the centers of gravity of the atoms or molecules. Of course the latter 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. 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 $d^3\mathbf{r}_1, d^3\mathbf{r}_2, \dots, d^3\mathbf{r}_N$ around positions $\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N$

$$P(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) d^3\mathbf{r}_1, d^3\mathbf{r}_2, \dots, d^3\mathbf{r}_N. \quad (1.4)$$

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

$$\int_V \prod_{\alpha=1}^N d^3\mathbf{r}_\alpha P(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) = 1. \quad (1.5)$$

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

$$\langle A \rangle = \int_V \prod_{\alpha=1}^N d^3\mathbf{r}_\alpha A(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) P(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N). \quad (1.6)$$

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

$$\rho^{(n)}(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_n) = \frac{N!}{(N-n)!} \int_V \prod_{i=n+1}^N d^3\mathbf{r}_i P(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N), \quad (1.7)$$

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

$$\rho(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) = \left(\frac{N}{V}\right)^n \equiv \rho_0^n. \quad (1.8)$$

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

$$\rho^{(n)}(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) = \rho_0^n g^{(n)}(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N). \quad (1.9)$$

In *homogeneous* systems we have

$$\rho^{(1)}(\mathbf{r}_1) = \rho_0 \quad (1.10)$$

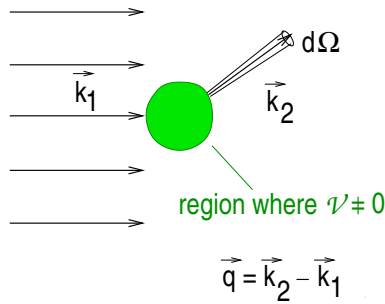
$$g^{(1)}(\mathbf{r}_1) = 1. \quad (1.11)$$

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

$$g^{(2)}(\mathbf{r}_1, \mathbf{r}_2) = g(|\mathbf{r}_1 - \mathbf{r}_2|) \quad (1.12)$$

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

1.2.2 Scattering theory



We want to describe the scattering of X-rays or neutrons from a simple liquid sample. We study an incoming plane wave (1st term) and an outgoing scattered spherical wave (2nd term) of the following asymptotic form

$$\psi(\mathbf{r}) \stackrel{|\mathbf{r}| \rightarrow \infty}{\approx} e^{i\mathbf{k}_1 \cdot \mathbf{r}} + f(\theta) \frac{1}{r} e^{ik_2 r} \quad (1.13)$$

The scattering cross-section into the solid angle element $d\Omega$ in the direction of \mathbf{k}_2 is then given by the modulus-square of the scattering amplitude

$$\frac{d\sigma}{d\Omega} = |f(\theta)|^2 \quad (1.14)$$

If the scattering potential (the potential between the scattered rays and the particles) can be decomposed as

$$\mathcal{V}(\mathbf{r}) = \sum_{\alpha=1}^N v(\mathbf{r} - \mathbf{r}_\alpha) \quad (1.15)$$

the scattering amplitude is given in 2nd approximation (*Born approximation*)

$$f(\theta) = -\frac{m}{2\pi\hbar^2} \langle \mathbf{k}_2 | \mathcal{V} | \mathbf{k}_1 \rangle = -\frac{m}{2\pi\hbar^2} \mathcal{V}(\mathbf{q}) = -\frac{m}{2\pi\hbar^2} \sum_{\alpha=1}^N e^{i\mathbf{q} \cdot \mathbf{r}_\alpha} v(\mathbf{q}) \equiv \sum_{\alpha=1}^N e^{i\mathbf{q} \cdot \mathbf{r}_\alpha} f(\mathbf{q}), \quad (1.16)$$

$f(\mathbf{q})$ is called *form factor* and has the unit of length. In the case of *energy unresolved* neutron or X-ray diffraction there is no net energy exchange with the sample, i.e. $|\mathbf{k}_1| = |\mathbf{k}_2|$. In an isotropic material the form factor depends only on the modulus of the exchanged momentum, which is given by

$$q = |\mathbf{k}_1 - \mathbf{k}_2| = k_1 \sqrt{2[1 - \cos(\theta)]} = \frac{4\pi}{\lambda} \sin\left(\frac{\theta}{2}\right), \quad (1.17)$$

where θ is the angle between \mathbf{k}_1 and \mathbf{k}_2 and $\lambda = \frac{2\pi}{k_1}$ is the wavelength.

In the case of neutrons, which scatter from the nuclei, whose potential $v(\mathbf{r})$ is extremely short-ranged, $f(q)$ does not depend on q (in the range of interest $q < 20 \text{ \AA}^{-1}$) and is called *scattering length* and is denoted by the letter b .

Inserting (1.16) into (1.14) and averaging over an ensemble of different configurations we obtain

$$\frac{d\sigma}{d\Omega} = |f(q)|^2 \left\langle \sum_{\alpha, \beta=1}^N e^{i\mathbf{q} \cdot [\mathbf{r}_\alpha - \mathbf{r}_\beta]} \right\rangle \equiv |f(q)|^2 NS(q), \quad (1.18)$$

where $S(q)$ is the *static structure factor*

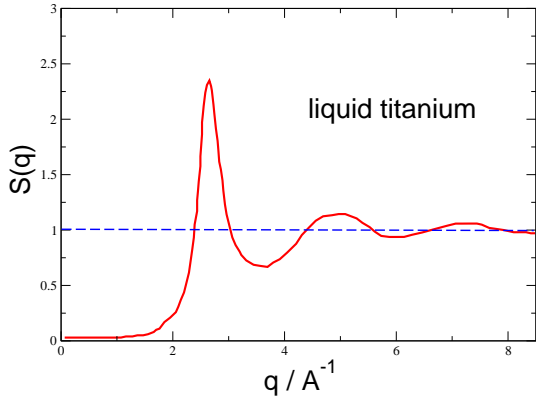
$$S(q) = \frac{1}{N} \left\langle \sum_{\alpha, \beta=1}^N e^{i\mathbf{q} \cdot [\mathbf{r}_\alpha - \mathbf{r}_\beta]} \right\rangle \quad (1.19)$$

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

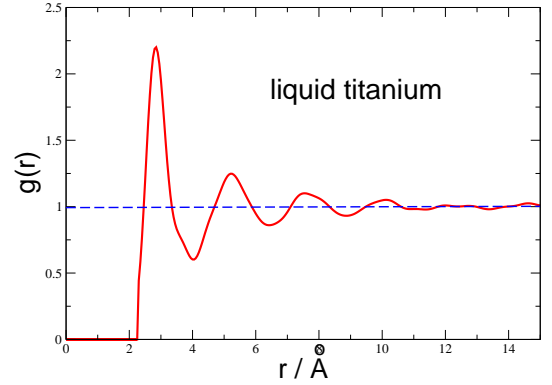
$$S(q) = 1 + \rho_0 \int_{-\infty}^{\infty} d^3\mathbf{r} e^{i\mathbf{q}\mathbf{r}} [g(r) - 1] \quad (1.20)$$

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

$$S(q) = 1 + \frac{4\pi\rho_0}{q} \int_0^{\infty} dr r \sin(qr) [g(r) - 1] \quad (1.21)$$



Structure factor of liquid titanium, measured by *Lee et al*



Corresponding pair distribution function calculated via Fourier-back transform from (1.21) with $\rho_0 = 0.05$

1.2.3 Models of disordered structures

1.2.4 Liquid structure and thermodynamics

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

$$\mathcal{H} = \sum_{\alpha=1}^N \frac{1}{2} m \dot{\mathbf{r}}_\alpha^2 + \frac{1}{2} \sum_{\alpha \neq \beta} \phi(|\mathbf{r}_\alpha - \mathbf{r}_\beta|). \quad (1.22)$$

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

Potential Energy

$$\frac{1}{N} \langle E_{\text{pot}} \rangle = 2\pi\rho_0 \int_0^{\infty} dr r^2 \phi(r) g(r) \quad (1.23)$$

Pressure

$$\langle P \rangle \frac{V}{Nk_B T} = \langle P \rangle \frac{1}{\rho_0 k_B T} = 1 - \frac{2\pi\rho_0}{3k_B T} \int_0^{\infty} dr r^3 \phi'(r) g(r) \quad (1.24)$$

Number fluctuations and isothermal compressibility κ_T

$$\frac{\langle N \rangle^2 - \langle N^2 \rangle}{N} = \rho_0 k_B T \left(-\frac{1}{V} \frac{\partial V}{\partial P} \right)_T = \rho_0 k_B T \kappa_T \quad (1.25)$$

$$= S(q=0) = 1 + 4\pi\rho_0 \int_0^{\infty} dr r^2 [g(r) - 1] \quad (1.26)$$

1.2.5 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:

$$S(q) = \frac{1}{N} \left\langle \sum_{\alpha, \beta=1}^N e^{i\mathbf{q} \cdot [\mathbf{r}_\alpha - \mathbf{r}_\beta]} \right\rangle = 1 + \frac{1}{N} \left\langle \sum_{\alpha \neq \beta}^N e^{i\mathbf{q} \cdot [\mathbf{r}_\alpha - \mathbf{r}_\beta]} \right\rangle \equiv 1 + \rho_0 h(q) \quad (1.27)$$

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.

$$h(r) = g(r) - 1. \quad (1.28)$$

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:

$$h(r_{12}) = c(r_{12}) + \rho_0 \int d^3 \mathbf{r}_3 c(r_{13}) c(r_{32}) + \rho_0^2 \int d^3 \mathbf{r}_3 \int d^3 \mathbf{r}_4 c(r_{13}) c(r_{34}) c(r_{42}) + \dots \quad (1.29)$$

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

$$h(r_{12}) = c(r_{12}) + \rho_0 \int d^3 \mathbf{r}_3 c(r_{13}) h(r_{32}) \quad (1.30)$$

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

$$h(q) = \frac{c(q)}{1 - \rho_0 c(q)} \quad (1.31)$$

which finally leads to

$$S(q) = \frac{1}{1 - \rho_0 c(q)} \quad (1.32)$$

1.2.6 Integral equation theories for $g(r)$

We recall again the Ornstein-Zernike (OZ) relation between $g(r) = 1 + h(r)$ and the direct correlation function $c(r)$ (in a slightly modified form):

$$h(r) = c(r) + \rho_0 \int d^3 \mathbf{r}' h(|\mathbf{r} - \mathbf{r}'|) c(r') \quad (1.33)$$

The function $c(r)$ can, on the other hand, be calculated by functional integral and functional derivative techniques. Using such techniques and an appropriate diagram formalism one can come up with a second relation between $c(r)$ and $g(r)$ which is called the *closure relation* and constitutes a specific *integral equation theory* for $g(r)$. The most popular closure relations are

Percus-Yevick (PY):

$$c(r) = g(r) \left[1 - e^{\beta\phi(r)} \right] \quad (1.34)$$

Hypernetted-Chain (HNC):

$$c(r) = -\beta\phi(r) + h(r) - \ln g(r) \quad (1.35)$$

These closures together with the OZ relation constitute a self-consistent set of integral equations for $h(r)$ or $g(r)$.

1.2.7 PY solution for hard spheres

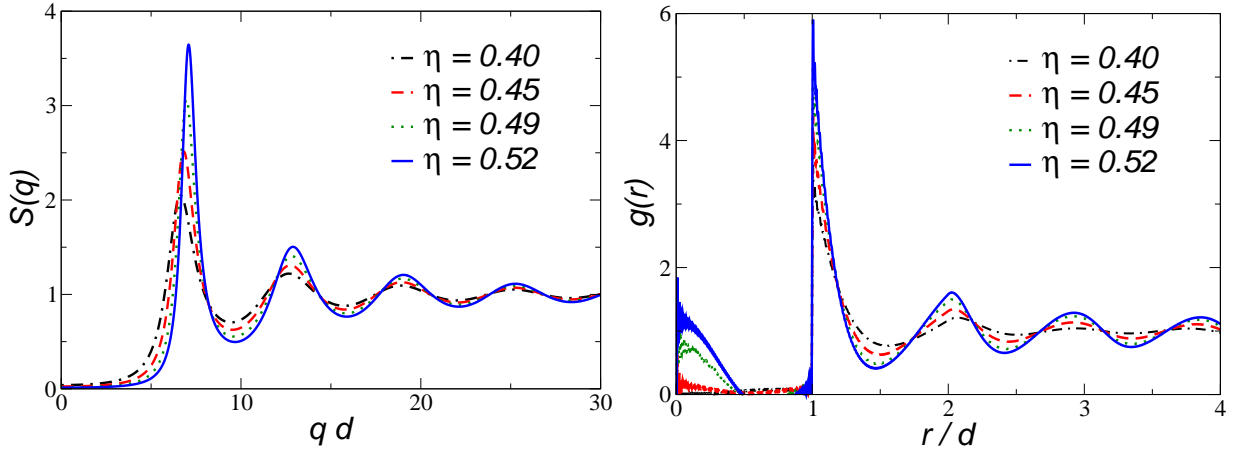


Fig. 4a and Fig. 4b: Hard-sphere PY structure factors $S(q)$ and pair correlation functions $g(r)$

We now consider the hard-sphere potential

$$\phi_{HS}(r) = \begin{cases} \infty & r < d \\ 0 & r > d \end{cases}, \quad (1.36)$$

where d is the *hard-sphere diameter*. In this case the PY integral equation can be solved *exactly*. The solution is given in terms of the *packing fraction*

$$\eta = \frac{\text{volume filled with spheres}}{\text{total volume}} = \frac{\pi}{6} d^3 \rho_0 \quad (1.37)$$

and the dimensionless variable $x = r/d$

$$c(r) = \begin{cases} \lambda_1 - 6\eta\lambda_2 x + \frac{1}{2}\eta\lambda_1 x^3 & x < 1 \\ 0 & x > 1 \end{cases}, \quad (1.38)$$

with

$$\lambda_1 = (1 + 2\eta)^2 / (1 - \eta)^4 \quad (1.39a)$$

$$\lambda_2 = (1 + \frac{1}{2}\eta)^2 / (1 - \eta)^4 \quad (1.39b)$$

1.2.8 disorder in crystals

1.3 Fractals

1.3.1 Logistic map and Mandelbrot set

1.3.2 Fractals and fractal dimension

In his book “The fractal geometry of nature”, which appeared in 1977, the french mathematician Benoit Mandelbrot coined the word *fractal* for geometrical objects, which do not have an inherent length scale, i.e. they are *self similar*. They just look the same at very different length scales. Such object are trees, sponges, termination deltas of rivers, tidal streaming traces, clouds, mountains – and coast lines. Although Mandelbrot made fractals a fashionable subject in physics, self-similar objects have been studied much earlier, e.g some 150 years ago by people like David Hilbert, Giuseppe Peano or Georg Cantor.

Let us start with coast lines. How long is the coast line of England/Scotland? You may measure it with conventional geodesic wooden sticks to come up with a number of about ten thousand km. (The figure given by www.coastalguide.org is 13560 km.) However, if you make your measuring device smaller, so that you can follow all small wrinkles you might be able to double the number: The length of the coast line depends on the scale of the measuring device, or, in other words, if you want to draw the coast line its length depends on the thickness or the sharpness of the pencil. In fact a coastline is a typical fractal object: It has similar wrinkles at different length scales.

In discussing the length of the coast line we found that there is some difficulty to identify it as a one-dimensional object, as it has a typical property of an object with dimensionality greater than one: Its length depends on something else: For an area this is the width, for the coast line it is the thickness of the pencil. In fact fractals turn out *not to have an integer dimensionality*. Its dimensionality is a *non-integer* number d_f , which is called *fractal dimension*. Let us resume, how in “normal” geometry the dimension is defined: If we multiply the linear size L of a d -dimensional object by a factor b the mass of the object changes by a factor b^d :

$$M(bL) = b^d M(L) \tag{1.40}$$

Let us discuss a regular geometric coast line, which is the *Koch curve* depicted in the figure. A straight line is divided into 3 and the inner part is replaced by the upper part of an equilateral triangle. This procedure is repeated for all 4 new sides. As the Koch curve is iteratively constructed from lines, i.e. one-dimensional objects its “mass” is just its length. This length steadily increases as the iteration is continued, just as in the coastline example. For the Koch curve we can deduce the value of the fractal dimension: Every time the length is increased by a factor of 3 its length increases by a factor of 4. If we call the length of the Koch curve also M we have

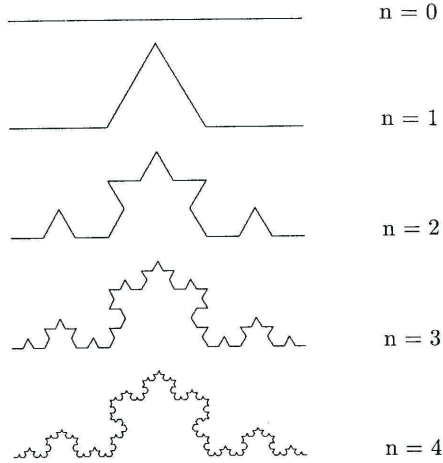
$$M(3L) = 4M(L) \tag{1.41}$$

We want to define the fractal dimension just as in (1.40)

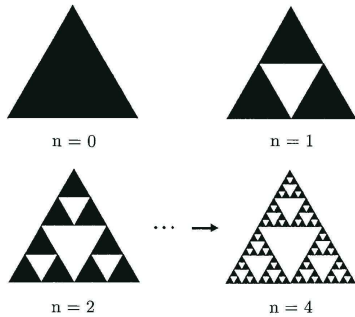
$$M(bL) = b^{d_f} M(L) \tag{1.42}$$

comparing (1.41) with (1.42) we obtain

$$d_f = \ln 4 / \ln 3 = 1.26185954 \dots \tag{1.43}$$



The first 4 iterations of the Koch curve



The first 4 iterations of the Sierpinski gasket

Instead of *augmenting* a one-dimensional object we can also *deplete* a two-dimensional object as done with the so-called *Sierpinski gasket*: An equilateral triangle of half the linear size of a bigger triangle is punched out of the middle of the big triangle. This procedure is repeated with all successively appearing triangles. For the “mass”, which is here the area, we have obviously

$$M(2L) = 3M(L) \Leftrightarrow d_f = \ln 3 / \ln 4 = 1.58496249 \dots \tag{1.44}$$

A similar procedure can also be repeated with a square or a cube. For the latter (“*Sierpinski sponge*”)

$$M(3L) = 20M(L) \Leftrightarrow d_f = \ln 20 / \ln 3 = 2.72683311 \dots \quad (1.45)$$

Note that this number is now between 2 and 3.

One even can generate fractals with dimensions *below* 1. These are point-like objects, called *dusts* by Mandelbrot. The *Cantor set* is iterated by taking just the middle third out of the unity interval, and then this procedure is repeated for every remaining interval. For the remaining dust we have the scaling relation

$$M(3L) = 2M(L) \Leftrightarrow d_f = \ln 2 / \ln 3 = 0.630929768 \dots \quad (1.46)$$

One can show that from a topological point of view the Cantor set has the Lebesgue measure 0, but its elements are *not* countable, i.e. it can not be mapped onto the set of integers.

In cases, in which the scaling law is not obvious one can calculate d_f *empirically* by the so-called *box counting algorithm*. For this we need to define the *imbedding dimension*, which is just called d . The imbedding dimension is the dimension of the space, in which the defining algorithm of the fractal is formulated. So for the Cantor set $d = 1$, for the Koch curve and the Sierpinski gasket $d = 2$, and for the Sierpinski sponge $d = 3$. We have strictly

$$d_f \leq d.$$

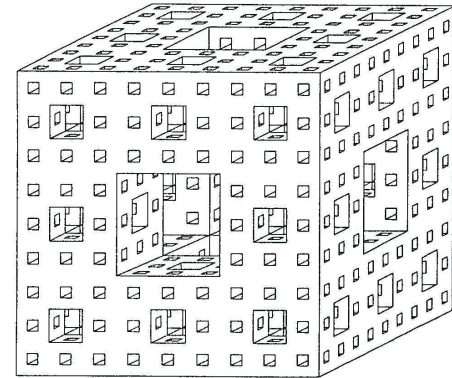
For the fractal, for which one wants to determine d_f one sets up a mesh of boxes inside a big hypercube of length L , which are hypercubes of “mass” $(\epsilon L)^d$, where $\epsilon = L/n$ and n is the number of boxes along one edge of the big box.

One then determines the number of boxes Z_n , which are filled or partially filled by the fractal object for several n . One then obtains from a log-log plot $\ln Z_n$ vs. $\ln n$ a straight line, the slope of which is d_f :

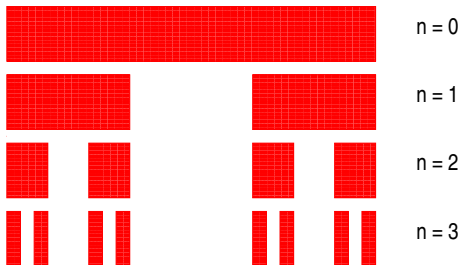
$$Z_n = \lim_{n \rightarrow \infty} n^{d_f} \Leftrightarrow d_f = \frac{\ln Z_n}{\ln n} \quad (1.47)$$

On the other Hand we can define Z_n to be the ratio of the “mass” of the fractal for a particular n $M(L)$, divided by the “mass” of an ϵ -pixel (or “voxel”) $Z_n = M(L)/M(\epsilon L)$. From this and $n = L/\epsilon$ we obtain

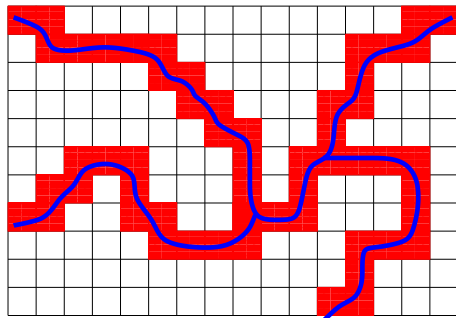
$$d_f = \lim_{\epsilon \rightarrow 0} \frac{\ln[M(\epsilon L)/M(L)]}{\ln \epsilon} \quad (1.48)$$



The 3rd iteration of the Sierpinski sponge



The first 4 iterations of the Cantor set



Box-counting determination of the fractal dimension

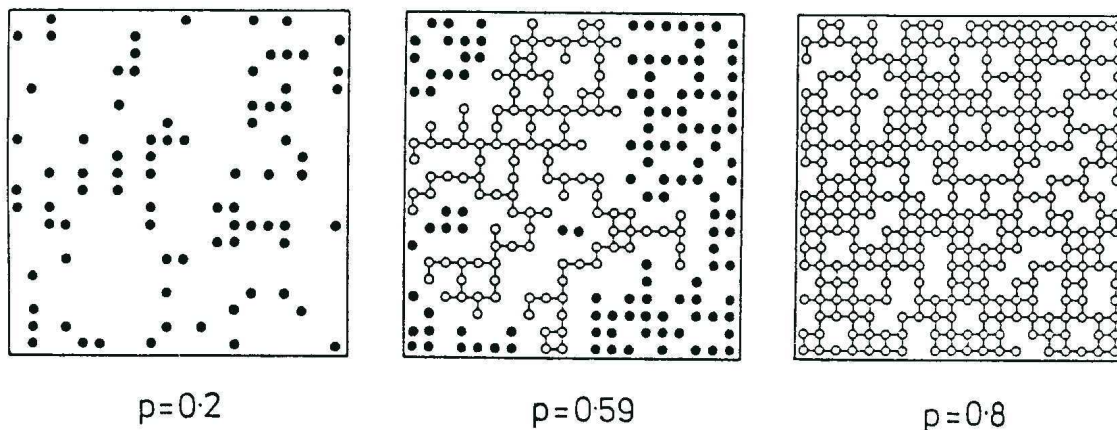
One can show that the *static structure factor* has a small- q dependence according to

$$S(q) \propto q^{-d_f} \quad (1.49)$$

This means that we can measure the fractal dimension of a real fractal can be measured by X-ray or neutron diffraction.

1.3.3 Percolation

An important model for a metal-nonmetal transition in a random mixture of a metal with a nonmetal is the *Percolation model*. At the same time it is a “toy model” for a thermodynamic phase transition. It has two versions, namely the *site percolation* model and the *bond percolation* model. In the site percolation model the sites of a d -dimensional lattice is occupied randomly by metal atoms according to the concentration p . If two neighboring sites are occupied they are called *connected*. Connected sites form a *cluster*. If a cluster extends through the system of linear extension L it is called percolation cluster. The critical concentration p_c for the metal-nonmetal transition is defined to be the smallest concentration for which a percolation cluster exists in the limit $L \rightarrow \infty$.



percolation clusters for 3 different concentrations p .

	site	bond
$d = 2$		
square l.	0.6	$\frac{1}{2}$
triangular l.	$\frac{1}{2}$	0.35
honeycomb l.	0.7	0.65
$d = 3$		
simple c.	0.31	0.25
f.c.c	0.20	0.12
b.c.c	0.25	0.18
simple c.	0.31	0.25
diamond	0.43	0.39

Fractal dimensions d_f of the site and bond percolation model

Lattice	β	ν
quadratic	$\frac{5}{36}$	$\frac{4}{3}$
simple c.	0.417	0.875

Critical dimensions β and ν corresponding to the order parameter $P(p)$ and correlation length $\xi(p)$. bond percolation model

In the bond percolation model *bonds* are randomly distributed on the elementary bonds on the lattice. All sites belonging to a bond are metallic sites and belong to a cluster of connected sites.

As can be seen from the table the percolation concentrations p_c depend not only on dimensionality but on the type of lattice and whether we have site percolation.

Right at $p = p_c$ the percolation cluster forms a fractal. The fractal dimension is *universal* as it depends only on the embedding dimension. For $d = 2$ we have $d_f = 1.9$, for $d = 3$ $d_f = 2.55$.

As in thermodynamic phase transitions one can define an *order parameter* $P(p)$, which is the probability of a site to belong to the percolation cluster. Obviously $P(p) = 0$ for $p < p_c$. For $p \geq p_c$ we have

$$P(p) \propto (p - p_c)^\beta \quad (1.50)$$

for p near p_c .

For $p \approx 1$ the percolation cluster is obviously not a fractal, as there are only a few vacancies which do not involve a scaling law. As in the theory of phase transitions one can define a *correlation length* $\xi(p)$, which has the property that for length scales $L < \xi$ the percolation cluster looks like a fractal, i.e. $M(L) \propto L^{d_f}$, whereas for $L > \xi$ $M(L) \propto L^d$ holds. Near p_c we have the critical law

$$\xi(p) \propto (p - p_c)^{-\nu} \quad (1.51)$$

1.4 Diffusion equation and mean-square displacement

We consider the diffusion process of a Brownian particle in a solvent, which is historically the first “random walk”, which was treated in one of Einstein’s seminal papers of 1905.

We first consider only motions in the x -direction. We start with the continuity equation for the time dependence of the particle density $\rho(x, t)$ and the current density $j(x, t) = \rho v$, which holds due to the conservation of the total number of Brownian particles:

$$\frac{\partial \rho}{\partial t} + \frac{\partial j}{\partial x} = 0. \quad (1.52)$$

For the current density we have *Fick’s law*, which states that the compensating diffusion current flows always against a momentary concentration gradient. The proportionality constant is called *diffusion constant* D .

$$j(x, t) = -D \nabla \rho(x, t) \quad (1.53)$$

if we then insert (1.53) into (1.52) we obtain the (one-dimensional) *diffusion equation*

$$\frac{\partial \rho}{\partial t} - D \frac{\partial^2 \rho}{\partial x^2} = 0. \quad (1.54)$$

Going over to a spatial Fourier transform

$$\rho(k, t) = \int_{-\infty}^{\infty} dx e^{ikx} \rho(x, t) \quad (1.55)$$

and a temporal Laplace transform

$$\rho(k, p) = \int_0^{\infty} dt e^{-pt} \rho(k, t) \quad (1.56)$$

we obtain from (3.3)

$$p\rho(k, p) - \rho(k, t=0) + Dk^2\rho(k, p) = 0 \quad (1.57)$$

with the solution

$$\rho(k, p) = \frac{\rho(k, t=0)}{p + Dk^2} = \rho(k, t=0)G(k, p) \quad (1.58)$$

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

$$G(k, t=0) = 1 \quad (1.59)$$

corresponding to

$$G(x, t=0) = \delta(x) \quad (1.60)$$

$G(x, t)$ 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

$$G(k, t) = e^{-Dk^2t} \quad (1.61)$$

and

$$G(x, t) = \frac{1}{\sqrt{4\pi Dt}} e^{-x^2/4Dt} \quad (1.62)$$

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

$$\langle x^2(t) \rangle = \int_{-\infty}^{\infty} dx x^2 G(x, t) \quad (1.63a)$$

$$= -\frac{\partial^2}{\partial k^2} \int_{-\infty}^{\infty} dx e^{ikx} G(x, t) \Big|_{k=0} \quad (1.63b)$$

$$= -\frac{\partial^2}{\partial k^2} e^{-Dk^2t} \Big|_{k=0} \quad (1.63c)$$

$$= 2Dt \quad (1.63d)$$

This is the second formula in the theory of Brownian motion which carries Einstein's name. It states that the 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

$$\frac{\partial \rho(\mathbf{r}, t)}{\partial t} - D \nabla^2 \rho(\mathbf{r}, t) = 0. \quad (1.64)$$

with solution

$$G(\mathbf{k}, t) = \int_{-\infty}^{\infty} d^3 \mathbf{r} e^{i\mathbf{k} \cdot \mathbf{r}} G(\mathbf{r}, t) = e^{-Dk^2 t}, \quad (1.65)$$

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

$$G(\mathbf{r}, t) = \left[\frac{1}{\sqrt{4\pi Dt}} \right]^3 e^{-r^2/4Dt} \quad (1.66)$$

with $r^2 = |\mathbf{r}|^2 = x^2 + y^2 + z^2$. For the three-dimensional mean-square distance we obtain the Einstein relation

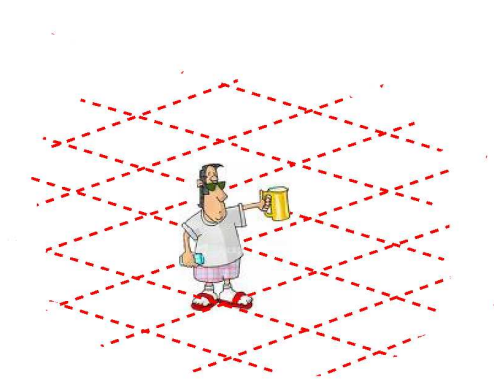
$$\langle r^2(t) \rangle = \int_{-\infty}^{\infty} d^3 \mathbf{r} (x^2 + y^2 + z^2) G(\mathbf{r}, t) \quad (1.67a)$$

$$= - \left(\frac{\partial^2}{\partial k_x^2} + \frac{\partial^2}{\partial k_y^2} + \frac{\partial^2}{\partial k_z^2} \right) \int_{-\infty}^{\infty} d^3 \mathbf{r} e^{i\mathbf{k} \cdot \mathbf{r}} G(\mathbf{r}, t) \Big|_{k_x=k_y=k_z=0} \quad (1.67b)$$

$$= - \left(\frac{\partial^2}{\partial k_x^2} + \frac{\partial^2}{\partial k_y^2} + \frac{\partial^2}{\partial k_z^2} \right) e^{-Dk^2 t} \Big|_{k_x=k_y=k_z=0} \quad (1.67c)$$

$$= 6Dt \quad (1.67d)$$

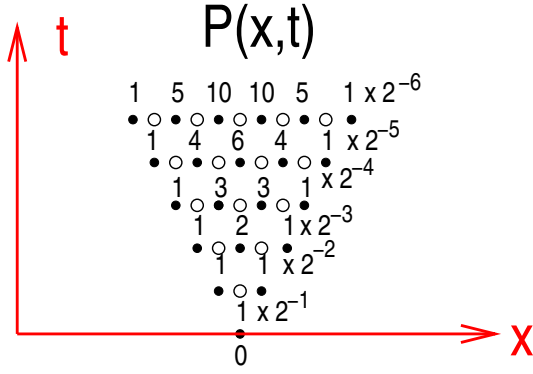
1.5 Random walk on a lattice



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 probabilities $P(x = a, t = \tau)$ 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 ν th 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 $\binom{\nu}{k}$, 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.

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

$$P(x_n, t + \tau) = \left(\frac{1}{2}\right)^{\nu+1} \binom{\nu+1}{k_{n,\nu+1}} = \frac{1}{2}P(x_{n+1}, t) + \frac{1}{2}P(x_{n-1}, t) \quad (1.70)$$

This can be re-written as

$$\frac{P(x_n, t + \tau) - P(x, t)}{\tau} = D \left[\frac{P(x_n + a) + P(x_n - a, t) - 2P(x, t)}{a^2} \right] \quad (1.71)$$

with

$$D = \frac{a^2}{2\tau} \quad (1.72)$$

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

$$\frac{\partial P(x, t)}{\partial t} = D \frac{\partial^2}{\partial x^2} P(x, t) \quad (1.73)$$

This is just the diffusion equation for the Brownian motion encountered in the previous section. So the Function $G(x, t)$ is just the continuum limit of the random walk probability.

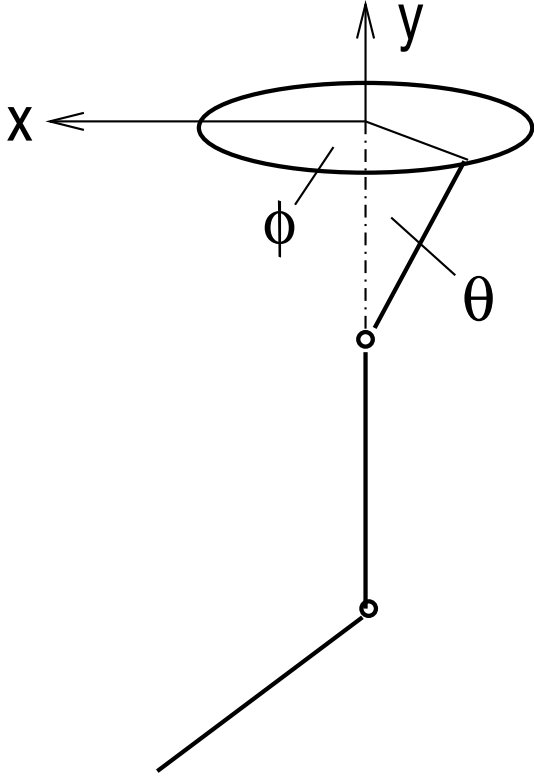
$$P(x_n, \nu\tau) = \left(\frac{1}{2}\right)^\nu \binom{\nu}{k} \quad k = \left\lceil \frac{1}{2}(n + \nu) \right\rceil, \quad (1.68)$$

where $\lceil \nu \rceil$ is the smallest integer κ with $\kappa \geq \nu$. It is worth while 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

$$\binom{n+1}{k} = \binom{n}{k} + \binom{n}{k-1} \quad (1.69)$$

1.6 Random Walks and polymers



Three 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. In particular, we can calculate the *radius of gyration* R_0 , which is the square-root of the mean square end-to-end distance:

$$R_0^2 = \left\langle \left[\sum_{n=1}^N \mathbf{b}_n \right]^2 \right\rangle = Nb^2 + \sum_{n=1}^N \sum_{\nu=1}^{\nu_{\max}} [C(\nu) + C(-\nu)] = Nb^2 \quad (1.75)$$

The second equality holds, because the correlations have all values between a^2 and $-a^2$ with equal probability, i.e they average to zero. However, in reality this might not be so, but in cases, where one can neglect the *volume exclusion* of the polymer chain the radius of gyration will be proportional to \sqrt{N} and we use a instead of b for the proportionality coefficient:

$$R_0^2 = a^2 N \quad (1.76)$$

So – for the time being – we can state that a polymer chain behaves like an ideal chain as modelled by a random walk with

$$2Dt = Na^2 \quad (1.77)$$

Let us discuss relation (1.6) for a moment. It states that the size of a random walk or ideal polymer chain scales with its “mass” as

$$N(L) \propto L^2 \quad (1.78)$$

This means that the fractal dimension d_f of a random walk is equal to 2 in any embedding dimension. In order to do statistical mechanics of Polymers we would like to calculate the statistical weight for averaging over different ways of random walks with a fixed end-to-end distance R . We first calculate the probability that a walker is inside a sphere with radius R

$$P_R = 4\pi \int_0^R dr r^2 P(r, N) \quad (1.79)$$

The desired quantity is

On a microscopic level a polymer chain mainly consists of a *backbone* of beads to which some *side groups* are attached. In addition there can be *branching* and *cross-linking*. There is usually a very limited range of possible *bond angles* between the beads. The angle θ between the beads is usually fixed, but the *azimuthal* or *Dieder* angle ϕ can have different values, e.g. $\phi = 0^\circ$ (*cis*), $\phi = 60^\circ$ (*gauche*), or $\phi = 180^\circ$ (*cis*), where the latter is usually the most stable position. Between the bond angle positions there are energetic barriers $\Delta\epsilon$, which the chain has to overcome for changing the angle. If the temperature is much higher than these energy barriers, the chain will acquire some freedom to form a curvature, i.e. the directions of the beads will start to fluctuate statistically. Let us denote by \mathbf{b}_n the vector pointing from one chain connection to another. Let us assume that they have all the same length a . Then we can be interested in the following correlation function

$$C(\nu) = \langle \mathbf{b}_{n+\nu} \cdot \mathbf{b}_n \rangle \quad (1.74)$$

This function will decay exponentially with increasing ν with a characteristic decay constant $\nu_0 = \ell_0/a$, where ℓ_0 is the decay length. For length scales larger than ℓ_0 the chain will behave as an *ideal polymer chain* i.e. like a *random walk* if we for a moment disregard the volume exclusion condition.

$$Z(R, N) = \frac{dP_R}{dR} = 4\pi R^2 [2\pi R_0^2]^{-3/2} e^{-R^2/2R_0^2} \quad (1.80)$$

From this we obtain the entropy

$$S_{\text{id}}(R, N) = k_B \ln[Z(R, N)] = -k_B \frac{R^2}{2R_0^2} + k_B \ln[4\pi R^2] - (3/2)k_B \ln[2\pi R_0^2] \quad (1.81)$$

and free energy

$$F_{\text{id}} = -TS_{\text{id}} = k_B T \frac{R^2}{2R_0^2} - k_B T \ln[4\pi R^2] - (3/2)k_B \ln[2\pi R_0^2] = F_0 + k_B T \frac{R^2}{2R_0^2} \quad (1.82)$$

From this we can calculate for example 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

$$F_f = -fx + F_0 + k_B T \frac{x^2 + y^2 + z^2}{2R_0^2} \quad (1.83)$$

Minimizing F_f with respect to x yields

$$x = f \frac{R_0^2}{k_B T} = f \frac{Na^2}{k_B T} \quad (1.84)$$

A quantity of interest is the *radial pair correlation function of monomers* $\tilde{g}(r)$ which is just the counter part of this quantity in simple liquids. In simple liquids $g(r)$ was defined in such a way that for large r the integral

$$\rho_0 4\pi \int_0^{R_{\text{max}}} dr r^2 g(r) = \frac{4}{3} R_{\text{max}}^3 \frac{N}{V} = N \quad (1.85)$$

where $\rho_0 = N/V$ is the number density of molecules. Here we identify ρ_0 with the number density of monomers and include the factor ρ_0 in the definition of the correlation function:

$$\tilde{g}(r) = \rho_0 g(r) \quad (1.86)$$

so that we have

$$4\pi \int_0^\infty dr r^2 \tilde{g}(r) = N \quad (1.87)$$

We now try to figure out a scaling form of $\tilde{g}(r)$. As this function has the dimension Length^{-3} we make the ansatz

$$\tilde{g}(r) = A \frac{N}{R_0^3} f\left(\frac{r}{R_0}\right) \quad (1.88)$$

We now realize that inside a sphere of radius r^* we must have

$$4\pi \int_0^{r^*} dr r^2 \tilde{g}(r) = n, \quad (1.89)$$

where n is the number of monomers inside the sphere of radius r^* . According to the random walk rule of the ideal chain we must have

$$(r^*)^2 \propto na^2, \quad (1.90)$$

which can only be reconciled with (1.89) if the function $f(x)$ is proportional to x^{-1} . We therefore obtain

$$\tilde{g}(r) = A \frac{N}{R_0^3} \frac{R_0}{r} = A \frac{1}{ra^2}. \quad (1.91)$$

This is the so-called *Debye correlation function*. It has the Fourier transform

$$\tilde{S}(k) = 4\pi A \frac{1}{q^2}. \quad (1.92)$$

1.7 The fractal dimension of a self-avoiding walk

In subsection 1.6 we mentioned that the *random walk* if studied as a function of the steps N is, in fact a fractal with $d_f = 2$ in any imbedding dimension d . Such an object might be a model for a polymer, if – and this is an important if – it were not for the fact that a polymer cannot intersect itself, i.e. the 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 estimate the mean repulsive energy as follows:

$$E = \rho_0^2 \int_V d^3\mathbf{r} \int_V d^3\mathbf{r}' g(|\mathbf{r} - \mathbf{r}'|) \phi(|\mathbf{r} - \mathbf{r}'|) \quad (1.93)$$

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

$$g(r)\phi(r) \approx \epsilon \delta(r - d), \quad (1.94)$$

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

$$E = \rho_0^2 V \epsilon = \epsilon N^2 / R^3 \quad (1.95)$$

We can now write down the free energy

$$\begin{aligned} F &= E - TS \\ &= \epsilon N^2 / R^3 + k_B T \ln[Z(R, N)] \\ &= \epsilon N^2 / R^3 + k_B T \frac{R^2}{2a^2 N} - k_B T \ln[4\pi R^2] - (3/2)k_B \ln[2\pi a^2 N] \end{aligned} \quad (1.96)$$

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.

$$0 = \frac{\partial F(R, N)}{\partial R} = -3 \frac{\epsilon N^2}{R^4} + \frac{k_B T R}{a^2 N} - \frac{2k_B T}{R}, \quad (1.97)$$

from which follows

$$\frac{R^2}{Na^2} = 3 \frac{N^2 \epsilon}{R^3 k_B T} + 2 \quad (1.98)$$

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

$$N(R) = \left[\frac{k_B T}{3\epsilon a^2} \right]^{1/3} R^{5/3} \quad (1.99)$$

1.8 Cayley tree and gelation

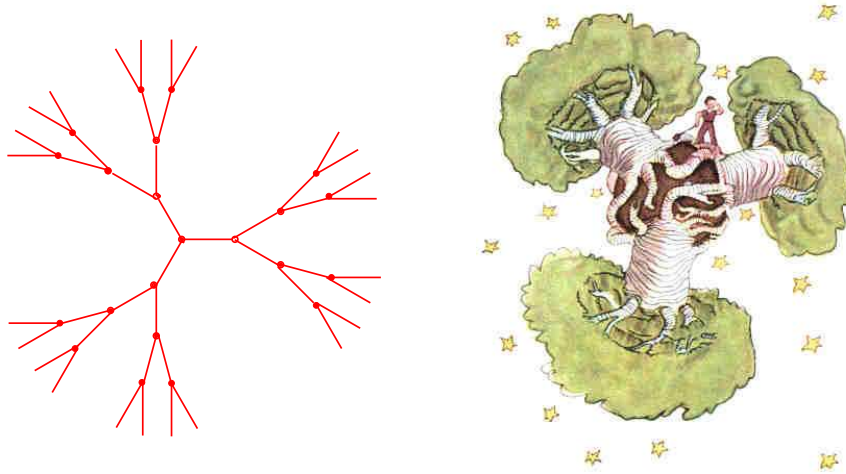
We now no more consider polymers with monomer units that have bonds to $Z = 2$ nearest neighbors but *branched* macromolecules with $Z > 2$. Of course the branching may occur in reality only every N_m th monomer unit with $N_m \gg 1$. This can be easily incorporated into the considerations by rescaling the fundamental length scale.

One can take a d -dimensional lattice with coordination number Z , which is for a hypercubic lattice just $Z = 2d$ and consider the case that only a fraction of p nearest-neighbor bonds are completed. This just defines a *bond percolation model* as discussed in section 4.6. if p is very small, only isolated clusters appear. A system of network-forming polymer units, in which only a small fraction has formed clusters of finite size is called a *sol*. Beyond a critical concentration p_c the network extends through the entire system and a *gel* is formed. The percolation transition in the gelation process is called *sol-gel* transition and is – as the percolation transition – a second-order phase transition, although the control parameter is not the

temperature but the bond concentration. However, if one considers a bond-breaking mechanism, which is thermally activated

$$q = 1 - p \propto e^{-E_A/k_B T} \quad (1.100)$$

one has transformed the p controlled phase transition to an ordinary T controlled transition, in which the sol phase is the high-temperature phase. In other important gelation processes (e.g. rubber vulcanisation egg boiling, baking) the *bond forming* is thermally activated, which leads to gelation at high temperatures.



Left: Bethe lattice or Cayley tree with $Z = 3$ and $n = 4$. Right: Cayley tree as drawn by Antoine de Saint-Exupéry

The first mean-field-type ideas in discussing this transition have been formulated by Flory and Stockmayer (1943), who considered a network without closed loops. Such a network is called a *Bethe lattice* (or *Cayley tree*, see the Figure) with branching order (or *functionality*) Z : One starts with a point from which Z branches start. These branches lead at every vertex to $Z - 1$ further outgoing branches. The number of nodes N increases with the number n of generations as

$$\Delta N(n) = N(n) - N(n - 1) = Z(Z - 1)^{n-1} \quad (1.101)$$

One can now consider the case in which the bonds are formed with probability p . In this case ΔN is given by

$$\Delta N(p, n) = pZ[p(Z - 1)]^{n-1} \quad (1.102)$$

If $p < p_c = 1/(Z - 1)$ the series $N(n)$ can be summed, i.e. on the average one obtains only a finite Cayley tree of size

$$\langle N \rangle = 1 + \frac{pZ}{1 - p(Z - 1)} = \frac{1 + p}{1 - p(Z - 1)} = p_c \frac{1 + p}{p_c - p}. \quad (1.103)$$

For $p \rightarrow p_c$ $\langle N \rangle$ diverges, which is then identified with the gelation threshold. As we did not make any assumption for the *angles* between successive bonds they are to be taken randomly, so that the *size* of the cluster will obey the random walk rule and is proportional to $\sqrt{\langle N \rangle}$:

$$R_Z \propto \xi \propto (p_c - p)^{-\nu} \quad (1.104)$$

with $\nu = 1/2$, which is the Flory-Stockmayer mean-field correlation length exponent.

We are now going to discuss the regime inside the gel phase. Let Q be the probability for the termination of a branch which emanates from a certain node. If the bond is absent (probability $1 - p$) $Q = 1$. If the bond is present (probability p) Q is equal to the probability for the termination of $Z - 1$ further branches. Therefore we have

$$Q = 1 - p + pQ^{Z-1}, \quad (1.105)$$

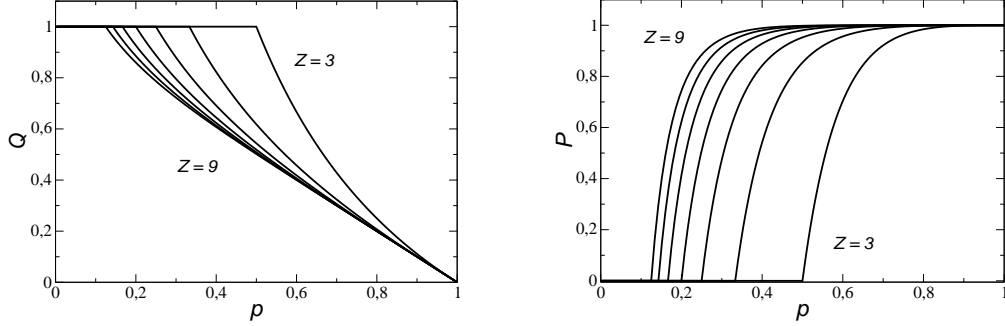
which is a closed equation for Q , albeit a nonlinear one. Obviously $Q = 1$ for $p < p_c$. For $p > p_c$ Q must be smaller than one. For $p \rightarrow p_c$ the deviation from 1 will be infinitesimally small:

$$Q = 1 - \epsilon \quad (1.106)$$

so that we can linearize (1.105):

$$1 - \epsilon = 1 - p + p[1 - (Z - 1)\epsilon] \quad (1.107)$$

Equating the coefficients of ϵ yields again $p_c = 1/(Z - 1)$.



Left: Probability Q for termination of a branch for $Z = 3$ to $Z = 9$. Right: Probability P for a node to be part of an infinite cluster for $Z = 3$ to $Z = 9$.

The numerical solution of (1.105) for $Q(p)$ is depicted in the left part of the figure. For $Z = 3$ the self consistent equation (1.105) can be evaluated analytically, as it is in this case a quadratic equation. The two solutions are

$$Q_1(p) = 1 \quad Q_2(p) = \frac{1-p}{p} = 1 - 2\frac{p-p_c}{p} \quad (1.108)$$

They coincide at $p = p_c = 1/2$. As Q cannot be larger than one and must be smaller than one for $p > p_c$ the physical solution is $Q_1(p)$ for $p < p_c$ and $Q_2(p)$ for $p > p_c$.

In the gel phase $p > p_c$ we can be interested in the probability P for a given node to be part of an infinite cluster. This probability together with its critical exponent β has already been introduced in the section on percolation. It is the *order parameter* of the percolation transition. In the Flory-Stockmayer Cayleytree model this probability is, of course, zero for $p < p_c$. For $p > p_c$ there is a finite probability that all three branches terminate, which is just

$$1 - P = Q^Z \quad \Rightarrow \quad P = 1 - Q^Z. \quad (1.109)$$

In the case $Z = 3$ we obtain from (1.108)

$$P = 6\frac{p-p_c}{p} + O(|p-p_c|^2), \quad (1.110)$$

i.e. $\beta = 1$. As one can see from the right part of the figure, obviously $\beta = 1$ holds also for $Z > 3$. This result can be obtained rigorously in the following way: From (1.105) we can obtain the *inverse* of the function $Q(p) \equiv 1 - \epsilon$:

$$p(Q) = \frac{1-Q}{1-Q^{Z-1}} = \frac{\epsilon}{1-(1-\epsilon)^{Z-1}} \approx \frac{1}{Z-1} \frac{1}{1-\frac{1}{2}(Z-2)\epsilon} \approx \frac{1}{Z-1} \left(1 + \frac{1}{2}(Z-2)\epsilon\right) \quad (1.111)$$

From $P = 1 - (1 - \epsilon)^Z \approx Z\epsilon$ we obtain

$$P = \frac{2Z}{Z-2} \frac{p-p_c}{p_c}, \quad (1.112)$$

which, interestingly enough, becomes independent of Z for large Z .

The critical exponent of the mean-field theory of the Flory-Stockmayer model are, of course, quite different from those of the percolation model, which includes closed loops. However, in the vulcanization transition of rubber both the chain length N_m in between the cross-linking nodes as well as the functionality Z_{eff} is so high that the effect of closed loops in the network is negligible. So the Cayley-tree model gives quite realistic results for this case. In other cases the percolation theory is more adequate.

2 Green's functions and the electronic structure of disordered systems

2.1 Model Hamiltonians

2.1.1 Tight-Binding models

Tight-binding models of disordered systems start usually with an “ordered” Hamiltonian of a simple-cubic lattice

$$\mathcal{H}_0 = \sum_{\substack{i \neq j \\ \text{n.N.}}} t |i\rangle \langle j| \quad (2.1)$$

where t is the tight-binding matrix element, $\langle \mathbf{r} | i \rangle$ are Wannier functions corresponding to the lattice site at \mathbf{r}_i and “n.N” denotes “nearest Neighbor”. The eigenvalues (band structure) are

$$E(\mathbf{k}) = -2t \left[\cos(ak_x) + \cos(ak_y) + \cos(ak_z) \right] \quad (2.2)$$

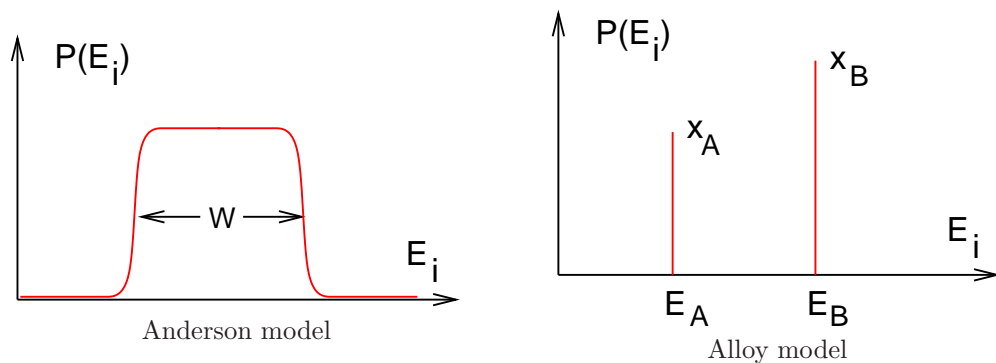
where a is the lattice constant. Near the lower band edge at $E_0 = -6t$ $E(\mathbf{k})$ can be expanded around $\mathbf{k} = 0$ to give

$$E(\mathbf{k}) = E_0 + ta^2 \left[k_x^2 + k_y^2 + k_z^2 \right] \equiv \frac{\hbar^2 k^2}{2m^*} \quad (2.3)$$

where the effective mass is given by $m^* = 1/2t\hbar^2 a^2$. By this identification one can have a correspondence with models starting from a free-electron Hamiltonian (see next paragraph).

The *disorder* can now be inserted by adding a local potential $E_i = v(\mathbf{r}_i)$:

$$\mathcal{H} = \mathcal{H}_0 + \underbrace{\sum_i E_i |i\rangle \langle i|}_v \quad (2.4)$$



The E_i are random variables with a continuous distribution (density) $P(E)$ of Width W , which can be a rectangular or a Gaussian distribution:

$$P(E) = \frac{1}{W} \begin{cases} -\frac{W}{2} \leq E & \text{for } \leq \frac{W}{2} \\ 0 & \text{else} \end{cases} \quad P(E) = \frac{1}{W\sqrt{2\pi}} e^{-E^2/2W^2} \quad (2.5)$$

This Hamiltonian has become very famous, as P. W. Anderson published 1958 his famous paper¹ stating that electrons in a random potential can become “localized”, i.e. their diffusion coefficient, which is related to their conductivity become zero if W exceeds a certain value (see chapter 4).

Another type of disorder is *alloy disorder*

$$P(E) = x_A \delta(E - E_A) + x_B \delta(E - E_B) \quad (2.6)$$

with $x_A + x_B = 1$.

We assume that the fluctuating potentials are uncorrelated

$$\langle E_i E_j \rangle = W^2 \delta_{ij} \quad \text{or} \quad \langle v(\mathbf{r}_i) v(\mathbf{r}_j) \rangle \propto W^2 \delta(\mathbf{r}_i - \mathbf{r}_j) \quad (2.7)$$

¹P. W. Anderson, *Absence of diffusion in certain random lattices* Phys. Rev. **109**, 1492 (1958)

so that we have

$$P(E_1, \dots, E_N) = \prod_{i=1}^N P(E_i) \quad (2.8)$$

One can also make the non-diagonal term disordered, which mimicks a covalently bonded disordered solid:

$$\mathcal{H} = \sum_{\substack{i \neq j \\ \text{n.N.}}} t(|\mathbf{r}_i - \mathbf{r}_j|) |i\rangle \langle j| \quad (2.9)$$

The distribution for this type of disorder is just given by the probability density $P(\mathbf{r}_1, \dots, \mathbf{r}_N)$ introduced in the last chapter.

2.1.2 Nearly-free-electron model

Starting point for this type of model Hamiltonians of disorder is the free-electron Hamiltonian

$$\mathcal{H} = \sum_{\mathbf{k}} \frac{\hbar^2 k^2}{2m} |\mathbf{k}\rangle \langle \mathbf{k}| \quad (2.10)$$

where

$$\langle \mathbf{r} | \mathbf{k} \rangle = \frac{1}{\sqrt{V}} e^{i\mathbf{k}\mathbf{r}} \quad (2.11)$$

are free electron wave functions normalized in a box of volume V with periodic boundary conditions, so that the \mathbf{k} sum is performed as $\sum_{\mathbf{k}} = \frac{V}{(2\pi)^3} \int d^3\mathbf{k}$. The *nearly-free electron* model (for amorphous metals) now adds a weak *Pseudopotential* at the atomic sites, from which the electrons are scattered:

$$\mathcal{H} = \mathcal{H}_0 + \mathcal{V} = \mathcal{H}_0 + \sum_{\mathbf{k}} \sum_{\mathbf{q}} W(\mathbf{q}) |\mathbf{k} + \mathbf{q}\rangle \langle \mathbf{k}| \quad (2.12)$$

\mathcal{V} is as in the tight-binding case a sum of potentials centered at the atomic sites.

$$\mathcal{V} = \sum_{i=1}^N v(\mathbf{r} - \mathbf{r}_i) \quad (2.13)$$

The disorder enters via that of the sites as in the tight-binding model with off-diagonal disorder. $W(q)$ is the matrix element $\langle \mathbf{k} | \mathcal{V} | \mathbf{k} + \mathbf{q} \rangle$, which is evaluated as

$$\begin{aligned} W(\mathbf{q}) &= \langle \mathbf{k} | \mathcal{V} | \mathbf{k} + \mathbf{q} \rangle = \int d^3\mathbf{r} \frac{1}{V} e^{-i\mathbf{k}\mathbf{r}} \sum_{i=1}^N v(\mathbf{r} - \mathbf{r}_i) e^{i(\mathbf{k}+\mathbf{q})\mathbf{r}} \\ &= \frac{1}{V} \sum_{i=1}^N e^{i\mathbf{q}\mathbf{r}_i} v(\mathbf{q}) \end{aligned} \quad (2.14)$$

where $v(\mathbf{q})$ is the Fourier transform of $v(\mathbf{r})$.

In the theory of metals the concept of *pseudopotentials* have been developed, because they take care of the fact that the outer valence electrons of the metals, the conduction electrons must avoid the bound electrons of the ionic core, because of the Pauli principle. More mathematically, their wave functions have to be orthogonal to the core functions. This “screens” the very deep nuclear potential, so that a most simple pseudopotential has been invented by Ashcroft² replaces just the Coulomb potential by zero inside a suitable core radius R_c

$$v(r) = \begin{cases} -\frac{Ze}{4\pi\epsilon_0 r} & \text{for } r > R_c \\ 0 & \text{else} \end{cases} \quad (2.15)$$

A further modification of the disorder-induced scattering potential is introduced by the *screening of the conduction electrons*. The most important effect of the repulsive Coulomb interaction between the negatively charged electrons has been shown to be the mutual screening of their interaction, turning it to a short-ranged interaction of the type

$$-\frac{Ze}{4\pi\epsilon_0 r} \rightarrow -\frac{Ze}{4\pi\epsilon_0 r} e^{-\lambda} \quad (2.16)$$

²N. W. Ashcroft, Phys. Lett. **23**, 48 (1966)

where λ is the *Debye-Hückel-Thomas-Fermi* screening length given by

$$\lambda^2 = \frac{e^2}{\epsilon_0} \frac{\partial n}{\partial \mu} \quad (2.17)$$

where n is the number of charge carriers per volume and μ is the chemical potential. For classical charged particles in a plasma $\partial n / \partial \mu = n / k_B T$, for a degenerate electron gas $\partial n / \partial \mu = N(E_F) = n g(E_F)$, which is the density of states at the Fermi level $E_F = \mu$. Our model expression for $w(\mathbf{q})$ now becomes

$$w(\mathbf{q}) = -\frac{1}{\epsilon_0} \frac{Z e^2}{q^2 + \lambda^2}. \quad (2.18)$$

2.2 Green's functions

2.2.1 Definition

In the field of disordered materials the Green's function concept is indispensable. We start with the one-electron Schrödinger equation

$$\mathcal{H} \psi(\mathbf{r}, t) = i\hbar \frac{\partial}{\partial t} \psi(\mathbf{r}, t) \quad (2.19)$$

As one wants to make use extendedly of models with Hamiltonians $\mathcal{H} = \mathcal{H}_0 + \mathcal{V}$, where \mathcal{V} describes the disorder, one wants to treat the part $\mathcal{V}\psi$ like an unknown source term, i.e. one treats the Schrödinger equation like an inhomogeneous differential equation. Special solutions of inhomogeneous differential equations are given in terms of the Green's function, which obeys the inhomogeneous equation with a δ function inhomogeneity:

$$\left(i\hbar \frac{\partial}{\partial t} - \mathcal{H}_0 \mp i\epsilon \right) G_{\pm}^{(0)}(\mathbf{r}, \mathbf{r}', t, t') = \delta(\mathbf{r} - \mathbf{r}') \delta(t - t') \quad (2.20)$$

The term $\mp i\epsilon$ has been inserted, because in its absence the term inside the bracket would be singular. One can also define the *full Greens' function* as

$$\left(i\hbar \frac{\partial}{\partial t} - \mathcal{H} \mp i\epsilon \right) G_{\pm}(\mathbf{r}, \mathbf{r}', t, t') = \delta(\mathbf{r} - \mathbf{r}') \delta(t - t') \quad (2.21)$$

G_+ is called *advanced* Green's function, G_- *retarded* Green's function, We now assume that \mathcal{H} is stationary, so that we obtain the Eigenvalue problem

$$\mathcal{H} |\psi_n \rangle = E_n |\psi_n \rangle \quad (2.22)$$

and we have

$$\psi(\mathbf{r}, t) = e^{-\frac{i}{\hbar} E_n t} \underbrace{\psi_n(\mathbf{r})}_{\langle \mathbf{r} | \psi_n \rangle} \quad (2.23)$$

One can show (Exercises!) that (2.21) is solved by

$$G_{\pm}(\mathbf{r}, \mathbf{r}', t, t') = \pm \frac{i}{\hbar} \sum_n \psi_n(\mathbf{r}) \psi_n^*(\mathbf{r}') e^{-(i/\hbar)[E_n \pm i\epsilon](t-t')} \theta(\mp(t-t')) \quad (2.24)$$

As the Green's function depends only on the time difference $\tau = t - t'$ we can perform a Fourier transform with respect to τ :

$$G_{\pm}(\mathbf{r}, \mathbf{r}', \omega) = \int_{-\infty}^{\infty} d\tau e^{i\omega\tau} G_{\pm}(\mathbf{r}, \mathbf{r}', \tau) = \sum_n \frac{\psi_n(\mathbf{r}) \psi_n^*(\mathbf{r}')}{\underbrace{\hbar\omega \mp i\epsilon - E_n}_{z_{\pm}}} \quad (2.25)$$

We define now the *resolvent operator* (or "Green operator") as

$$\mathcal{G}(z) = [z\mathbb{1} - \mathcal{H}]^{-1} \equiv \frac{1}{z - \mathcal{H}} \quad (2.26)$$

from which we obtain

$$G_{\pm}(\mathbf{r}, \mathbf{r}', \omega) = \langle \mathbf{r} | \frac{1}{z_{\pm} - \mathcal{H}} | \mathbf{r}' \rangle = \langle \mathbf{r} | \mathcal{G}(z_{\pm}) | \mathbf{r}' \rangle \quad (2.27)$$

One can, of course also consider matrix elements of $\mathcal{G}(z)$ in an arbitrary basis $|\alpha\rangle$

$$G_{\alpha\beta}(z) = \langle \alpha | \mathcal{G}(z) | \beta \rangle . \quad (2.28)$$

In particular we shall make use of the plane wave basis normalized with the sample volume V and periodic boundary conditions

$$\langle \mathbf{r} | \mathbf{k} \rangle = \frac{1}{\sqrt{V}} e^{i\mathbf{k}\mathbf{r}}; \quad \langle \mathbf{k} | \mathbf{r} \rangle = \frac{1}{\sqrt{V}} e^{-i\mathbf{k}\mathbf{r}} . \quad (2.29)$$

Relation to the density of states Let us consider the difference of the trace of the resolvent taken with z just above and below the real axis:

$$\begin{aligned} \text{Tr}\{\mathcal{G}(z_+) - \mathcal{G}(z_-)\} &= \sum_n \left[\frac{1}{\underbrace{\hbar\omega}_{E} - i\epsilon - E_n} - \frac{1}{\underbrace{\hbar\omega}_{E} + i\epsilon - E_n} \right] \\ &= 2i \text{Im} \left\{ \text{Tr}\{\mathcal{G}(z_+)\} \right\} = -2i \text{Im} \left\{ \text{Tr}\{\mathcal{G}(z_-)\} \right\} \\ &= \sum_n \frac{2i\epsilon}{(E - E_n)^2 + \epsilon^2} \xrightarrow{\epsilon \rightarrow 0} 2\pi i \sum_n \delta(E - E_n) \end{aligned} \quad (2.30)$$

In the limit $\epsilon \rightarrow 0$ we obtain

$$g(E) = \frac{1}{n} N(E) = \frac{1}{\pi N} \text{Im} \left\{ \text{Tr}\{\mathcal{G}(z_+)\} \right\} = -\frac{1}{\pi N} \text{Im} \left\{ \text{Tr}\{\mathcal{G}(z_-)\} \right\} \quad (2.31)$$

2.3 Approximation methods

2.3.1 Perturbation expansion and self-consistent Born approximation (SCBA)

We now consider a Hamiltonian of the form

$$\mathcal{H} = \mathcal{H}_0 + \mathcal{V} \quad (2.32)$$

From the operator identity $\frac{1}{A+B} = \frac{1}{A} \left(1 - \frac{B}{A+B}\right)$ we obtain

$$\mathcal{G}(z) = \frac{1}{z - \mathcal{H}_0} \left(1 + \mathcal{V} \frac{1}{z - \mathcal{H}}\right) = \mathcal{G}_0(z) \left(1 + \mathcal{V} \mathcal{G}(z)\right), \quad (2.33)$$

which one can iterate to obtain

$$\begin{aligned} \mathcal{G} &= \mathcal{G}_0 + \mathcal{G}_0 \mathcal{V} \mathcal{G}_0 + \mathcal{G}_0 \mathcal{V} \mathcal{G}_0 \mathcal{G}_0 \mathcal{V} \mathcal{G}_0 + \dots \\ &= \mathcal{G}_0 + \mathcal{G}_0 \frac{\mathcal{V}}{1 - \mathcal{V} \mathcal{G}_0} \mathcal{G}_0 \\ &\equiv \mathcal{G}_0 + \mathcal{G}_0 \mathcal{T} \mathcal{G}_0, \end{aligned} \quad (2.34)$$

where we have defined the *scattering matrix* or *T-matrix* \mathcal{T} .

We now consider a *disordered metal* composed of atoms centered at \mathbf{r}_n in an irregular way, so that the $\{\mathbf{r}_n\}$ do *not* form a lattice. The structural information is contained in the probability distribution $P(\mathbf{r}_1, \dots, \mathbf{r}_{N_a})$, (where N_a is the number of atoms) and in particular the radial pair distribution function $g(|\mathbf{r}_i - \mathbf{r}_j|)$ and its Fourier transform $S(q) = 1 + \rho \int d^3\mathbf{r} e^{i\mathbf{q}\mathbf{r}} [g(r) - 1]$ (see paragraph 2.1.1). The electron-atom potential is assumed to have the form

$$\mathcal{V}(\mathbf{r}) = \sum_{n=1}^{N_a} v(|\mathbf{r} - \mathbf{r}_n|) \quad (2.35)$$

from which follows

$$\langle \mathbf{k} + \mathbf{q} | \mathcal{V} | \mathbf{k} \rangle = \frac{1}{V} \sum_{n=1}^{N_a} e^{i\mathbf{q}\mathbf{r}_n} v(q) \quad (2.36)$$

where $v(\mathbf{q}) = v(q)$ is the Fourier transform of $v(\mathbf{r}) = v(r)$. The electronic Hamiltonian is then composed as

$$\mathcal{H} = \mathcal{H}_0 + \mathcal{V} \quad (2.37)$$

where \mathcal{H}_0 is assumed to be a *free-electron Hamiltonian*

$$\mathcal{H}_0 | \mathbf{k} \rangle = E_{\mathbf{k}}^{(0)} | \mathbf{k} \rangle = \left(\frac{\hbar^2 k^2}{2m} + C \right) | \mathbf{k} \rangle \quad (2.38)$$

where C is an arbitrary constant.

We further denote an average over the distribution $P\{\mathbf{r}_n\}$ by $\langle \dots \rangle$.

Before we proceed further we interest ourselves in the average $\langle \mathcal{V} \rangle$ of the potential. This is just a number and we shift our energy scale (i.e. the parameter C such that this number is set to zero:

$$\langle \mathcal{V} \rangle = 0 \quad (2.39)$$

In order to be able to calculate the density of states of the disordered metal we become interested in the *configurationally averaged resolvent*

$$\mathbf{G}(z) = \langle \mathcal{G}(z) \rangle = \left\langle \frac{1}{z - \mathcal{H}_0 - \mathcal{V}} \right\rangle \equiv \frac{1}{z - \mathcal{H}_0 - \Sigma(z)} \quad (2.40)$$

Here we have introduced an unknown operator $\Sigma(z)$ which looks like an effective potential of a fictitious system which is not disordered but, instead, depends on a complex parameter z . This (yet unknown) operator is called *self-energy operator*. We now insert the perturbation expansion (2.34) into (2.40) and solve for $\Sigma(z)$:

$$\begin{aligned} \Sigma(z) &= z - \mathcal{H}_0 - \frac{1}{\langle \mathcal{G}(z) \rangle} \\ &= \frac{1}{\mathcal{G}_0} - \frac{1}{\mathcal{G}_0 + \underbrace{\mathcal{G}_0 \langle \mathcal{V} \rangle \mathcal{G}_0}_{0} + \mathcal{G}_0 \langle \mathcal{V} \mathcal{G}_0 \mathcal{V} \rangle \mathcal{G}_0 + \dots} \\ &= \frac{1}{\mathcal{G}_0} \left(1 - \frac{1}{1 + \langle \mathcal{V} \mathcal{G}_0 \mathcal{V} \rangle \mathcal{G}_0 + \dots} \right) \end{aligned} \quad (2.41)$$

To second order in \mathcal{V} we get

$$\Sigma(z) = \frac{1}{\mathcal{G}_0(z)} \langle \mathcal{V} \mathcal{G}_0(z) \mathcal{V} \rangle \mathcal{G}_0(z). \quad (2.42)$$

We now use the $| \mathbf{k} \rangle$ basis. The density of states is given by

$$N(E) = \frac{1}{\pi V} \sum_{\mathbf{k}} \underbrace{\langle \mathbf{k} | \mathbf{G}(z_+) | \mathbf{k} \rangle}_{G(k,z)} \quad (2.43)$$

$G(k, z)$ is at the same time the Fourier transform of the averaged Green's function

$$\langle G(\mathbf{r}, \mathbf{r}', z) \rangle = G(\mathbf{r} - \mathbf{r}', z) \quad (2.44)$$

with respect to the variable $\mathbf{r} - \mathbf{r}'$. The relation (2.44) holds because the averaged material is assumed to be homogeneous. This is tantamount to stating that both $\mathbf{G}(z)$ as well as $\Sigma(z)$ are diagonal in the $| \mathbf{k} \rangle$ representation.

We now can write down the diagonal element of the self-energy operator, which is called the *self-energy function* to second order in \mathcal{V} :

$$\begin{aligned} \Sigma(k, z) &= \langle \mathbf{k} | \Sigma(z) | \mathbf{k} \rangle = \sum_{\mathbf{q}} \frac{1}{G_0(k, z)} \left\langle \langle \mathbf{k} | \mathcal{V} | \mathbf{k} + \mathbf{q} \rangle G_0(|\mathbf{k} + \mathbf{q}|, z) \langle \mathbf{k} + \mathbf{q} | \mathcal{V} | \mathbf{k} \rangle \right\rangle G_0(k, z) \\ &= \frac{N}{V^2} \sum_{\mathbf{q}} \frac{1}{N} \underbrace{\left\langle \sum_{\ell m} e^{i\mathbf{q}(\mathbf{r}_\ell - \mathbf{r}_m)} \right\rangle}_{S(q)} |v(q)|^2 G_0(|\mathbf{k} + \mathbf{q}|, z) = \Sigma'(k, E) + i\Sigma''(k, E) \end{aligned} \quad (2.45)$$

This approximation is known as the *Born approximation for disorder* in the literature.

Let us discuss our result:

The real part of $\Sigma(\mathbf{k}, z)$ produces a *shift* (“renormalization”) of the “band structure”:

$$E_{\mathbf{k}} \equiv E_{\mathbf{k}}^{(0)} + \Sigma'(k, E) \quad (2.46)$$

The density of states now takes the form

$$N(E) = \frac{1}{\pi V} \sum_{\mathbf{k}} \frac{\Sigma''(k, E)}{[E_{\mathbf{k}}]^2 + [\Sigma''(k, E)]^2} \quad (2.47)$$

The imaginary part of $\Sigma(\mathbf{k}, z)$ introduces a new element into the density of states of our amorphous metal: The function $E_{\mathbf{k}}$ is no more sharply defined but is “washed out” by the disorder-induced imaginary part of $\Sigma(k, E)$. This is so, because neither a lattice \mathbf{k} vector nor the free-electron \mathbf{k} vector can serve as a “good quantum number” for labeling the electronic states. However, the latter serves as “approximate quantum number” but one has to deal with the fact that in this “approximate” basis the $E_{\mathbf{k}}$ resonances are washed out by disorder.

2.3.2 Single-site t matrices

We study now a Hamiltonian with “impurity disorder”, i.e. the disorder enters via a fluctuating energy, which is diagonal at a certain site i

$$\mathcal{V} = \sum_i E_i |i\rangle \langle i| \equiv \sum_i v_i \quad (2.48)$$

We now consider again the expansion of the resolvent (2.34) and insert (??)

$$\begin{aligned} \mathcal{G}(z) &= \mathcal{G}_0 + \mathcal{G}_0 \mathcal{V} \mathcal{G}_0 \cdots = \mathcal{G}_0 \sum_i v_i \mathcal{G}_0 \\ &= \mathcal{G}_0 + \sum_i \left(\mathcal{G}_0 v_i \mathcal{G}_0 + \mathcal{G}_0 v_i \mathcal{G}_0 + \dots \right. \\ &\quad \left. + \sum_{j \neq i} \mathcal{G}_0 v_i \mathcal{G}_0 v_j \mathcal{G}_0 + \dots + \sum_{k \neq j, i} \dots \right) \\ &= \mathcal{G}_0 + \sum_i \mathcal{G}_0 t_i \mathcal{G}_0 + \sum_i \sum_{j \neq i} \mathcal{G}_0 t_i \mathcal{G}_0 t_j \mathcal{G}_0 \\ &\quad + \sum_i \sum_{j \neq i} \sum_{k \neq j, i} \mathcal{G}_0 t_i \mathcal{G}_0 t_j \mathcal{G}_0 t_k \mathcal{G}_0 \dots \end{aligned} \quad (2.49)$$

Here we have introduced the so-called *single-site t matrix*

$$t_i = v_i \sum_{\nu=0}^{\infty} (v_i \mathcal{G}_0)^\nu = \frac{v_i}{1 - v_i \mathcal{G}_0} \quad (2.50)$$

Because the matrix element of v_i are taken with respect to the *same* sites i t_i is diagonal, i.e t is a complex number

$$t_i = v_i \sum_{\nu=0}^{\infty} (v_i \mathcal{G}_0)^\nu = \frac{v_i}{1 - v_i \mathcal{G}_0^{ii}} \quad (2.51)$$

where \mathcal{G}_0^{ii} is the matrix element of \mathcal{G}_0 with respect to i .

2.3.3 Lattice disorder: The coherent-potential approximation (CPA)

We study now a tight-binding Hamiltonian, which can be formally written as

$$\mathcal{H}_{\text{tb}} = \sum_{i=1}^{N_a} |i\rangle E_i \langle i| + \sum_{i \neq j} |i\rangle t_{ij} \langle j| \quad (2.52)$$

where E_i are the diagonal elements and t_{ij} the off-diagonal elements. $\langle \mathbf{r}|i \rangle = a(\mathbf{r} - \mathbf{r}_i) \approx \psi_{\text{at}}(\mathbf{r} - \mathbf{r}_i)$ are orbitals associated with the site i . We now consider a *simple cubic* lattice and assume that the local energies (“local potentials”) fluctuate from site to site, say with a Gaussian distribution

$$P(E_i) = \frac{1}{\sqrt{2\pi}\sigma} e^{-\frac{1}{2\sigma^2}(E_i - E_0)^2} \quad (2.53)$$

or, alternatively, with a binary-alloy distribution

$$P(E_i) = c_A \delta(E_i - E_A) + c_B \delta(E_i - E_B) \quad (2.54)$$

with $c_A + c_B = 1$. The off-diagonal elements are assumed to be constant and the reference energy E_0 is assumed to be zero (in the alloy case $E_0 = c_A E_A + c_B E_B = 0$). The Hamiltonian now takes the form

$$\mathcal{H}_{\text{dis}} = \sum_i |i \rangle E_i \langle i| + t \sum_{i \neq j} |i \rangle \langle j| \quad (2.55)$$

We now define an *effective medium*, in which the Green’s function is equal to the averaged Greens function and the on-site energies are set equal to a complex number $\Sigma(z)$, so that we obtain an effective frequency-dependent Hamiltonian of the effective medium

$$\mathcal{H}_{\text{eff}}(z) = \sum_i |i \rangle \Sigma(z) \langle i| + t \sum_{i \neq j} |i \rangle \langle j| \quad (2.56)$$

We now “dig a hole” into the effective medium near a specific site i_0 , where we replaxe the uniform self energy by the fluctuating energy E_{i_0} . This introduces a “Perturbation” into the effective medium at site i_0

$$\mathcal{H}_{\text{hole}} = \mathcal{H}_{\text{eff}}(z) + \underbrace{|i_0 \rangle (E_{i_0} - \Sigma(z)) \langle i_0|}_{\mathcal{V}_{i_0}} \quad (2.57)$$

We now want to have (*CPA postulate*)

$$\begin{aligned} \mathcal{G}_{\text{eff}}(z) &= \frac{1}{z - \mathcal{H}_{\text{eff}}(z)} \\ &= \left\langle \frac{1}{z - \mathcal{H}_{\text{hole}}(z)} \right\rangle \\ &= \mathcal{G}_{\text{eff}} + \left\langle \mathcal{G}_{\text{eff}} + \left(\mathcal{V}_{i_0} \mathcal{G}_{\text{eff}} + \mathcal{V}_{i_0} \mathcal{G}_{\text{eff}} \mathcal{V}_{i_0} \mathcal{G}_{\text{eff}} + \dots \right) \right\rangle \\ &= \mathcal{G}_{\text{eff}} + \underbrace{\mathcal{G}_{\text{eff}} \left\langle \frac{\mathcal{V}_{i_0}}{\mathbb{1} - \mathcal{V}_{i_0} \mathcal{G}_{\text{eff}}} \right\rangle}_{\text{T-matrix}} \mathcal{G}_{\text{eff}} \end{aligned} \quad (2.58)$$

Since the T-matrix series contains only diagonal $\langle i_0 | \dots | i_0 \rangle$ matrix elements the T-matrix becomes diagonal $\langle i_0 | T | i_0 \rangle \equiv t_{i_0}$ so that the CPA postulate becomes

$$\boxed{\langle t_{i_0} \rangle = \left\langle \frac{\mathcal{V}_{i_0}}{1 - \underbrace{\mathcal{V}_{i_0} \mathcal{G}_{\text{eff}}(z) \mathcal{V}_{i_0}}_{G_0(z)}} \right\rangle = \left\langle \frac{E_i - \Sigma(z)}{1 - [E_i - \Sigma(z)] G_0(z)} \right\rangle = 0} \quad (2.59)$$

We can re-write this equation as follows

$$\begin{aligned} \left\langle \frac{\Sigma(z)}{1 - [E_i - \Sigma(z)] G_0(z)} \right\rangle &= \left\langle \frac{E_i}{1 - [E_i - \Sigma(z)] G_0(z)} \right\rangle \\ = \Sigma(z) \left(1 + \underbrace{\left\langle \frac{[E_i - \Sigma(z)] G_0(z)}{1 - [E_i - \Sigma(z)] G_0(z)} \right\rangle}_{=0} \right) &= \Sigma(z) \end{aligned} \quad (2.60)$$

We now consider the case of *small* fluctuations of E_i , so that we can expand the denominator with respect to $[E_i - \Sigma(z)]$. Taking into account $\langle E_i \rangle = 0$ we obtain to lowest nonvanishing order

$$\Sigma(z) = \langle (E_i)^2 \rangle G_0(z) \quad (2.61)$$

which is just the SCBA result.

We still have the task to evaluate the effective-medium Green's function. We have

$$G_0(z) = \langle i_0 | \frac{1}{z - \mathcal{H}_{\text{eff}}(z)} | i_0 \rangle \quad (2.62)$$

Taking the diagonal element with respect to a lattice site is equivalent to a sum over the first Brillouin zone:

$$G_0(z) = \sum_{\mathbf{k} \in \text{BZ}} \frac{1}{z - \Sigma(z) - E_{\mathbf{k}}} = G_{\text{lattice}}(z - \Sigma(z)) \quad (2.63)$$

where $E_{\mathbf{k}}$ is the simple-cubic tight-binding band structure

$$E_{\mathbf{k}} = -2t[\cos(ak_x) + \cos(ak_y) + \cos(ak_z)] \quad (2.64)$$

and G_{lattice} is the diagonal lattice tight-binding Green's function.

2.3.4 Muffin-Tin potentials and KKR method

In order to study random alloys of crystalline metals a very interesting - and, in fact powerful - model has been established, namely the ‘‘Muffin-tin’’ model. The tin is the form in which the muffin is baked and restricts the muffin to a certain volume. The muffin-tin potential is restricted to be finite only inside a sphere, outside it is zero:

$$\mathcal{V} = \sum_n v(|\mathbf{r} - \mathbf{r}_n|) \equiv \sum_n v_n \quad v_{\text{MT}}(r) = \begin{cases} v(r) & r < R_{\text{MT}} \\ 0 & \text{else} \end{cases}, \quad (2.65)$$

where R_{MT} is the so-called muffin-tin radius. We now consider a ‘‘metallic’’ Hamiltonian of the form

$$\mathcal{H} = \mathcal{H}_0 + \mathcal{V} = k^2 + \sum_n v_n \quad (2.66)$$

where we have set $m = 1/2$ for simplicity. We now return to the expansion (??), in which we used the fact that v_i is ‘‘diagonal’’ with respect to the ‘‘site’’ n . We now identify the site n with the center of the muffin-tin potential and represent the t matrix of the potential v_i by a partial-wave description and restrict ourselves to the ‘‘energy shell’’ represented by $k = \sqrt{E}$

$$\langle \mathbf{k} | t_n | \mathbf{k} \rangle = \sum_{\ell m} \langle \mathbf{k} | \ell m \rangle t_n^\ell(k) \langle \ell m | \mathbf{k} \rangle \quad (2.67)$$

Here $\langle \mathbf{k} | \ell m \rangle = 2\pi Y_{\ell m}(\hat{\mathbf{k}})$, where $Y_{\ell m}$ are the spherical harmonics with respect to \mathbf{k} space. The partial wave amplitudes are given by

$$t_n^\ell(k) = -\frac{1}{k} e^{i\delta_\ell(k)} \sin \delta_\ell(k) \quad (2.68)$$

We further assume that the muffin-tin spheres K_i are *non-overlapping* i.e.

$$\bigcap_i K_i = \emptyset \quad (2.69)$$

So outside the union $\bigcup_i K_i$ the Hamiltonian is \mathcal{H}_0 , so we consider plane waves from scattering centers at sites i . This method is due to J. Koringa³ and W. Kohn, N. Rostoker⁴, and therefore called KKR-method. Due to the condition (2.69) we can represent the total t matrix as

$$T = \mathcal{G}_0 \frac{\mathcal{V}}{\mathbb{1} + \mathcal{V}\mathcal{G}_0} = \sum_n t_n + \sum_n t_n \mathcal{G}_0 T^{\{n\}}, \quad (2.70)$$

³J. Koringa, Physica **13**, 392 (1947)

⁴W. Kohn, N. Rostoker, Phys. Rev. **94**, 1111 (1954)

where $T^{\{n\}}$ is the t matrix, where n is missing. T can now be written as a double sum

$$T = \sum_{n_1 n_2} T_{n_1 n_2} \quad (2.71)$$

$$T_{n_1 n_2} = t_{n_1} \delta_{n_1 n_2} + t_{n_1} \mathcal{G}_0 t_{n_2} + \sum_{\substack{n_3 \\ \neq n_1 \neq n_2}} t_{n_1} \mathcal{G}_0 t_{n_3} \mathcal{G}_0 t_{n_2} + \dots \quad (2.72)$$

$$= t_{n_1} \delta_{n_1 n_2} + \sum_{\substack{n_3 \\ \neq n_1 \neq n_2}} t_{n_1} \mathcal{G}_0 T_{n_3 n_2} \quad (2.73)$$

Expanding with respect to the angular-momentum basis $|L\rangle \equiv |\ell m\rangle$ we obtain⁵

$$T_{nn'}^{LL'}(\kappa) = t_n^\ell(k) \left(\delta_{nn'} \delta_{LL'} + \sum_{n_1 L_1} B_{nn_1}^{LL_1}(\kappa) T_{nn_1}^{LL_1}(\kappa) \right) \quad (2.74)$$

where $\kappa = \sqrt{z}$. The matrix elements of the free propagator are given by

$$B_{nn_1}^{LL_1}(\kappa) = \left(1 - \delta_{nn_1} \right) \frac{4\pi\kappa}{i} \sum_{L_3} i^{\ell - \ell_1 - \ell_2} C_{LL_1 L_2} Y_{L_2}(\mathbf{r}_n - \mathbf{r}_1) h_{\ell_1}(\kappa|\mathbf{r}_n - \mathbf{r}_1) \quad (2.75)$$

with

$$h_\ell(z_\pm) = j_\ell(z_\pm) \pm n_\ell(z_\pm) \quad (2.76)$$

where $j_\ell(z)$, $h_\ell(z)$, and $n_\ell(z)$ are the spherical Bessel, Hankel, and Neumann functions, resp. . $C_{LL_1 L_2}$ are the so-called Gaunt coefficients

$$C_{L_1 L_2 L_3} \int d\Omega Y_{L_1}(\Omega) Y_{L_2}(\Omega) Y_{L_3}(\Omega) \quad (2.77)$$

The density of states is now given as the sum of the free density of states and the imaginary part of the t matrix, which can in principle be calculated, if the scattering phases δ_ℓ and the positions \mathbf{r}_n are known. We can now make the following correspondence:

Tight-binding		KKR	
E_n	\longleftrightarrow	t_n^ℓ	(2.78)
$t_{nn'}$	\longleftrightarrow	$B_{nn'}^{LL_1}$	

In the case of a random crystalline alloy the \mathbf{r}_n are fixed on the lattice and we have scattering phases corresponding to A and B . In most cases it is sufficient to restrict ℓ to 0, 1 and 2, so that for an alloy one has three phases, which represent each alloy partner. One can then cast the CPA equation via the correspondence (2.78) into an equation in which the fluctuating t^ℓ enter. The solution of this equation for evaluating the electronic structure of alloys has nowadays become an industry like band structure calculations for ordered crystals.

However, using random arrangements \mathbf{r}_n of atoms the KKR method has not yet been applied. Here is something to do for you, the readers!

3 Vibrational excitations in disordered systems

3.1 Why is the sky so blue?

(Rayleigh scattering)

⁵H. Ehrenreich, L. M. Schwartz, *Solid State Physics*, Vol. 31, H. Ehrenreich, Ed. Springer-Verlag 1975

We start with Maxwell's equations in a medium, which allows for spatial fluctuations of the dielectric constant (e.g. air in the sky):

$$\begin{aligned}\nabla \cdot \mathbf{B} &= 0 & \nabla \cdot \mathbf{E} &= 0 \\ \nabla \times \mathbf{B}(\mathbf{r}, t) &= \frac{\epsilon(\mathbf{r})}{c^2} \frac{\partial}{\partial t} \mathbf{E}(\mathbf{r}, t) \\ \nabla \times \mathbf{E}(\mathbf{r}, t) &= -\frac{\partial}{\partial t} \mathbf{B}(\mathbf{r}, t)\end{aligned}\tag{3.1}$$

from which we obtain the wave equation

$$\begin{aligned}\frac{\partial^2}{\partial t^2} \mathbf{B}(\mathbf{r}, t) &= -\nabla \times \overbrace{\frac{c^2}{\epsilon(\mathbf{r})}}^{D(\mathbf{r})} \nabla \times \mathbf{B}(\mathbf{r}, t) \\ &= \nabla \cdot D(\mathbf{r}) \cdot \nabla \mathbf{B}(\mathbf{r}, t)\end{aligned}\tag{3.2}$$

From now on we study for simplicity the scalar wave equation

$$\ddot{\psi}(\mathbf{r}, t) = \nabla D(\mathbf{r}) \nabla \psi(\mathbf{r}, t) \quad -\omega^2 \psi(\mathbf{r}, t) = \nabla D(\mathbf{r}) \nabla \psi(\mathbf{r}, t)\tag{3.3}$$

We can take the average D_0 of $D(\mathbf{r})$ outside and define

$$D(\mathbf{r}) = D_0 + \delta D(\mathbf{r})\tag{3.4}$$

The Green's function of (3.3) obeys the equation of motion

$$(s - D_0 \nabla^2) G(\mathbf{r}, \mathbf{r}', s) - \nabla \delta D(\mathbf{r}) \nabla G(\mathbf{r}, \mathbf{r}', s) = \delta(\mathbf{r} - \mathbf{r}')\tag{3.5}$$

Fourier-transformed we obtain

$$sG(\mathbf{k}\mathbf{k}', s) - \delta(\mathbf{k} + \mathbf{k}') + D_0 k^2 G(\mathbf{k}\mathbf{k}', s) = -\frac{1}{(2\pi)^3} \int d^3 \mathbf{k}_1 \mathbf{k} \cdot \mathbf{k}_1 \delta D(\mathbf{k} - \mathbf{k}_1) G(\mathbf{k}_1 \mathbf{k}', s)\tag{3.6}$$

We now define

$$G_0(\mathbf{k}\mathbf{k}', s) = \frac{1}{s + D_0 k^2} \delta(\mathbf{k} + \mathbf{k}') \equiv G_0(\mathbf{k}, s) \delta(\mathbf{k} + \mathbf{k}')\tag{3.7}$$

to be the Green's function without fluctuations so that we have

$$\frac{G(\mathbf{k}\mathbf{k}', s)}{G_0(\mathbf{k}, s)} = 1 - \frac{1}{(2\pi)^3} \int d^3 \mathbf{k}_1 \mathbf{k} \cdot \mathbf{k}_1 \delta D(\mathbf{k} - \mathbf{k}_1) G(\mathbf{k}_1 \mathbf{k}', s)\tag{3.8}$$

We represent the averaged Green's function, which contains fluctuations, by means of a self-energy function $\Sigma(\mathbf{k}, s)$ as follows

$$\mathbf{G}(\mathbf{k}, s) \equiv \langle G(s, \mathbf{k}\mathbf{k}') \rangle \delta(\mathbf{k} + \mathbf{k}') = \frac{1}{s + D_0 k^2 - \Sigma(\mathbf{k}, s)} = \frac{1}{\frac{1}{G_0(\mathbf{k}, s)} - \Sigma(\mathbf{k}, s)}\tag{3.9}$$

From this we obtain

$$\Sigma(\mathbf{k}, s) = \frac{1}{G_0(\mathbf{k}, s)} - \frac{1}{\langle G(\mathbf{k}\mathbf{k}', s) \rangle} = \frac{1}{G_0(\mathbf{k}, s)} \left(1 - \frac{G_0(\mathbf{k}, s)}{\langle G(\mathbf{k}\mathbf{k}', s) \rangle} \right)\tag{3.10}$$

Inserting (3.8) and expanding the denominator with respect to the fluctuations δD we get

$$\Sigma(\mathbf{k}, s) = \frac{1}{G_0(\mathbf{k}, s)} \left\langle \frac{1}{(2\pi)^3} \int d^3 \mathbf{k}_1 \mathbf{k} \cdot \mathbf{k}_1 \delta D(\mathbf{k} - \mathbf{k}_1) G(\mathbf{k}_1 \mathbf{k}', s) \right\rangle\tag{3.11}$$

Inserting (3.8) again, recognizing that the average over a fluctuation is 0 and restricting ourselves to lowest (second) order in the fluctuations we obtain

$$\begin{aligned}\Sigma(\mathbf{k}, s) &= \left\langle \frac{1}{(2\pi)^3} \int d^3 \mathbf{k}_1 \mathbf{k} \cdot \mathbf{k}_1 \delta D(\mathbf{k} - \mathbf{k}_1) G_0(\mathbf{k}_1) \right. \\ &\quad \left. \times \frac{1}{(2\pi)^3} \int d^3 \mathbf{k}_2 \mathbf{k}_1 \cdot \mathbf{k}_2 \delta D(\mathbf{k}_1 - \mathbf{k}_2) G_0(\mathbf{k}_2) \right\rangle\end{aligned}\tag{3.12}$$

The correlation function of the fluctuations is

$$K(\mathbf{r}_1, \mathbf{r}_2) = \langle \delta D(\mathbf{r}_1) \delta D(\mathbf{r}_2) \rangle = K(\mathbf{r}_1 - \mathbf{r}_2) \quad (3.13)$$

Its Fourier transform obeys

$$K(\mathbf{k}_1, \mathbf{k}_2) = \langle \delta D(\mathbf{k}_1) \delta D(\mathbf{k}_2) \rangle = K(\mathbf{k}_1) (2\pi)^3 \delta(\mathbf{k}_1 + \mathbf{k}_2) \quad (3.14)$$

from which we obtain the identification

$$\mathbf{k} - \mathbf{k}_1 = \mathbf{k}_2 - \mathbf{k}_1 \quad \Rightarrow \quad \mathbf{k}_2 = \mathbf{k} \quad (3.15)$$

So we finally obtain

$$\Sigma(\mathbf{k}, s) = \frac{1}{(2\pi)^3} \int d^3 \mathbf{k}_1 K(\mathbf{k} - \mathbf{k}_1) (\mathbf{k} \cdot \mathbf{k}_1)^2 G_0(\mathbf{k}_1, s) \quad (3.16)$$

We now assume short-range correlations

$$K(\mathbf{r}_1, \mathbf{r}_2) = \Delta^2 \delta(\mathbf{r}_1 - \mathbf{r}_2) \quad \Leftrightarrow \quad K(\mathbf{k}) = \Delta^2 \quad (3.17)$$

and define a *frequency dependent speed of light* by

$$c^2(\omega) = c_0^2 - \Sigma(s) \quad (3.18)$$

with

$$\Sigma(\omega) = \frac{1}{k^2} \Sigma(\mathbf{k}, s) \Big|_{\mathbf{k}=0} = \frac{\Delta^2}{6\pi^2} \underbrace{\int_0^\infty dk_1 \frac{k_1^4}{s + D_0 k_1^2}}_{\propto s^{3/2}} \quad (3.19)$$

We further define a *frequency dependent wave number* by

$$\begin{aligned} \kappa(\omega) &= \frac{\omega}{c(\omega)} = \frac{\omega}{\sqrt{\underbrace{c_0^2 - \Sigma'(0)}_{c^2} - i\Sigma''(\omega)}} \\ &= \frac{\omega}{c} \frac{1}{1 - i\Sigma''(\omega)/c^2} \approx \frac{\omega}{c} \left(1 + i \frac{1}{2} \frac{\Sigma''(\omega)}{c^2} \right) \equiv \bar{k} + i \frac{1}{2\ell(\omega)} \end{aligned} \quad (3.20)$$

Here c is the speed of light in the medium. Now the averaged Green's function can be written as

$$\mathbf{G}(\mathbf{k}, \omega) = \frac{1}{c(\omega)^2} \frac{1}{\kappa(\omega)^2 - k^2} \approx \frac{1}{c^2} \frac{1}{\kappa(\omega)^2 - k^2} \quad (3.21)$$

which has a Fourier transform

$$\mathbf{G}(\mathbf{r}, \omega) = \frac{1}{4\pi c^2 r} e^{i\kappa(\omega)r} = \frac{1}{4\pi c^2 r} e^{i\bar{k}r} e^{-r/2\ell(\omega)} \quad (3.22)$$

For the scattered intensity we obtain

$$\left| \mathbf{G}(\mathbf{r}, \omega) \right|^2 \propto e^{-r/\ell(\omega)} \quad (3.23)$$

with a mean-free path

$$\frac{1}{\ell(\omega)} \propto \omega \Sigma''(\omega) \propto \omega [\omega^2]^{3/2} = \omega^4, \quad (3.24)$$

From this we conclude (as Lord Rayleigh) that the blue light rays are much stronger scattered than the red ones.

3.2 Elements of random matrix theory

3.2.1 Integrability in classical mechanics and level statistics in quantum mechanics

Suppose we have a classical-mechanics system with f degrees of freedom. If the number s of *invariants*, i.e. physical observables A_i with

$$\frac{d}{dt}A_i = 0 \quad i = 1 \dots s \quad (3.25)$$

is equal to f , and, in addition, these quantities are in *involution*, i.e.

$$\{A_i, A_j\} = 0 \quad i, j = 1 \dots s, \quad (3.26)$$

where $\{\dots, \dots\}$ is a Poisson bracket, the system is called *integrable*. In this case the f invariants (energy is always one of them) can be chosen as generalized momenta, and - as demonstrated in the theory of Hamilton and Jacobi - the motion in phase space is on an f -torus, where the f radii are given by the constant values of the invariants. So the motion of the system is known, once the initial conditions are given. In particular, if the initial conditions are only known approximately, the motion can still be predicted - just with the precision of the initial conditions.

On the other hand, if the number of invariants (in involution) s is smaller than f , the system is called *non-integrable*. Such a system can exhibit *sensitive dependence on initial conditions*. This case is called *chaos* in physics slang. It means that the distance of two trajectories $q_1(t)$ and $q_2(t)$ which were separated from each other at $t = 0$ by a very small amount ϵ will grow exponentially according to

$$|q_1(t) - q_2(t)| \propto e^{\lambda t}, \quad (3.27)$$

where λ is the *Lyapunov* exponent. This sensitive dependence on initial conditions, which applies in particular to *nonlinear* dynamic systems like the atmosphere or water currents, inhibits any prediction of the dynamics for a longer time than $t_\lambda = 1/\lambda$. For the earth-near atmosphere t_λ is of the order of a few days.

We turn now to *quantum-mechanical* systems corresponding to the cases considered above. In the integrable case (involution means now commutability) all eigenvalues are f -fold degenerate. On the other hand, if the only invariant is the energy, no eigenvalue is degenerate. In this case the energy levels are said to “repel” each other (*level repulsion*). This is the case for an *atomic nucleus*. For the description of nuclear spectra Wigner, Dyson and Mehta developed a model of *random matrices* and found that the nuclear spectra could be described in terms of Hamilton matrices with elements taken from a (Gaussian) statistical distribution. Here we give a pedagogical discussion of the energy level statistics of a random Hamiltonian.

3.3 Isotropic solids: Debye model

In 1912 Debye realized that something was inconsistent with the Einstein model. It was well known that low-energetic excitations of a solid material were *not* oscillations of a single atom, but *collective* vibrations, which are sound waves. Such waves were well known from *elasticity theory*. The main object of elasticity theory is the generalized Hooke law between the *stress tensor* σ_{ij} and the *strain tensor* ϵ_{kl}

$$\boxed{\sigma_{ij} = \sum_{kl} C_{ijkl} \epsilon_{kl}} \quad i, j, k, \ell = 1, 2, 3 \quad (3.28)$$

The stress tensor is defined in terms of a force in i direction acting on a surface element dA_j with normal vector in j direction

$$dF_i = \sum_j \sigma_{ij} dA_j \quad (3.29)$$

The strains are defined in terms of infinitesimal displacements $\mathbf{u}_i(\mathbf{r})$ at \mathbf{r} in i direction

$$\epsilon_{ij} = \frac{1}{2} (u_{i|j} + u_{j|i}) \quad u_{i|j} = \frac{\partial u_i}{\partial x_j} \quad (3.30)$$

In an *isotropic* system the Hooke tensor C_{ijkl} has only 2 independent entries and we have

$$C_{ijkl} = \lambda \delta_{ij} \delta_{kl} + \mu \left(\delta_{ik} \delta_{jl} + \delta_{il} \delta_{jk} \right) \quad (3.31)$$

The general Lagrangian density is ($\rho = N/V$)

$$\begin{aligned}\mathcal{L}(\mathbf{r}, t) &= \frac{1}{2}\rho\dot{\mathbf{u}}\cdot\dot{\mathbf{u}} - \frac{1}{2}\sum_{ijkl}u_{i|j}C_{ijkl}u_{k|l} \\ &= \frac{1}{2}\rho\dot{\mathbf{u}}\cdot\dot{\mathbf{u}} - \frac{\lambda}{2}\left(\sum_i\epsilon_{ii}\right)^2 - \mu\sum_{ij}\epsilon_{ij}^2\end{aligned}\quad (3.33)$$

where the second equality holds for the isotropic system.

λ and μ are Lamé's elastic constants. μ is identical with the shear modulus, in other textbooks also called G . The *bulk modulus*, which is the inverse of the compressibility is given by

$$K = \lambda + \frac{2}{3}\mu = \frac{E}{2(1-2\nu)}\quad (3.34)$$

where E is Young's modulus and ν the Poisson number.

The equations of motion are

$$\sum_{i=0}^3\frac{\partial}{\partial x_i}\frac{\partial\mathcal{L}}{\partial u_{k|i}} - \frac{\partial\mathcal{L}}{\partial u_k} = 0 \quad x_0 = t \quad k = 1, 2, 3\quad (3.35)$$

They can be reformulated as

$$\rho\ddot{u}_i = \sum_{\ell=1}^3 A_{i\ell}u_{\ell}\quad (3.37)$$

$$A_{i\ell} = \lambda\partial_i\partial_{\ell} + \mu\left(\partial_{\ell}\partial_i + \nabla^2\delta_{i\ell}\right)\quad (3.38)$$

With the Ansatz

$$\mathbf{u}(\mathbf{r}, t) = \mathbf{u}e^{i[\mathbf{k}\mathbf{r}-\omega t]}\quad (3.39)$$

we obtain the matrix eigenproblem

$$\omega^2 u_i = \sum_{\ell} D_{i\ell} u_{\ell}\quad (3.41)$$

$$D_{i\ell} = \frac{1}{\rho}\left[(\lambda + \mu)k_i k_{\ell} + \mu k^2 \delta_{i\ell}\right]\quad (3.42)$$

D is called the *dynamical matrix*. We easily obtain the eigenvalues of this matrix by rotating into a system in which the z axis coincides with the direction of the vector \mathbf{k} . In this system $\mathbf{k} = (k, 0, 0)$, and we have

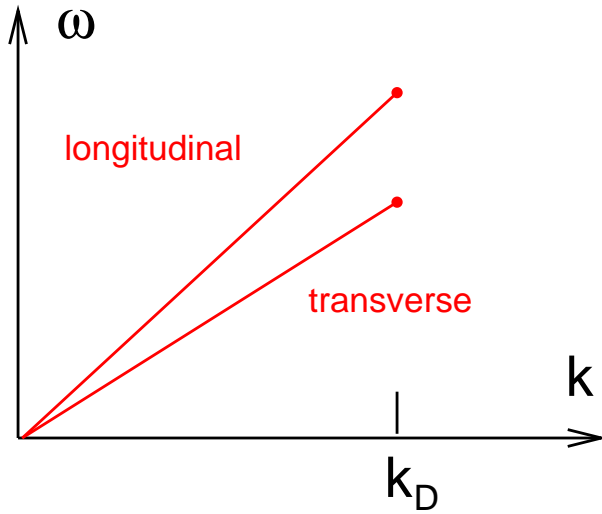
$$D = \frac{1}{\rho}\begin{pmatrix} \mu k^2 & 0 & 0 \\ 0 & \mu k^2 & 0 \\ 0 & 0 & (\lambda + 2\mu)k^2 \end{pmatrix}\quad (3.43)$$

We see that we have three independent sound waves, two transverse ones ($\mathbf{u} \perp \mathbf{k}$) with sound velocity $c_T = \sqrt{\mu/\rho}$ and one longitudinal one ($\mathbf{u} \parallel \mathbf{k}$) with sound velocity $c_L = \sqrt{(\lambda + 2\mu)/\rho}$.

We return now to the ideas of *Debye*. He realized that the number of vibrational modes (of a particular polarization direction) cannot exceed the number of atoms. So he imposed a *wavenumber cutoff* k_D (*k-Debye*) by demanding $N = \sum_{\mathbf{k}}$, where the sum is carried out with the help of the Born-von-Karman boundary conditions (just as in the calculation of the Fermi wavenumber):

$$N = \sum_{|\mathbf{k}| < k_D} = \frac{V}{(2\pi)^3} \int_{|\mathbf{k}| < k_D} d^3\mathbf{k} = \frac{V}{2\pi^2} \int_0^{k_D} dk k^2 = \frac{V}{6\pi^2} k_D^3\quad (3.44)$$

$$\Rightarrow \boxed{k_D = \sqrt[3]{6\pi^2 N/V}} \quad (3.45)$$



The Debye model now states that the solid, composed of N atoms allows for two transverse sound modes and one longitudinal one with wavenumbers $k \leq k_D$.

The total energy of the Debye solid is

$$\begin{aligned} E &= \sum_{\lambda=1}^2 \sum_{\mathbf{k}} \frac{\hbar \omega_{\mathbf{k}\lambda}}{e^x - 1} & \omega_{\mathbf{k}\lambda} &= c_{\lambda} k \\ &= \sum_{\lambda} c_{\lambda} \frac{V}{2\pi^2} \int_0^{k_D} dk \frac{k^3}{e^x - 1} & x &= \hbar c_{\lambda} k / k_B T \equiv \Theta_D / T \\ &= \sum_{\lambda} \frac{(k_B T)^4}{(\hbar c_{\lambda})^3} \frac{V}{2\pi^2} \int_0^{\Theta_D/T} dx \frac{x^3}{e^x - 1} \end{aligned} \quad (3.47)$$

Dispersion of the Debye model

Θ_D is called the *Debye temperature*.

For $T \rightarrow 0$ the integral over x becomes a constant $I = 6.43$. In this limit, therefore we can write

$$\begin{aligned} \frac{E}{N} &= \frac{V}{N} \frac{I}{2\pi^2} \frac{1}{\hbar^3} \left(\frac{1}{c_L^3} + \frac{2}{c_T^3} \right) (k_B T)^4 \\ &= \frac{3I}{(\hbar k_D)^3} \left(\frac{1}{c_L^3} + \frac{2}{c_T^3} \right) (k_B T)^4 \end{aligned} \quad (3.49)$$

$$\Rightarrow \boxed{C_N = \frac{3I k_B}{(\hbar k_D)^3} \left(\frac{1}{c_L^3} + \frac{2}{c_T^3} \right) (k_B T)^3} \quad (3.50)$$

This is the famous T^3 law of Debye. As a matter of fact this is not an approximation but it holds rigorously for any insulating crystalline material.

3.4 Harmonic approximation and interatomic potentials

Until now the fact that the crystalline (or non-crystalline) material is composed of atoms or molecules entered only via the Debye cutoff wavenumber k_D . We are now going to formulate a microscopic theory of atomic vibrations in a solid.

Considering displacements of atoms from their equilibrium positions in a lattice leads to the question:

- What does the lattice hold together in the first place?

This question is intimately related to the nature of the *chemical bond*.

We know from elementary chemistry that there are four fundamentally different kinds of bonds (forces) which hold the atoms together

- Van-der-Waals bonds (rare gases and polymers)
- Ionic bonds (ionic crystals and glasses)
- Covalent bonds (insulating homopolar materials)
- Metallic bonds (metals)

In almost all of these different cases one can formulate the concept of an *effective interatomic potential* $\phi(r_{ij})$, $r_{ij} = |\mathbf{r}_i - \mathbf{r}_j|$, such that the total energy of cohesion of the solid can be written

$$E = E_0 + \frac{1}{2} \sum_{\substack{i,j=1 \\ i \neq j}}^N \phi(r_{ij}) \quad (3.51)$$

Such potentials can have very different form.

Let us now assume that all atoms have their equilibrium positions on a lattice site \mathbf{R}_i and we perform a Taylor expansion of the lattice energy

$$E = E_0 + \frac{1}{2} \sum_{\substack{i,j=1 \\ i \neq j}}^N \phi(R_{ij}) + \frac{1}{4} \sum_{ij} \left[(\mathbf{u}_i - \mathbf{u}_j) \cdot \nabla \right]^2 \phi(r_{ij}) \Big|_{r_{ij}=R_{ij}} \quad (3.52)$$

with $R_{ij} = |\mathbf{R}_i - \mathbf{R}_j|$ and $\mathbf{u}_i = \mathbf{r}_i - \mathbf{R}_i$. The latter are the *displacement vectors*. The *linear* term in the expansion does not exist, because we assume that the \mathbf{R}_i are *equilibrium* positions of the atoms. The quadratic term is called the *harmonic* part of the lattice energy and has the form

$$E_{\text{harm}} = \frac{1}{4} \sum_{\substack{ij \\ \mu\nu}} (u_{i\mu} - u_{j\mu}) \phi_{\mu\nu}^{ij} (u_{i\nu} - u_{j\nu}) \quad (3.54)$$

$$\phi_{\mu\nu}^{ij} = \frac{\partial}{\partial x_\mu} \frac{\partial}{\partial x_\nu} \phi(r_{ij}) \Big|_{r_{ij}=R_{ij}} \quad (3.54)$$

The $\phi_{\mu\nu}^{ij}$ are called harmonic force constants. We can re-write E_{harm} as

$$E_{\text{harm}} = \frac{1}{2} \sum_{\substack{ij \\ \mu\nu}} u_{i\mu} D_{\mu\nu}^{ij} u_{j\nu} \quad (3.56)$$

$$\text{with } D_{\mu\nu}^{ii} = \sum_{\ell} \phi_{\mu\nu}^{i\ell} \quad (3.56)$$

$$D_{\mu\nu}^{ij} = -\phi_{\mu\nu}^{ij} \quad i \neq j.$$

We can now write down the *equation of motion* for the displacements

$$M \ddot{u}_{i\mu} = - \sum_j D_{\mu\nu}^{ij} u_{j\nu} \quad (3.57)$$

which is the *microscopic version* of Hooke's law. $D_{\mu\nu}^{ij}$ is the *dynamical matrix*.

3.5 Phonon dispersions in crystals

The task is, of course, to *diagonalize* $D_{\mu\nu}^{ij}$. The eigenvectors are called *normal modes* of the lattice. The *eigenvalues* in reciprocal space are the squares of the characteristic frequencies $\omega_\alpha(\mathbf{k})$, which are called *phonon dispersions*.

3.5.1 Normal modes of a monatomic three-dimensional lattice

We recall the expression for the harmonic part of the cohesion energy

$$E_{\text{harm}} = \frac{1}{2} \sum_{\substack{ij \\ \mu\nu}} u_{i\mu} D_{\mu\nu}^{ij} u_{j\nu} \quad (3.58)$$

which corresponds to the set of equations of motion

$$m \ddot{u}_{i\mu}(t) = - \sum_{j\nu} D_{\mu\nu}^{ij} u_{j\nu} \quad (3.59)$$

The dynamical matrix has the symmetries

$$D_{\mu\nu}^{ij} = D_{\nu\mu}^{ji} \quad (3.61)$$

$$D_{\mu\nu}^{ij} = D_{\mu\nu}^{ji} \quad (3.62)$$

$$\sum_i D_{\mu\nu}^{ij} = \sum_j D_{\mu\nu}^{ij} = 0 \quad (3.63)$$

We seek solutions of the form

$$u_{i\mu}(t) = u_\mu e^{i(\mathbf{k}\cdot\mathbf{R}_i - \omega t)} \quad (3.64)$$

Due to the periodic boundary condition the reciprocal space is discretized again in such a way that we can write

$$\mathbf{k} = \frac{n_1}{N_1}\mathbf{b}_1 + \frac{n_2}{N_2}\mathbf{b}_2 + \frac{n_3}{N_3}\mathbf{b}_3 \quad (3.65)$$

where the \mathbf{b}_i are the reciprocal basis, $L_i = aN_i$ are the edges of the sample volume and n_i, N_i are integers. We obtain the characteristic equations

$$m\omega^2 u_\mu = \sum_\nu D_{\mu\nu}(\mathbf{k}) u_\nu \quad (3.66)$$

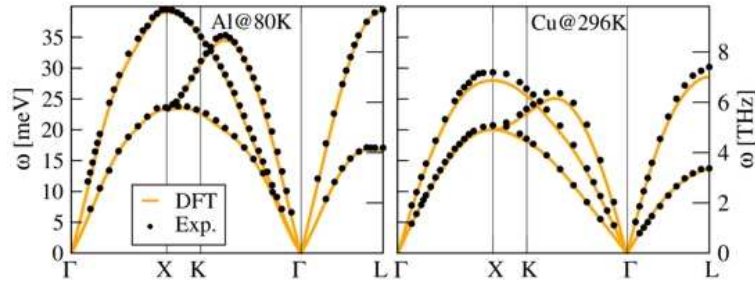
$$D_{\mu\nu}(\mathbf{k}) = \sum_{\ell \text{ lattice}} e^{i\mathbf{k}\cdot\mathbf{R}_\ell} D_{\mu\nu}(\mathbf{R}_i - \mathbf{R}_j) \Big|_{\mathbf{R}_\ell = \mathbf{R}_i - \mathbf{R}_j} \quad (3.67)$$

Taking advantage of the symmetries (3.60) of the dynamical matrix we re-write (3.67) as follows

$$\begin{aligned} D_{\mu\nu}(\mathbf{k}) &= \frac{1}{2} \sum_{\ell} e^{i\mathbf{k}\cdot\mathbf{R}_\ell} \left[D_{\mu\nu}(\mathbf{R}_\ell) + D_{\mu\nu}(-\mathbf{R}_\ell) \right] - \underbrace{\sum_{\ell} D_{\mu\nu}(\mathbf{R}_\ell)}_{=0} \quad (3.69) \\ &= \frac{1}{2} \sum_{\ell} D_{\mu\nu}(\mathbf{R}_\ell) [\cos \mathbf{k}\cdot\mathbf{R}_\ell - 1] = \sum_{\ell} D_{\mu\nu}(\mathbf{R}_\ell) \sin^2 \left(\frac{1}{2} \mathbf{k}\cdot\mathbf{R}_\ell \right) \quad (3.70) \end{aligned}$$

The matrix $\overleftrightarrow{D}(\mathbf{k})$ has 3 eigenvalues $\gamma_1, \gamma_2, \gamma_3$ and 3 eigenvectors, which can be orthogonalized $\mathbf{u}_s \cdot \mathbf{u}_{s'} = \delta_{ss'}$, so that we have

$$\omega_s(\mathbf{k}) = \sqrt{\frac{1}{m} \gamma_s(\mathbf{k})} \quad \text{with } \overleftrightarrow{D}(\mathbf{k}) \mathbf{u}_s = \gamma_s \mathbf{u}_s \quad (3.71)$$



Phonon dispersions of Al and Cu. The points are experimental data obtained by inelastic neutron scattering. The lines are obtained by electronic structure calculations of the adiabatically deformed crystal.

The phonon dispersions $\omega_s(\mathbf{k})$ can be directly measured by inelastic neutron scattering, where the transferred energy is just $\Delta E = \hbar\omega(\mathbf{k})$ and the transferred momentum is $\Delta\mathbf{p} = \hbar\mathbf{k}$. In materials, where it is possible to apply the density-functional theory the force constants entering into the dynamical matrix can be calculated by applying the adiabatical principle: the crystal inside the computer is deformed according to the vibrational mode considered. Then the corresponding change in the total energy is calculated, which yields the force constants (“frozen phonon” method).

3.5.2 Vibrational density of states

The normalized density of vibrational frequencies (density of states, DOS) is given by

$$g(\omega) = \frac{1}{3N} \sum_s \sum_{\mathbf{k}} \delta(\omega - \omega_s(\mathbf{k})) = \frac{1}{3N} \sum_s \frac{1}{(2\pi)^2} \int d^3\mathbf{k} \delta(\omega - \omega_s(\mathbf{k})) \quad (3.72)$$

For the Debye model

$$\omega_s(\mathbf{k}) = \begin{cases} c_s k & k \leq k_D \\ 0 & k > k_D \end{cases} \quad (3.73)$$

This gives

$$g(\omega) = \frac{V}{6\pi^2 N} \sum_s \int_0^{k_D} dk \delta(\omega - kc_s) \quad (3.75)$$

$$= \sum_s \frac{V}{6\pi^2 N c_s^3} \omega^2 \quad (3.76)$$

$$= 3 \frac{\omega^2}{\omega_D^3} \quad (3.77)$$

where we have introduced the *Debye frequency*

$$\omega_D = k_D \left[\frac{1}{c_L^3} + \frac{2}{c_T^3} \right]^{-1/3} \equiv k_D c_D \quad (3.78)$$

Instead the dynamical matrix \overleftrightarrow{D} we can also introduce a modified dynamical matrix

$$K_{\mu\nu}^{ij} = \frac{1}{m_i} D_{\mu\nu}^{ij} \quad (3.79)$$

which allows for different masses, and define the eigenvalues of \overleftrightarrow{K} as

$$\lambda \mathbf{u} = \overleftrightarrow{K} \mathbf{u} \quad (3.80)$$

Then we have $\omega_s(\mathbf{k}) = \lambda_s(\mathbf{k})$. The density of eigenvalues is then

$$\tilde{g}(\lambda) = \frac{1}{3N} \sum_s \sum_{\mathbf{k}} \delta(\lambda - \lambda_s(\mathbf{k})) \quad (3.81)$$

and we have

$$g(\omega) = \frac{d\lambda}{d\omega} \tilde{g}(\lambda) = 2\omega \tilde{g}(\lambda) \quad (3.82)$$

Use of the density of states Let us consider the vibrational energy per atom

$$E_N = \frac{1}{N} \sum_{s=1}^3 \sum_{\mathbf{k}} \hbar \omega_s(\mathbf{k}) \frac{1}{e^{\hbar \omega_s(\mathbf{k})/k_B T} - 1} \quad (3.84)$$

$$= 3 \int d\omega \frac{1}{3N} \sum_{s\mathbf{k}} \delta(\omega - \omega_s(\mathbf{k})) \frac{\hbar \omega_s(\mathbf{k})}{e^{\hbar \omega_s(\mathbf{k})/k_B T} - 1} \quad (3.85)$$

$$= 3 \int d\omega g(\omega) \frac{\hbar \omega}{e^{\hbar \omega/k_B T} - 1} \quad (3.86)$$

$$\Rightarrow C_N = 3 \int d\omega g(\omega) \hbar \omega \frac{\partial}{\partial T} \left(\frac{1}{e^{\hbar \omega/k_B T} - 1} \right) \quad (3.87)$$

The density of states appears if one wants to consider the frequency dependence of the contributions to the energy instead the \mathbf{k} dependence. This point of view becomes important in disordered solids, where it is in general not possible to label the vibrational states by means of the components of a wave vector \mathbf{k} .

3.6 Harmonic vibrational dynamics in disordered Solids

3.6.1 Disordered cubic lattice and coherent-potential approximation (CPA)

Let us consider masses of value M fixed to a cubic lattice which are connected with springs the Hooke constants (force constants) MK_{ij} of which fluctuate according to a distribution density $P(K_{ij})$.

We simplify the system further by considering the displacements $u_i(t)$ at site i to be scalar quantities.

The equation of motion of this system is

$$\frac{d^2}{dt^2}u_i(t) = -\sum_j K_{ij}(u_i(t) - u_j(t)) \quad (3.88)$$

The green's function of this equation $\mathcal{G}_{ij}(t, t')$ obeys the equation

$$\frac{d^2}{dt^2}\mathcal{G}_{ij}(t, t') + \sum_\ell K_{i\ell}(\mathcal{G}_{ij} - \mathcal{G}_{\ell j}) = \delta_{ij}\delta(t - t') \quad (3.89)$$

Defining a "Hamiltonian Matrix"

$$\mathcal{H}_{ij} = \begin{cases} -\sum_j K_{ij} & i = j \\ K_{ij} & i \neq j \end{cases} \quad (3.90)$$

and Fourier transforming we obtain the following matrix equation for the Green matrix $\langle i|\mathcal{G}(\omega)|j \rangle = \mathcal{G}_{ij}(\omega)$

$$(\tilde{z} - \mathcal{H})\mathcal{G} = (-\omega^2 + i\tilde{\epsilon} - \mathcal{H})\mathcal{G} = 1 \quad (3.91)$$

where we, again introduced a complex frequency variable \tilde{z} which is, for convenience, constructed with respect to ω^2 .

If we look carefully at these equations they turn out to be identical to the Schrödinger equation of tight-binding electrons with transfer integrals K_{ij} and on-site energies $E_i = \mathcal{H}_{ii} = -\sum_j K_{ij}$. So we can make use of the approximation schemes which have been invented in the literature to deal with electrons in disordered systems with such a type of Hamiltonian.

One of the most powerful mean-field theories of disorder is the *coherent-potential approximation*, CPA. The CPA is derived as follows:

We invent an *effective medium*, which is not disordered (i. e. it has the cubic symmetry), but the force constants are frequency dependent:

$$K_{ij}^{eff}(\tilde{z}) = \Gamma(\tilde{z}). \quad (3.92)$$

Let $Z = 6$ be the coordination number of the sites. Then effective-Medium Hamiltonian is

$$H_{ij} = \begin{cases} -\sum_j K_{ij}^{eff}(\tilde{z}) - Z\Gamma(\tilde{z}) & i = j \\ K_{ij}^{eff}(\tilde{z}) = \Gamma(\tilde{z}) & i \neq j \end{cases} \quad (3.93)$$

and the Green's function of the effective medium obeys the equation of motion

$$\tilde{z}G_{ij} - \delta_{ij} = Z\Gamma(\tilde{z})(G_{\ell j} - G_{ij}) \quad \ell \text{ arbitrary neighboring site} \quad (3.94)$$

As in the Lorentz theory of dielectric polarizability¹ we now "dig a hole" into the effective medium. As we deal with *pairs* of sites this hole must contain a pair (i_0, j_0) . Inside the hole we replace the effective-medium force constant $\Gamma(\tilde{z})$ by the actual one $K_{i_0 j_0}$ so that we obtain a "perturbation" $v_{i_0 j_0}(\tilde{z}) = K_{i_0 j_0} - \Gamma(\tilde{z})$. The corresponding perturbing Hamiltonian matrix V has four non-zero entries, namely $V_{i_0 i_0}$, $V_{j_0 j_0}$, $V_{i_0 j_0}$, and $V_{j_0 i_0}$. In the $i_0 j_0$ subspace we have

$$V = \begin{pmatrix} -v_{i_0 j_0}(\tilde{z}) & v_{i_0 j_0}(\tilde{z}) \\ v_{i_0 j_0}(\tilde{z}) & -v_{i_0 j_0}(\tilde{z}) \end{pmatrix} \quad (3.95)$$

We now demand that introducing this perturbation should have *on the average* no influence on the effective medium which is equivalent to demanding that the Green's function of the effective medium should be equal

¹The first version of the CPA has been devised by Bruggeman, 1937 for composite dielectrics.

to the configuratonally averaged Green's function of the disordered system. One can again reformulate this postulate in demanding that the averaged T -matrix

$$\langle T \rangle = \left\langle \frac{V}{1 - VG} \right\rangle \quad (3.96)$$

should vanish. Working out the 2×2 inverse and using (3.94) with $i = j$ we obtain the following CPA self-consistent equation for $\Gamma(\tilde{z})$

$$\left\langle \frac{K - \Gamma(\tilde{z})}{1 + (K - \Gamma(\tilde{z})) \frac{2}{Z\Gamma(\tilde{z})} (1 - \tilde{z}G_{ii}(\tilde{z}))} \right\rangle = 0 \quad (3.97)$$

which can be reformulated as

$$\Gamma(\tilde{z}) = \left\langle \frac{K}{1 + (K - \Gamma(\tilde{z})) \frac{2}{Z\Gamma(\tilde{z})} (1 - \tilde{z}G_{ii}(\tilde{z}))} \right\rangle \quad (3.98)$$

We now define the local Green's function of the simple cubic lattice ($Z = 6$) as

$$G_{ii}^{(0)}(\tilde{z}) = \sum_{\mathbf{k} \in BZ} \frac{1}{\tilde{z} + 6 - E(\mathbf{k})} \quad (3.99)$$

with the simple-cubic band structure

$$E(\mathbf{k}) = 2[\cos(k_x a) + \cos(k_y a) + \cos(k_z a)] \quad (3.100)$$

where a is the lattice constant and BZ is the 1st Brillouin zone. Then we have for the local Green's function of the effective medium

$$G_{ii}(\tilde{z}) = \frac{1}{\Gamma(\tilde{z})} G_{ii}^{(0)} \left(\frac{\tilde{z}}{\Gamma(\tilde{z})} \right) \quad (3.101)$$

(3.98) and (3.101) now establish a self-consistent set of equations which can (and have to be) solved on a computer.

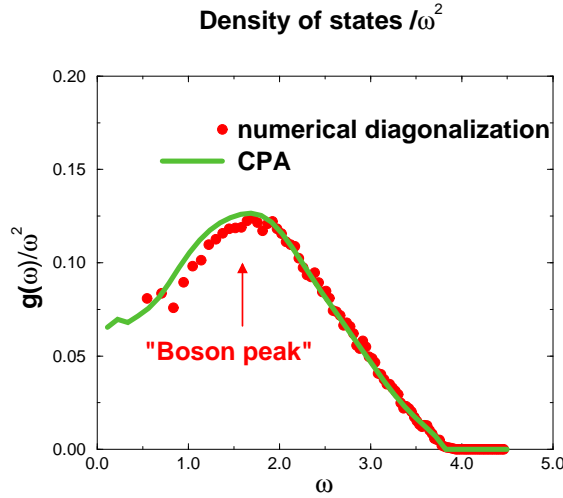


Fig. 8: Density of states, divided by ω^2 of a simple-cubic lattice with a Gaussian distribution of force constants with width parameter $\sigma/K_0 = 0.6$. The full line is a CPA calculation (solution of (3.98) and (3.101)), the points are the result of numerical diagonalizations of systems with periodic boundary conditions, averaged over different box sizes.

The density of states is obtained from the Green's function according to

$$g(\omega) = 2\omega g(\omega^2) = -\frac{2\omega}{\pi} \Im m \{ G(\tilde{z}) \} \quad (3.102)$$

in Fig. 8 we have plotted the so-called reduced density of states $g(\omega)/\omega^2$ resulting from a numerical diagonalization of a model with a Gaussian $P(K)$ with width-to-mean ratio $\sigma/K_0 = 0.6$ together with the CPA calculation. Clearly the CPA gives a good account of the data. It also is seen that there are no van-Hove singularities as in the ordered system (see the curve " $\sigma = 0$ " in Fig. 9), but instead a maximum, which can be identified as the so-called boson peak.

We are now giving a physical explanation of the forming of such a peak in the reduced density of states of disordered solids. First we note that if we increase the width of the distribution $P(K)$ the system becomes unstable, because some atoms are now sitting on top of a potential hill instead at the bottom of a potential well. This instability manifests itself by the existence of negative eigenvalues ω_i^2 in the numerics, or, in the CPA, by the appearance of a portion of the density of states for negative values of ω^2 . To have a "fine-tuning" of this instability we introduced a lower cutoff K_{min} in the Gaussian and put $\sigma = K_0$. The result is shown in Fig. 9

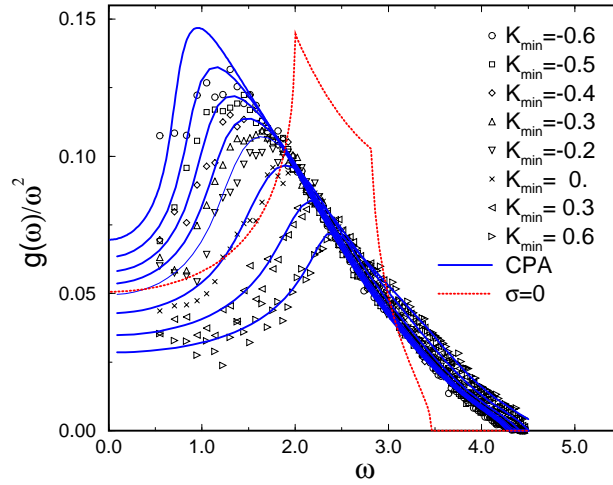


Fig. 9: Density of states, divided by ω^2 of a simple-cubic lattice with a varying lower cutoff K_{min} and width parameter $\sigma/K_0 = 1$. The full line is a CPA calculation (solution of (3.98) and (3.101)), the points are the result of numerical diagonalizations of systems with periodic boundary conditions, averaged over different box sizes.

It is seen that the more negative force constants we put in, the stronger becomes the boson peak. So it looks as if the boson peak is the precursor of the mentioned instability. This conclusion will be thoroughly corroborated in the rest of the present lectures.

3.6.2 The self-consistent Born approximation, SCBA

We would like to simplify the CPA by the following steps:

- getting rid of the unphysical cubic lattice by replacing the dispersion by a Debye law

$$6K_0^2[6 - E(\mathbf{k})] \rightarrow c_0^2 k^2 \theta(k - k_D)$$

- expanding the CPA equation with respect to the deviations $\delta K = K - K_0$ and $\delta \Gamma = \Gamma - K_0$

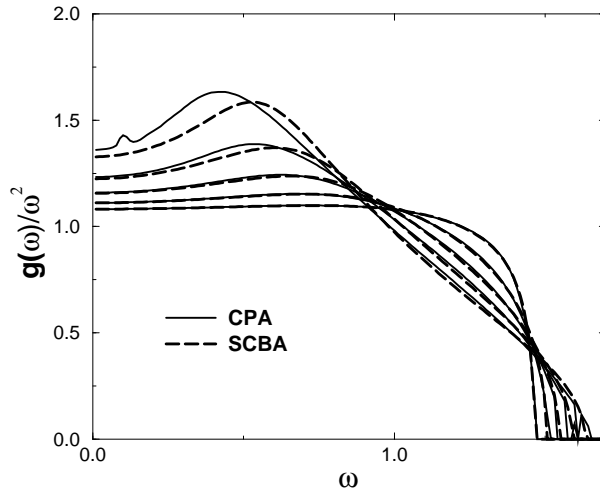


Fig. 10: Density of states, divided by ω^2 for a generalized Debye model with fluctuating elastic constants $\tilde{K} \equiv c^2$ calculated for different disorder parameters $\gamma \propto \langle \delta K^2 \rangle / \langle \tilde{K} \rangle^2$, calculated in SCBA and CPA

If we limit the expansion to second order in δK and $\delta \Gamma$ we obtain the so-called *self-consistent Born approximation*, *SCBA*

$$\delta \Gamma(\tilde{z}) = -\gamma \sum_{|\mathbf{k}| < k_D} \frac{k^2}{\tilde{z} + k^2 [c_0^2 + \delta \Gamma(\tilde{z})]} \quad (3.103)$$

where $\gamma \propto \langle (\delta K)^2 \rangle / \langle K \rangle^2$. In Fig. 10 we compare the CPA for a Gaussian $P(K)$ with the SCBA with the same width parameter. The difference is not striking, so that we can safely use the SCBA instead of the CPA, especially if we don't want to compare our results to a simulation on a lattice. It is clear from Fig. 10 that the boson peak has nothing to do with a broadened van-Hove singularity as claimed sometimes in the literature, because all lattice-specific features have been removed from the theory. To understand the origin of the boson peak we further simplify the SCBA equation (7.149) by replacing the sum over \mathbf{k} by its dominant term at the maximum $|\mathbf{k}| = k_D$. If we use frequency units where $c_0 = k_D = 1$ we obtain

$$\delta \Gamma(\tilde{z}) = \Gamma(\tilde{z}) - 1 = -\gamma \frac{1}{\tilde{z} + \Gamma(\tilde{z})} \quad (3.104)$$

which is a quadratic equation for $\Gamma(\tilde{z})$

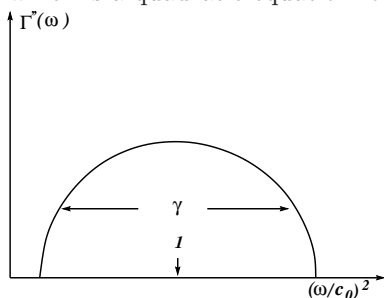


Fig. 11: Imaginary part of the "self energy" $\Gamma(\tilde{z})$ for the simplified SCBA equation (3.104). If γ becomes larger than unity the system becomes unstable.

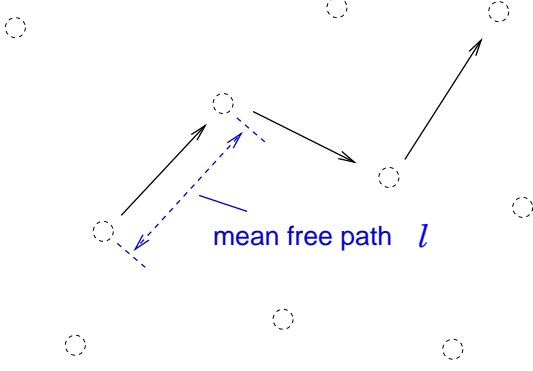
The solution of this equation yields a semicircular law for the imaginary part of the self energy Γ (Fig. 11) which is proportional to the "density of levels" $g(\omega^2)$. If the variance-to mean square ratio γ becomes comparable to unity the system becomes unstable. If it is smaller a rapid rise of the spectrum occurs for $\omega^2 \approx c_0^2 [1 - \gamma]$, which actually is the boson peak. The gap below this value occurs, because we omitted the \mathbf{k} summation. If included, there is a crossover from the Debye behavior to the semicircular behavior. However, as we know from random matrix theory, the occurrence of a semicircular spectrum with width proportional to the mean of the distribution density of the matrix elements is a generic property of any random matrix.

So we can state that the boson peak marks the crossover from Debye's law (which is actually dictated by the translational symmetry of the equation of motion) to the semicircular law of the random Hamiltonian.

If the variance of its matrix elements exceeds their mean the system is unstable. The boson peak can be interpreted as the precursor of this instability.

4 Electron transport in disordered metals

4.1 Scattering, diffusion and Drude formula



Scattering path of a nearly free electron

We now consider nearly free electrons in a metal, which are occasionally scattered by an impurity or a lattice vibration (phonon), which passes by (see our figure). The electronic velocity is its momentum $p_F = \hbar k_F$, divided by its mass

$$v_F = \frac{1}{m} \hbar k_F \quad (4.1)$$

So, during the repeated scattering the electron performs a kind of random walk, and we make the ansatz

$$D = \frac{1}{3} \ell^2 \frac{1}{\tau} \quad (4.2)$$

Here ℓ is the mean-free path of the electron, i.e. the length an electron moves freely (on average) without being scattered. $1/\tau$ is the (average) scattering rate per unit time, which is related to ℓ via

$$\ell = v_F \tau, \quad (4.3)$$

so that we have

$$D = \frac{1}{3} \ell v_F = \frac{1}{3} v_F^2 \tau. \quad (4.4)$$

From the degenerate version of the Einstein relation (??) we obtain

$$\sigma = N(E_F) e^2 D = \frac{3}{2} \frac{n}{E_F} e^2 \frac{1}{3} \frac{\hbar^2 k_F^2}{m^2} \tau = \frac{1}{m} n e^2 \tau \quad (4.5)$$

This is the *Drude formula* for the electric conductivity of a metal, which can be derived from kinetic theory as well. We shall do so in the next paragraph. Here we have emphasized the random-walk aspect, which states, that a repeated scattering process is equivalent to a diffusion mechanism.

4.2 Boltzmann equation

We now consider the repeated scattering process of electrons in a metal more formally. As the transport phenomena do not involve wave functions but electronic densities and currents one considers Wigner's *generalized phase space function*

$$\begin{aligned} f_{\mathbf{k},s}(\mathbf{r}, t) &= \sum_{\mathbf{q}} e^{i\mathbf{q}\mathbf{r}} \psi_s^*(\mathbf{k} - \frac{\mathbf{q}}{2}) \psi_s(\mathbf{k} + \frac{\mathbf{q}}{2}) \\ &= \int d^3 \vec{\rho} e^{i\vec{\rho}\mathbf{k}} \psi_s^*(\mathbf{r} - \frac{\vec{\rho}}{2}) \psi_s(\mathbf{r} + \frac{\vec{\rho}}{2}) \end{aligned} \quad (4.6)$$

$\mathbf{r}, \vec{\rho}$ are center-of-mass and relative coordinates, resp.:

$$\mathbf{r} = \frac{1}{2} [\mathbf{r}_1 + \mathbf{r}_2] \quad \vec{\rho} = \mathbf{r}_2 - \mathbf{r}_1 \quad (4.7)$$

The scattering of a wave of wave vector \mathbf{k} can be accounted for by making a balance of “scattering in and out of the \mathbf{k} channel” in the following manner:

$$\left. \frac{\partial}{\partial t} f_{\mathbf{k},s}(\mathbf{r}, t) \right|_{\text{coll}} = -\frac{1}{V} \sum_{\mathbf{k}',s'} W_{\mathbf{k}\mathbf{k}'}^{s's'} f_{\mathbf{k},s} [1 - f_{\mathbf{k}',s'}] + \frac{1}{V} \sum_{\mathbf{k}',s'} W_{\mathbf{k}'\mathbf{k}}^{s's} f_{\mathbf{k}',s'} [1 - f_{\mathbf{k},s}] \quad (4.8)$$

The index “coll” means that this is the collisional change of the electronic phase space density due to collisions with an impurity or a phonon.

We now disregard the spin index and consider the quantities \mathbf{r} and $\mathbf{p} = \hbar\mathbf{k}$ in $f_{\mathbf{k}}(\mathbf{r}, t) \equiv f(\mathbf{p}, \mathbf{r}, t)$ as classical quantities $\mathbf{r}(t)$ and $\mathbf{p}(t)$. Then the collisional change of $f(\mathbf{p}, \mathbf{r}, t)$ should be equal to the *total time derivative* of $f(\mathbf{p}, \mathbf{r}, t)$:

$$\begin{aligned}\left.\frac{\partial f}{\partial t}\right|_{\text{coll}} &= \frac{\partial f}{\partial t} + \sum_{\alpha=1}^3 \frac{\partial f}{\partial p_{\alpha}} \frac{\partial p_{\alpha}}{\partial t} + \sum_{\alpha=1}^3 \frac{\partial f}{\partial x_{\alpha}} \frac{\partial x_{\alpha}}{\partial t} \\ &= \frac{\partial f}{\partial t} + \mathbf{F} \cdot \nabla_{\mathbf{p}} f + \mathbf{v} \cdot \nabla_{\mathbf{r}} f\end{aligned}\quad (4.9)$$

(4.9), together with the spinless version of (4.8) form the celebrated *Boltzmann equation* of electronic transport. \mathbf{F} is the force on the electron, which — in “semiclassical approximation” — is taken to be the Lorentz force

$$\mathbf{F} = -e[\mathbf{E} + \mathbf{v} \times \mathbf{B}] \quad (4.10)$$

In the *relaxation time approximation* one writes (see exercise 9.1)

$$\begin{aligned}\left.\frac{\partial f}{\partial t}\right|_{\text{coll}} &= -\frac{1}{\tau}(f - f_0) \\ \text{with } \frac{1}{\tau} &= \frac{1}{V} \sum_{\mathbf{k}'} W_{\mathbf{k}\mathbf{k}'} (1 - \mathbf{e}_{\mathbf{k}} \cdot \mathbf{e}'_{\mathbf{k}}) \Big|_{|\mathbf{k}|=|\mathbf{k}'|=k_F}\end{aligned}\quad (4.11)$$

Here f_0 is the equilibrium Fermi distribution. We now call $f - f_0 = f_1$ and assume that f_1 is created by the small external electric field \mathbf{E} , so that f_1 can be neglected in the force term. We further assume an uniform spatial distribution of the scattered electrons, i.e. $\nabla_{\mathbf{r}} f = 0$, and no explicit time dependence, i.e. $\partial f / \partial t = 0$, so that we get the following strongly simplified version of the Boltzmann equation

$$\mathbf{F} \cdot \nabla_{\mathbf{p}} f_0 = -\frac{f_1}{\tau} \quad (4.12)$$

We re-arrange $\nabla_{\mathbf{p}} f_0$ as

$$\begin{aligned}\nabla_{\mathbf{p}} f_0 &= \underbrace{\nabla_{\mathbf{p}} E}_{\mathbf{v}} \frac{\partial f}{\partial E} \\ \Rightarrow f_1 &= \tau \left(-\frac{\partial f}{\partial E} \right) \mathbf{v} \cdot \mathbf{F} = -e\tau \left(-\frac{\partial f}{\partial E} \right) \mathbf{v} \cdot \mathbf{E}\end{aligned}\quad (4.13)$$

For the field-induced current density we finally obtain

$$\begin{aligned}\mathbf{j} &= -\frac{2e}{V} \sum_{\mathbf{k}} f_1 \mathbf{v} \\ &= \frac{2e^2\tau}{V} \sum_{\mathbf{k}} \left(-\frac{\partial f}{\partial E} \right) \underbrace{\mathbf{v} \cdot \mathbf{E} \mathbf{v}}_{v^2 \mathbf{e}_z \text{ if } \mathbf{j} \parallel \mathbf{E} \parallel \mathbf{e}_z}\end{aligned}\quad (4.14)$$

from which we obtain the quantum Drude formula

$$\sigma = \frac{2e^3\tau}{3V} \sum_{\mathbf{k}} \left(-\frac{\partial f}{\partial E} \right) v^2 \quad (4.15)$$

$\xrightarrow{\text{Exercise 9.2}} \frac{ne^2\tau}{m^*} \quad \text{for } E = \frac{\hbar^2 k^2}{2m^*}$

4.3 Quantum interference effects

We consider again the scattering of the electrons as a random walk and construct a time variable along the walk as we have done in discussing the polymer chains. In terms of this time variable the diffusivity is given as

$$D = \lim_{t \rightarrow \infty} \frac{1}{2t} \langle r^2(t) \rangle = \lim_{t \rightarrow \infty} \int d^3 \mathbf{r} \frac{r^2}{2t} P(\mathbf{r}, t) \quad (4.16)$$

where $P(\mathbf{r}, t)$ is the diffusion probability density. Defining ϵ to be the Laplace variable (instead of p) we have

$$D = \lim_{\epsilon \rightarrow 0} \frac{\epsilon^2}{2} \langle r^2(\epsilon) \rangle = \lim_{\epsilon \rightarrow 0} \frac{\epsilon^2}{2} \int d^3 \mathbf{r} r^2 P(\mathbf{r}, \epsilon) \quad (4.17)$$

Now there exists a relation by Kubo and Greenwood

$$D \propto \lim_{\epsilon \rightarrow 0} \frac{\epsilon^2}{2} \int d^3 \mathbf{r} r^2 P_{\text{quantum}}(\mathbf{r}, \epsilon) \quad (4.18)$$

$$\text{with } P_{\text{quantum}}(\underbrace{\mathbf{r}_1 - \mathbf{r}_2}_{\mathbf{r}}, \epsilon) = \langle G_+(\mathbf{r}_1 - \mathbf{r}_2, \epsilon) G_-(\mathbf{r}_2 - \mathbf{r}_1, \epsilon) \rangle_{\text{disorder}}$$

$G_{\pm}(\mathbf{r}_1, \mathbf{r}_2, \epsilon) = \langle \mathbf{r}_1 | \mathcal{G} | \mathbf{r}_2 \rangle = \langle \mathbf{r}_1 | \frac{1}{E \mp i\epsilon - \mathcal{H}} | \mathbf{r}_2 \rangle$ is our old friend, the Green's function, which can be represented as a multiple-scattering expansion with respect to the fluctuating potential V as

$$\begin{aligned} \mathcal{G} &= \mathcal{G}_0 + \mathcal{G}_0 V \mathcal{G}_0 + \dots \\ &= \mathcal{G}_0 T \mathcal{G}_0 \end{aligned} \quad (4.19)$$

The scattering operator T involves all possible scattering processes, which can be decomposed into scattering processes from specific impurities, located at a site i , associated with a single-site T matrix t_i . The Green's function can then be decomposed as (we drop all ϵ s from now on)

$$G(\mathbf{r}, \mathbf{r}') = \sum_{\substack{\text{paths} \\ \text{from } \mathbf{r} \text{ to } \mathbf{r}'}} G_0(\mathbf{r}_0) t_1 G_0(\mathbf{r}_{12}) t_2 G_0(\mathbf{r}_{23}) \dots t_{n-1} G_0(\mathbf{r}_{n-1, n}) \quad (4.20)$$

with $\mathbf{r}_0 = \mathbf{r}$ and $\mathbf{r}_n = \mathbf{r}'$.

If, now, we approximate $|G|^2$ in such a way that we put

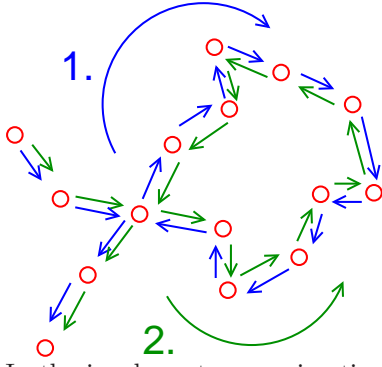
$$\left| \sum_{\text{paths}} G_0 t_1 G_0 t_2 \dots t_{n-1} G_0 \right|^2 \cong \sum_{\text{paths}} |G_0|^2 |t_1|^2 |G_0|^2 |t_2|^2 \dots |t_{n-1}|^2 |G_0|^2 \quad (4.21)$$

we obtain the diffusion propagator for $P_{\text{quantum}}(\mathbf{r}, \epsilon)$. with $\tau^{-1} \propto |t_i|^2$. By this procedure all interferences have been assumed to be cancelled out by the impurity averages, i.e. one has assumed that the $T_{ij} = A_{ij} e^{i\phi_{ij}}$ have all random phases ϕ_{ij} , which cancel out by the impurity average. As the free Green's functions have the form

$$G_0(r_{\nu, \nu+1}) \propto e^{ik_F r_{\nu, \nu+1}} \quad (4.22)$$

the phases ϕ_{ij} are just given by k_F times the length s_{ij} of the path from i to j . This fact leads to an *important exception* from the rule that the interference terms cancel out:

Assume that a multiple-scattering path contains a *loop*. As the positions of the impurities do not change in time, the phases along this path are fixed once forever. Let us now consider two paths one, which leads *clockwise* around the loop, the other *anticlockwise*. The phases along both paths are exactly the same so that we have for the intensities of the two processes



$$\begin{aligned}
|T_1 + T_2|^2 &= \left| A_1 e^{i\phi_1} + A_2 e^{i\phi_2} \right|^2 \\
&= |A_1|^2 + |A_2|^2 + 2A_1 A_2 \underbrace{\cos(\phi_1 - \phi_2)}_{=1 \text{ for } \phi_1 = \phi_2} \\
&= 4|A_1|^2 \quad \text{for } A_1 = A_2
\end{aligned}
\tag{4.23}$$

In the incoherent approximation (4.21) one would obtain $|T_1 + T_2|^2 = 2|A_1|^2$ instead. In the incoherent approximation, which treats the quantum propagator $P_{\text{quantum}}(\mathbf{r}, \epsilon)$ as classical diffusion propagator the closed-loop interferences are missing. Obviously there must be a correction to the scattering rate due to the closed-loops:

$$\tau^{-1} = \tau_0^{-1} + \Delta\tau^{-1} \tag{4.24}$$

which is of the form

$$\Delta\tau^{-1} \propto \sum_{\text{loops}} \overbrace{t_1 G_0 t_2 G_0} \cdots \sum_{\text{loops}} \overbrace{t_1 G_0 t_2 G_0} \cdots \tag{4.25}$$

which can be approximated as

$$\Delta\tau^{-1} \propto G_{\text{diff}}(\mathbf{r} = 0, \epsilon \rightarrow 0) = \lim_{\epsilon \rightarrow 0} \int_0^\infty dt \frac{1}{[4\pi D_0 t]^{d/2}} e^{-\epsilon t} \tag{4.26}$$

where we have used the expression for the d dimensional diffusion propagator

$$G_{\text{diff}}(\mathbf{r}, t) = \frac{1}{[4\pi D_0 t]^{d/2}} e^{-r^2/4Dt} \tag{4.27}$$

For evaluating the interference contribution (4.26) we first consider $d = 3$:

$$\int_0^\infty dt t^{-3/2} e^{-\epsilon t} = \epsilon^{1/2} \Gamma(-1/2) \xrightarrow{\epsilon \rightarrow 0} 0 \tag{4.28}$$

So the contribution vanishes, unless there is a *maximum loop length*, given by the *inelastic mean-free path* ℓ_{in} due to scattering from phonons. In this case ϵ is replaced by $\tau_{\text{in}}^{-1} = v_F/\ell_{\text{in}}$. Assuming² $\tau_{\text{in}}^{-1} \propto T^p$ we obtain a correction with a temperature dependence $\propto T^{p/2}$.

Let us now consider the case $d = 2$. The integral $\int_0^\infty \frac{dt}{t}$ certainly *diverges*. This is a first indication for a *disorder and interference induced localization transition in $d = 2$* , which we shall discuss in the next subsection. If we insert a minimal and maximal scattering time (the minimal one corresponding to the elastic mean-free path $\ell_0 = v_F \tau_0$) we obtain

$$\Delta\tau^{-1} \propto \ln \tau_{\text{in}}/\tau_0 \propto -\ln T \tag{4.29}$$

Such a behavior is, indeed observed in two-dimensional devices.

4.4 Anderson localization

In 1958 P. W. Anderson published his famous paper “Absence of diffusion in certain random lattices”, in which he showed that the diffusion coefficient of an electron in a random potential V can be zero if the spatial fluctuations measured by $\langle (V - \langle V \rangle)^2 \rangle / (\langle V \rangle)^2$ exceed a certain critical value. This happens roughly when the mean free path due to the potential fluctuations becomes as short as the electronic wavelength or (equivalently) an interatomic distance. In 1979 Abrahams, Anderson, Licciardello and Ramakrishnan showed that this *localization* effect is due to a *quantum interference effect* first discussed by Langer and Neal in 1966. We just discussed this effect in the previous subsection.

²The exponent p can vary between 2 and 5, depending on the type of material.

We now discuss the Anderson localization transition (or *metal-nonmetal transition*) from the point of view of electrons in a random environment and present the scaling ideas of Abrahams *et al.* . In his original paper Anderson considered a tight-binding Hamiltonian with a spatially fluctuating local energy ϵ_i representing the fluctuations of the external potentials:

$$\mathcal{H} = \mathcal{H}_1 + \mathcal{H}_0 = \sum_i \epsilon_i |i\rangle\langle i| + t \sum_{\substack{ij \\ \text{n.N.}}} |i\rangle\langle j| \quad (4.30)$$

We assume that the on-site energies $\epsilon_i = \epsilon_0 + \Delta\epsilon_i$ are random variables with average ϵ_0 and relative variance $\sigma_\epsilon = \langle (\Delta\epsilon_i)^2 \rangle / \epsilon_0^2$. Near the lower band edge \mathcal{H}_0 can be represented by a free-electron Hamiltonian with effective mass $m^* = \hbar^2 / 2ta^2$, where a is the lattice constant of a simple-cubic lattice.

Anderson found that there exists a critical amount σ_c of disorder. For $\sigma_\epsilon < \sigma_c$ the mean-square displacements of the electrons increases linearly with time, whereas for $\sigma_\epsilon > \sigma_c$ it has an upper bound r_0^2 :

$$\langle r^2(t) \rangle \begin{cases} \propto t & \sigma_\epsilon < \sigma_c & \text{Diffusion} \\ \leq r_0^2 & \sigma_\epsilon > \sigma_c & \text{Localization} \end{cases} \quad (4.31)$$

r_0 is called *localization length*, and, in the localized state the electronic wave function has an envelope, which decays exponentially beyond r_0 :


$$\psi(\mathbf{r}) = \sum_{\alpha} a_W(\mathbf{r}) e^{-|\mathbf{r}-\mathbf{r}_\alpha|/r_0} \quad (4.32)$$

where $a_W(\mathbf{r})$ is a Wannier function and \mathbf{r}_α are some random points in the disordered material. The important point is, if one considers a piece of disordered material, the *conductance* G of the material will decay exponentially with the length L of a bar

$$G(L) \propto e^{-L/r_0} \quad (4.33)$$


We now turn to the *scaling argument of Abraham et al.*:

We consider the length dependence of the conductance a *metallic* piece of material of size L^d of resistivity ρ



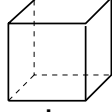
$\mathbf{d} = 1$

$G \propto \frac{1}{\rho L}$



$\mathbf{d} = 2$

$G \propto \frac{1}{\rho}$



$\mathbf{d} = 3$

$G \propto \frac{L}{\rho}$

$$\quad (4.34)$$

We want to construct a dimensionless conductance and define

$$\frac{1}{G_0} = \frac{\hbar}{e^2} = \frac{1.05 \cdot 10^{-34} \text{Ws}^2}{(1.6)^2 \cdot 10^{-38} (\text{As})^2} = 410\Omega \quad (4.35)$$

so that we have in the metallic regime

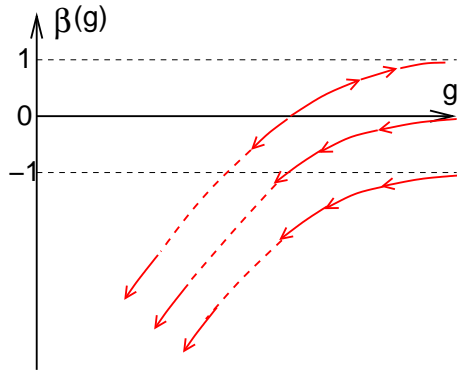
$$\lim_{L \rightarrow \infty} g(L) = \lim_{L \rightarrow \infty} \frac{G(L)}{G_0} \propto L^{d-2} \quad (4.36)$$

In the localized regime we expect

$$\lim_{L \rightarrow \infty} g(L) \propto e^{L/r_0} \rightarrow 0 \quad (4.37)$$

The *scaling hypothesis* now consists in postulating that in all dimension and whether there is localization or not $g(L)$ can be represented as

$$g(L) = g_0 L^\beta \quad \text{or inversely} \quad \beta(g) = \frac{d \ln g}{d \ln L} \quad (4.38)$$



where $\beta(g)$ is supposed to be a *universal* function of g . If $\beta(g)$ is known, one can decide from the *sign* of β , whether

$$\lim_{L \rightarrow \infty} g(L) \begin{cases} \rightarrow \infty & \text{metallic for } \beta > 0 \\ \rightarrow 0 & \text{localized for } \beta < 0 \end{cases} \quad (4.39)$$

How can $\beta(g)$ look like? For large g we have

$$\lim_{g \rightarrow \infty} \beta = d - 2 \quad (4.40)$$

Abrahams *et al.* calculated the *corrections* to this asymptotic law:

$$\beta(g) = d - 2 - \frac{\text{cons.}}{g} \quad (4.41)$$

On the other hand, we have for small g $g(L) \propto e^{-L/r_0}$, from which follows

$$\lim_{g \rightarrow 0} \beta(g) = \ln g - \text{const.} \quad (4.42)$$

Result:

The scaling transformation (increasing L) leads to a *vanishing conductance* in $d = 1$ and $d = 2$. This means that, in these dimensions, for *any* disorder there is always localization, i.e. $\lim_{L \rightarrow \infty} g(L) = 0$. In $d = 3$ this limit depends on the degree of disorder: if in a sample of a certain size L the dimensionless conductance is smaller than the critical one it will scale towards zero. If it is larger, it will scale towards infinity. The point, where $\beta(g)$ crosses the zero line is an *unstable fixed point* of the scaling transformation. These findings have been backed up by a field-theoretical treatment of the Anderson transition by F. Wegner and other authors. Within the field-theoretical formalism the scaling transformation corresponds to the *renormalization group transformation*.

4.5 Quantum-Hall effect, QHE

4.5.1 Normal Hall effect and the QHE

We write down the Boltzmann equation in relaxation-time approximation for an electron with momentum $\mathbf{p} = \hbar \mathbf{k}$ in static electric and magnetic fields $\mathbf{E} = (E_x, E_y, 0)$ and $\mathbf{B} = (0, 0, B)$:

$$0 = - \left[e\mathbf{E} + \frac{1}{m} \mathbf{p} \times \mathbf{B} \right] - \frac{1}{\tau} \mathbf{p} \quad (4.43)$$

We introduce the cyclotron frequency $\omega_c = eB/m$ and obtain component-by-component

$$\begin{aligned} 0 &= -eE_x - \omega_c p_y - \frac{p_x}{\tau} \\ 0 &= -eE_y + \omega_c p_x - \frac{p_y}{\tau} \end{aligned} \quad (4.44)$$

With $\mathbf{j} = -ne\mathbf{p}/m$ and $\sigma_0 = ne^2\tau/m$ we obtain

$$\begin{aligned} \sigma_0 E_x &= \omega_c \tau j_y + j_x \\ \sigma_0 E_y &= -\omega_c \tau j_x + j_y \end{aligned} \quad (4.45)$$

i.e.

$$\sigma_0 \mathbf{E} = \begin{pmatrix} 1 & \omega_c \tau \\ -\omega_c \tau & 1 \end{pmatrix} \mathbf{j} \quad (4.46)$$

which we re-write as

$$\mathbf{E} = \vec{\rho} \begin{pmatrix} \rho_0 & -R_H B \\ R_H B & \rho_0 \end{pmatrix} \mathbf{j} \quad (4.47)$$

Here

$$R_H = -\frac{1}{ne} \quad (4.48)$$

is the *Hall-coefficient* and we have

$$|\rho_{xy}| = \frac{B}{ne} = \underbrace{\frac{eB}{\hbar}}_{\ell_B^2} \frac{1}{n} \frac{\hbar}{e^2} = \underbrace{\frac{2\pi\ell_B^2}{n}}_{1/\nu} \frac{h}{e^2} \quad (4.49)$$

ν is the so-called *fill factor*, and it turns out that the Hall resistivity for large fields is *quantized* in such a way that ν takes only *integer* numbers³.

4.5.2 Quantum Mechanics: Landau Levels

Here we review the quantum mechanics of an electron in a magnetic field (without taking spin effects into account). The Schrödinger equation for a electron (living in the $x - y$ plane) in a magnetic field in z direction is given by

$$\left[\frac{1}{2m} (i\hbar\nabla + e\mathbf{A})^2 + V(\mathbf{r}) \right] \psi(\mathbf{r}) = E\psi(\mathbf{r}) \quad (4.50)$$

Here the *Landau gauge* is used $\mathbf{A} = (-By, 0)$ If we further assume V to be only y dependent the Schrödinger equation is separable:

$$\psi(\mathbf{r}) = e^{ikx} \chi(y) \quad (4.51)$$

In x direction the solutions are plane waves. In y direction the solution can, of course, only be given if $V(y)$ is specified.

We first set $V = 0$ and obtain

$$\left[-\frac{\hbar^2 \partial_y^2}{2m} + \underbrace{\frac{(eBy + \hbar k)^2}{2m}}_{\frac{1}{2} m \omega_c^2 (y-Y)^2} \right] \chi(y) = E\chi(y) \quad (4.52)$$

Here $Y = -\hbar k / eB = -\ell_B^2 k$ is the “mid-point coordinate” of an effective one-dimensional harmonic oscillator with angular frequency ω_c . The energy levels are, of course

$$E_n = \left(n + \frac{1}{2}\right) \omega_c \quad (4.53)$$

and the wave-functions are given by

$$\chi(y) = e^{-\frac{1}{2}(y-Y)^2/\ell_B^2} H_n\left(\frac{y-Y}{\ell_B}\right) \quad (4.54)$$

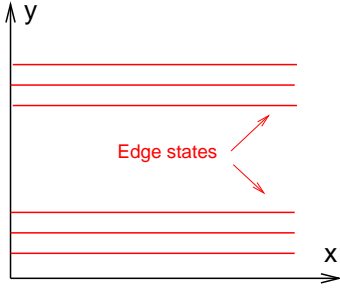
where H_n are the Hermite polynomials.

We now turn to the inclusion of $V(y)$. If the field B is big enough 1st-order perturbation theory is sufficient, and we have

$$\begin{aligned} \Delta E_n &= \langle \chi_n^{(0)} | V | \chi_n^{(0)} \rangle \\ &= \int dy (\chi_n^{(0)})^2 (y - Y) V(y) \approx V(Y) \\ E_N &= E_n(Y) = E_n^{(0)} + V(Y) \end{aligned} \quad (4.55)$$

We now assume that $V(y)$ specifies the profile of a confining potential in y direction, i.e. we consider a *lead* in x direction. The corresponding band structure in y direction is depicted in the figure.

³For very large fields it can also take rationally fractional numbers (*fractional QHE*)



The Edge states are localized, where the band structure “pinches” through E_F

We now generalize the above reasoning. In another gauge one has

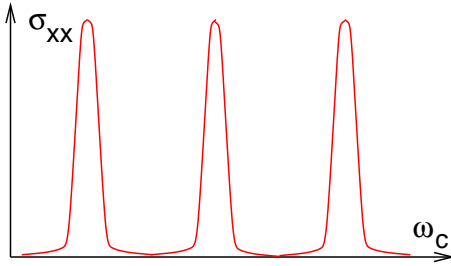
$$E_n = E_n^{(0)} + V(\mathbf{R}) \quad (4.57)$$

where $\mathbf{R} = (X, Y)$ is the midpoint coordinate of a cyclotron orbit. We now assume that the potential, in addition to the confining part, has a *spatially fluctuating* part as in the Anderson problem:

$$V(\mathbf{r}) = V_{\text{edge}}(y) + \Delta V(\mathbf{r}) \quad (4.58)$$

For the states contributing to the electric current we now have the condition

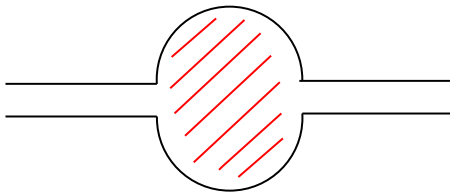
$$E_F = E_n^{(0)} + V_{\text{edge}}(Y) + \Delta V(\mathbf{R}) \quad (4.59)$$



Schematic dependence of σ_{xx} on ω_c

We now consider the appearance or disappearance of an edge channel, which occurs by changing the magnetic field (i.e. ω_c). If the bottom of the surface defined by $E_n(\mathbf{R})$ moves to the vicinity of E_F the situation may occur, in which a conducting path can lead in y direction. This path is the result of a *percolation transition*. By changing ω_c , first E_F touches the “valleys” in $\Delta V(\mathbf{r})$, leading to “islands”, around which conducting edges exist. At the percolation transition the islands turn to land paths and the “water passages” turn to “lakes”. Just at the transition the edges of the land paths co-existing with water passages form conducting paths in y direction. This leads to a spike in the $x - x$ conductivity as depicted in the 3rd figure.

4.5.3 Landauer-Büttiker formula and the QHE



Geometry for the Landauer formula

We consider quantum-mechanical electrons traveling along some “quantum channels” in a 2-dimensional plane and coming across some “obstacles”, which give rise to reflection and transmission of the channel waves. The influence of such an obstacle can be treated like a resistance $R_{12} = 1/g_{12}$, i.e.

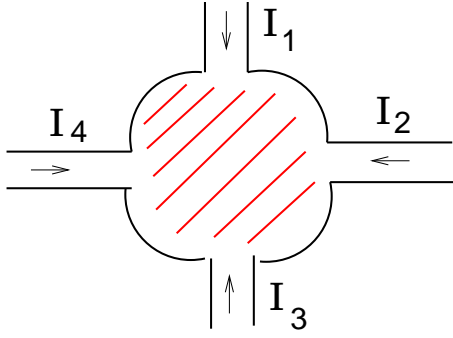
$$I = g_{12}(V_1 - V_2) \quad (4.60)$$

where the conductance is given by

$$g_{12} = 2 \frac{e^2}{h} T_{12} \quad (4.61)$$

The factor 2 takes each spin into account. $T_{12} = |t_{12}|^2$ is the quantum-mechanical transmission probability through the obstacle, where $t_{12} = t_{12}(E_F)$ is the transmission amplitude. Landauer realized that the voltage drop of microscopic electrons in a quantum environment is only governed by scattering processes and is *not* associated with dissipation⁴. The dissipation of the complete circuit in a device occurs exclusively in the thermal bath connected to the device. This version of Ohm’s law is called *Landauer formula*.

⁴The residual resistance of a metal is also a zero-temperature property of the ground state of the metal and is exclusively related to scattering processes of the electrons from the impurities.



Geometry for the Landauer-Büttiker formula

The *coefficients of resistance* at the Quantum-Hall device are defined by

$$R_{k\ell, mn} = \frac{V_m - V_n}{I} \quad I = I_k = -I_\ell \quad (4.64)$$

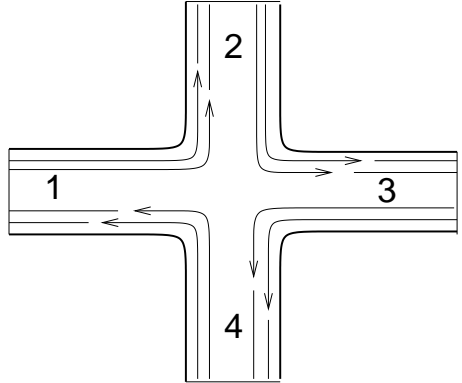
I_k is the source current, I_ℓ the drain current.

One can generalize the Landauer formula for an obstacle connected to more than two leads, where one counts - as in Kirchoff's laws - the in-going currents as positive:

$$I_m = - \sum_n g_{mn} V_n \quad (4.62)$$

From current conservation we have $\sum_n g_{mn} = 0 \Leftrightarrow g_{mm} = - \sum_{n \neq m} g_{mn}$ so that the *Landauer-Büttiker formula* takes the form

$$I_m = \sum_{n \neq m} g_m n (V_m - V_n) \quad (4.63)$$



Geometry for the quantum Hall-effect

The edge states now form channels along which the electron can move. Each channel gives a quantum contribution to the conductance, so that we have

$$g_{12} = g_{23} = g_{34} = g_{41} = g_c = 2N \frac{e^2}{h} \quad (4.65)$$

$$g_{ij} = 0 \quad \text{else}$$

N is the number of channels and the factor 2 accounts for the spin degrees of freedom. The Hall resistance, therefore, is given by

$$R_{\text{Hall}} = R_{13,42} = \frac{V_4 - V_2}{I_2} \quad (4.66)$$

From the Landauer Formula we have

$$I_2 = g_c(V_2 - V_3) = 0 \quad \Rightarrow \quad V_2 = V_3$$

$$I_4 = g_c(V_4 - V_1) = 0 \quad \Rightarrow \quad V_4 = V_1$$

$$I_1 = g_c(V_1 - V_2) = g_c(V_4 - V_2)$$

So we finally obtain

$$R_{\text{Hall}} = R_{13,42} = \frac{1}{g_c} = \frac{h}{2Ne^2} \quad (4.67)$$

On the other hand, if the voltage leads are *not* transverse to the current, e.g. at 3,4

$$I_3 = g_c(V_3 - V_4) = 0 \quad \Rightarrow \quad V_3 = V_4$$

$$I_4 = g_c(V_4 - V_1) = 0 \quad \Rightarrow \quad V_4 = V_1$$

$$\Rightarrow \quad R_{12,34} = \frac{V_3 - V_4}{I_1} = 0 \quad \text{etc...}$$

This scenario is valid if E_F is *not* in the vicinity of the bottom of the potential $V(y)$, where the fluctuations lead to the percolation transition discussed above.

How is the Fermi level E_F determined? We have for the density of electrons

$$n_e = \int_{-\infty}^{E_F} N(E) dE \quad (4.68)$$

where $N(E)$ is the density of states. In the absence of disorder we would have

$$N_0(E) \propto \sum_n \delta(E - E_n) \quad (4.69)$$

In this case the Fermi level would be “pinned” at one of the E_n and could never be situated between the Landau levels. In the presence of disorder we have

$$N(E) \propto \sum_n \frac{\Gamma}{\Gamma^2 + (E - E_n)^2} \quad (4.70)$$

The states in between the levels are *localized*, so that now E_F can take any position, depending on the applied field B or the gate voltage. If one of these parameters is changed, such that E_F passes one of the E_n a *step* in R_{Hall} occurs.

For large field strength B the localized states are the edge states corresponding to the fluctuating potential $V(x, y) = V_0(y) + \Delta V(x, y)$. For B smaller than the application range of the semiclassical approximation a version of Anderson localization theory including an applied field must be used in order to devise a theory for the QHE. Such a theory has been outlined⁵, but not yet satisfactorily been established.

It should be noted, that for very large fields the *fractional* quantum Hall effect is observed, i.e. steps in R_{Hall} with fractional filling factors of the form $N = 1/\nu$, where ν are odd numbers⁶.

5 Theory of hopping transport in doped semiconductors

6 Field-theoretical treatment of quenched disorder

6.1 Gaussian integrals

6.2 Functional-integral representation of the Green’s function

6.3 Configurational average and replica trick

6.4 Effective field theory for the Anderson problem

6.5 Effective field theory for the scalar phonon problem

⁵M. Janssen, O. Viehweger, U. Fastenrath, J. Hajdu, *Introduction to the theory of the integer quantum Hall effect*, Verlag Chemie, 1994

⁶D.C. Tsui, H.L. Störmer, and A.C. Gossard, Phys. Rev. Lett. 48, 1559 (1982); R.B. Laughlin, Phys. Rev. Lett. 50, 1395 (1983)

7 Elasticity theory with fluctuating shear modulus

We consider an inhomogeneous disordered solids in which we allow the Lam'e constants λ and μ to fluctuate in space. This leads to the Lagrange density

$$\mathcal{L} = \frac{m_0}{2} \sum_{i=x,y,z} \dot{u}_i(\vec{r}, t)^2 - \frac{\lambda(\vec{r})}{2} \left(\sum_i \epsilon_{ii}(\vec{r}, t) \right)^2 (\vec{r}, t) - \mu(\vec{r}) \sum_{ij} \epsilon_{ij}(\vec{r}, t)^2. \quad (7.1)$$

The strain tensor is defined as above

$$\epsilon_{ij}(\vec{r}, t) = \frac{1}{2} (\partial_i u_j(\vec{r}, t) + \partial_j u_i(\vec{r}, t)) \quad i, j = x, y, z \quad (7.2)$$

Combining (7.2) and (7.1) leads to

$$\mathcal{L} = \frac{m_0}{2} \sum_i \dot{u}_i(\vec{r}, t)^2 - \frac{\lambda(\vec{r})}{2} \sum_{ij} \partial_i u_i(\vec{r}, t) \partial_j u_j(\vec{r}, t) \quad (7.3)$$

$$- \frac{\mu(\vec{r})}{2} \sum_{ij} \left((\partial_i u_j(\vec{r}, t) \partial_i u_j(\vec{r}, t) + \partial_i u_j(\vec{r}, t) \partial_j u_i(\vec{r}, t)) \right). \quad (7.4)$$

With the help of the Euler-Lagrange equations

$$\sum_{l=x,y,z,t} \partial_l \left(\frac{\partial \mathcal{L}}{\partial (\partial_l u_k)} \right) - \frac{\partial \mathcal{L}}{\partial u_k} = 0, \quad k = x, y, z$$

we obtain the equations of motion

$$m_0 \ddot{u}_i(\vec{r}, t) - \sum_j \left[\partial_i \lambda(\vec{r}) \partial_j u_j(\vec{r}, t) + \partial_j \mu(\vec{r}) \partial_i u_j(\vec{r}, t) + \partial_j \mu(\vec{r}) \partial_j u_i(\vec{r}, t) \right] = 0 \quad i = x, y, z \quad (7.5)$$

Now we transform into frequency space with the transformation rules

$$u_j(\vec{r}, t) = \frac{1}{2\pi} \int_{-\infty}^{\infty} d\omega_\xi u_j(\vec{r}, \omega_\xi) \cdot e^{-i\omega_\xi t} \quad (7.6)$$

$$u_j(\vec{r}, \omega_\xi) = \int_{-\infty}^{\infty} dt u_j(\vec{r}, t) \cdot e^{i\omega_\xi t} \quad (7.7)$$

$$\omega_\xi := \omega + i\xi\eta \quad (7.8)$$

where $\xi = \pm 1, \eta \rightarrow 0$. The equations of motion can be written as

$$A_{ij}(\vec{r}, \omega_\xi) u_j(\vec{r}, \omega_\xi) = 0 \quad i = x, y, z \quad (7.9)$$

with

$$A_{ij}(\vec{r}, \omega_\xi) = -\omega_\xi^2 \delta_{ij} - m_0^{-1} (\partial_i \lambda(\vec{r}) \partial_j + \partial_j \mu(\vec{r}) \partial_i + \partial_l \mu(\vec{r}) \partial_l \delta_{ij}). \quad (7.10)$$

In the following $\lambda(\vec{r})$ is assumed to be constant while $\mu(\vec{r})$ is assumed to fluctuate randomly in space. The reason for this is motivated by the fact that $\mu(\vec{r})$ would be zero in liquids as liquids do not have a shear modulus. So we expect $\mu(\vec{r})$ to have strong fluctuations in amorphous solids.

Now we want to split (7.10) into a constant part and a part which depends on the location. So we replace

$$\lambda(\vec{r}) = m_0 \cdot \bar{\lambda}_0 \quad (7.11a)$$

$$\mu(\vec{r}) = m_0 \cdot (\bar{\mu}_0 + \Delta\bar{\mu}(\vec{r})) \quad (7.11b)$$

where $m_0 \cdot \bar{\mu}_0$ is the average of $\mu(\vec{r})$

$$m_0 \cdot \bar{\mu}_0 = \langle \mu(\vec{r}) \rangle. \quad (7.12)$$

This means also that the average of $\Delta\bar{\mu}(\vec{r})$ is zero

$$\langle \Delta\bar{\mu}(\vec{r}) \rangle = 0. \quad (7.13)$$

We now introduce a complex variable

$$z_\xi = -\omega_\xi^2 \quad (7.14)$$

and drop the suffix ξ further on. We further split $A_{ij}(\vec{r}, z)$ into a spatially fluctuating part $A_1(\vec{r})_{ij}$ and an ‘‘unperturbed’’ part $A_0(z)_{ij}$ which does not fluctuate in space

$$A_{ij}(\vec{r}, z) = A_0(z)_{ij} + A_1(\vec{r})_{ij} \quad (7.15a)$$

$$A_0(z)_{ij} = -z^2 \delta_{ij} - (\bar{\lambda}_0 + \bar{\mu}_0) \partial_i \partial_j - \bar{\mu}_0 \delta_{ij} \partial_l \partial_l \quad (7.15b)$$

$$A_1(\vec{r})_{ij} = -\partial_j \Delta \bar{\mu}(\vec{r}) \partial_i - \delta_{ij} \partial_l \Delta \bar{\mu}(\vec{r}) \partial_l \quad (7.15c)$$

7.1 Fluctuations of the elastic constants

The elastic constant $\mu(\vec{r})$ fluctuates in space. Although the average of $\Delta \bar{\mu}(\vec{r})$ is defined to be zero, $\langle \Delta \bar{\mu}(\vec{r})^2 \rangle$ is expected to have a finite value. As we are interested in average values of all quantities, we define the *configurational average* $\langle \dots \rangle$. The configurational average of a quantity A is defined to be

$$\langle A \rangle \equiv \int \mathcal{D}[\Delta \bar{\mu}(\vec{r})] P([\Delta \bar{\mu}(\vec{r})]) A([\Delta \bar{\mu}(\vec{r})]) \quad (7.16)$$

$\int \mathcal{D}[\Delta \bar{\mu}(\vec{r})]$ is a functional integral over all possible functions $\Delta \bar{\mu}(\vec{r})$. A system with a specific function $\Delta \bar{\mu}(\vec{r})$ is defined to be a configuration $[\Delta \bar{\mu}(\vec{r})]$. $P([\Delta \bar{\mu}(\vec{r})])$ is then the probability density for this configuration to occur. $A([\Delta \bar{\mu}(\vec{r})])$ is the value the quantity A takes with this configuration. So the configurational average of $\Delta \bar{\mu}(\vec{r}_0)^2$ is expected to be independent of \vec{r}_0

$$\langle \Delta \bar{\mu}(\vec{r}_0)^2 \rangle \equiv \langle \Delta \bar{\mu}^2 \rangle \quad (7.17)$$

Additionally the fluctuations of $\Delta \bar{\mu}(\vec{r}_0)$ and $\Delta \bar{\mu}(\vec{r}_0 + \vec{r})$ can be correlated. So we introduce the *correlation function* $\gamma(\vec{r})$

$$\boxed{\gamma(\vec{r}) := \langle \Delta \bar{\mu}(\vec{r}_0) \Delta \bar{\mu}(\vec{r}_0 + \vec{r}) \rangle} \quad (7.18)$$

Now we need an ansatz for the probability $P([\Delta \bar{\mu}(\vec{r})])$ for a certain configuration $[\Delta \bar{\mu}(\vec{r})]$. The main condition for this function $P([\Delta \bar{\mu}(\vec{r})])$ is that the resulting integrals of the kind (7.16) can be evaluated somehow. As this is only the case for a Gaussian function we make the ansatz

$$P([\Delta \bar{\mu}(\vec{r})]) = P_0 \cdot e^{-\frac{1}{2} \int d^3 r d^3 r' \Delta \bar{\mu}(\vec{r}) \Delta \bar{\mu}(\vec{r}') B(\vec{r}, \vec{r}')} \quad (7.19)$$

where the function $B(\vec{r}, \vec{r}')$ is still to be determined. P_0 is a normalization constant which has to be chosen in such a way that the equation

$$\int \mathcal{D}[\Delta \bar{\mu}(\vec{r})] P([\Delta \bar{\mu}(\vec{r})]) = P_0 \int \mathcal{D}[\Delta \bar{\mu}(\vec{r})] e^{-\frac{1}{2} \int d^3 r d^3 r' \Delta \bar{\mu}(\vec{r}) \Delta \bar{\mu}(\vec{r}') B(\vec{r}, \vec{r}')} \stackrel{!}{=} 1 \quad (7.20)$$

is fulfilled.

In order to simplify the notation we introduce Dirac’s bra and ket notation. As there are some different possibilities for the normalization of the bra and ket vectors their main properties are summed up in the following:

- $|\vec{r}\rangle$ and $|\vec{k}\rangle$ are eigenvectors of the real and momentum space, respectively, with

$$\langle \vec{r} | \vec{k} \rangle = \frac{1}{\sqrt{V}} e^{i\vec{k}\vec{r}} \quad (7.21)$$

The ket vector of an arbitrary function $\psi(\vec{r})$ has the properties

$$\langle \vec{r} | \psi \rangle = \psi(\vec{r}) \quad (7.22a)$$

$$\langle \vec{k} | \psi \rangle = \frac{1}{\sqrt{V}} \psi(\vec{k}) = \frac{1}{\sqrt{V}} \int d^3 r e^{-i\vec{k}\vec{r}} \psi(\vec{r}) \quad (7.22b)$$

Nonlocal functions $A(\vec{r}, \vec{r}')$ can be defined in terms of operators \hat{A} with the properties

$$\langle \vec{r}' | \hat{A} | \vec{r}' \rangle = A(\vec{r}, \vec{r}') \quad (7.23a)$$

$$\langle \vec{k} | \hat{A} | \vec{k}' \rangle = \frac{1}{V} A(\vec{k}, \vec{k}') = \frac{1}{V} \int d^3r d^3r' e^{-i\vec{k}\vec{r} + i\vec{k}'\vec{r}'} A(\vec{r}, \vec{r}'). \quad (7.23b)$$

If $\langle \vec{r}' | \hat{A} | \vec{r}' \rangle$ depends only on the distance between \vec{r} and \vec{r}'

$$\langle \vec{r}' | \hat{A} | \vec{r}' \rangle = A(\vec{r} - \vec{r}') \quad (7.24)$$

you can write

$$\langle \vec{k} | \hat{A} | \vec{k}' \rangle = \delta_{\vec{k}, \vec{k}'} A(\vec{k}) \quad (7.25)$$

with

$$A(\vec{k}) = \int d^3r e^{-i\vec{k}\vec{r}} A(\vec{r}) \quad (7.26)$$

- The bra and ket vectors fulfil the following orthogonality relations

$$\langle \vec{r}' | \vec{r}' \rangle = \delta^{(3)}(\vec{r} - \vec{r}') \quad (7.27a)$$

$$\langle \vec{k} | \vec{k}' \rangle = \delta_{\vec{k}, \vec{k}'} \quad (7.27b)$$

- The bra and ket vectors fulfil the following completeness relations

$$\int d^3r |\vec{r}\rangle \langle \vec{r}| = \hat{1} \quad (7.28)$$

$$\sum_{\vec{k}} |\vec{k}\rangle \langle \vec{k}| = \hat{1} \quad (7.29)$$

where $\hat{1}$ is the unity operator with

$$\hat{1} |\psi\rangle = |\psi\rangle \quad (7.30)$$

for any $|\psi\rangle$.

- The trace of an operator \hat{A} is defined to be

$$\text{Tr} \hat{A} := \int d^3r \langle \vec{r}' | \hat{A} | \vec{r}' \rangle = \sum_{\vec{k}} \langle \vec{k} | \hat{A} | \vec{k} \rangle \quad (7.31)$$

The dimension N of the Hilbert space is then

$$\begin{aligned} N &= \text{Tr} \hat{1} = \int d^3r \sum_{|\vec{k}| < k_D} \langle \vec{r} | \vec{k} \rangle \langle \vec{k} | \vec{r} \rangle \\ &= \frac{V}{(2\pi)^3} \frac{4\pi}{3} k_D^3. \end{aligned} \quad (7.32)$$

The Debye cutoff is needed to take care of the fact that the disordered solid is composed by N atoms, which restricts the number of modes to $3N$.

Equation (7.19) can now be written as

$$P([\Delta\bar{\mu}(\vec{r})]) = P_0 \cdot e^{-\frac{1}{2} \langle \Delta\bar{\mu} | \hat{B} | \Delta\bar{\mu} \rangle} \quad (7.33)$$

and the functional integrals are denoted by

$$\int \mathcal{D}[\Delta\bar{\mu}(\vec{r})] \rightarrow \int \mathcal{D}[\Delta\bar{\mu}]. \quad (7.34)$$

We now make use of the integral transform theorems (see above)

$$\int \mathcal{D}|u\rangle e^{-\frac{1}{2} \langle u | \hat{A} | u \rangle} e^{\langle j | u \rangle} = \sqrt{2\pi}^N e^{-\frac{1}{2} \text{Tr} \ln \hat{A}} e^{\frac{1}{2} \langle j | \hat{A}^{-1} | j \rangle} \quad (7.35)$$

or equivalently

$$\int \mathcal{D}|u\rangle e^{-\frac{1}{2}\langle u|\hat{A}|u\rangle} e^{\langle j|u\rangle} = e^{\frac{1}{2}\langle j|\hat{A}^{-1}|j\rangle} \int \mathcal{D}|u\rangle e^{-\frac{1}{2}\langle u|\hat{A}|u\rangle} \quad (7.36)$$

We now obtain for the correlation function

$$\begin{aligned} & \langle \Delta\bar{\mu}(\vec{r}_0) \Delta\bar{\mu}(\vec{r}_0 + \vec{r}) \rangle = \\ & = P_0 \int \mathcal{D}|\Delta\bar{\mu}\rangle \langle \vec{r}_0|\Delta\bar{\mu}\rangle \langle \vec{r}_0 + \vec{r}|\Delta\bar{\mu}\rangle e^{-\frac{1}{2}\langle \Delta\bar{\mu}|\hat{B}|\Delta\bar{\mu}\rangle} \end{aligned} \quad (7.37a)$$

$$= P_0 \frac{\partial}{\partial \langle \vec{r}_0|j\rangle} \frac{\partial}{\partial \langle \vec{r}_0 + \vec{r}|j\rangle} \int \mathcal{D}|\Delta\bar{\mu}\rangle e^{-\frac{1}{2}\langle \Delta\bar{\mu}|\hat{B}|\Delta\bar{\mu}\rangle} e^{\langle j|\Delta\bar{\mu}\rangle} \Big|_{|j\rangle=0} \quad (7.37b)$$

$$= \frac{\partial}{\partial \langle \vec{r}_0|j\rangle} \frac{\partial}{\partial \langle \vec{r}_0 + \vec{r}|j\rangle} e^{\frac{1}{2}\langle j|\hat{B}^{-1}|j\rangle} P_0 \int \mathcal{D}|\Delta\bar{\mu}\rangle e^{-\frac{1}{2}\langle \Delta\bar{\mu}|\hat{B}|\Delta\bar{\mu}\rangle} \Big|_{|j\rangle=0} \quad (7.37c)$$

$$= \langle \vec{r}_0|\hat{B}^{-1}|\vec{r}_0 + \vec{r}\rangle \quad (7.37d)$$

where in the step from (7.37b) to (7.37c) equation (7.36), and from (7.37c) to (7.37d) equation (7.20) was used. To fulfil (7.18) we have to presume

$$\langle \vec{r}_0|\hat{B}^{-1}|\vec{r}_0 + \vec{r}\rangle \stackrel{!}{=} \gamma(\vec{r}) = \langle \vec{r}_0|\hat{\gamma}|\vec{r}_0 + \vec{r}\rangle \quad (7.38)$$

which also means that

$$\hat{B} = \hat{\gamma}^{-1}. \quad (7.39)$$

So we arrive for the probability for a certain configuration (7.19)

$$\boxed{P(|\Delta\bar{\mu}\rangle) = P_0 \cdot e^{-\frac{1}{2}\langle \Delta\bar{\mu}|\hat{\gamma}^{-1}|\Delta\bar{\mu}\rangle}} \quad (7.40)$$

7.2 The Green's function

The Green's function is in fact something very simple. If the equations of motion for a field $|u\rangle$ can be written in the form

$$\hat{A}(z)|u(z)\rangle = 0 \quad (7.41)$$

then the Green's function

$$G(\vec{r}, \vec{r}', z) = \langle \vec{r}|\hat{G}(z)|\vec{r}'\rangle \quad (7.42)$$

is just defined as the spatial matrix element of the inverse of the operator $\hat{A}(z)$

$$\hat{A}(z)\hat{G}(z) = \hat{1} \quad (7.43)$$

where the properties of the unity operator $\hat{1}$ were defined in (7.30). Multiplying (7.43) with $\langle \vec{r}|\dots|\vec{r}'\rangle$ and using (7.28) this can be written in real space

$$\int d^3r' A(\vec{r}, \vec{r}', z) G(\vec{r}', \vec{r}'', z) = \delta^{(3)}(\vec{r} - \vec{r}'') \quad (7.44)$$

and in momentum space equivalently

$$\sum_{\vec{k}'} A(\vec{k}, \vec{k}', z) G(\vec{k}', \vec{k}'', z) = V^2 \delta_{\vec{k}, \vec{k}''}. \quad (7.45)$$

If the system is translationally invariant⁷

$$A(\vec{r}, \vec{r}', z) = A(\vec{r} - \vec{r}', z) \quad (7.46a)$$

$$G(\vec{r}, \vec{r}', z) = G(\vec{r} - \vec{r}', z) \quad (7.46b)$$

which also means that \hat{A} and \hat{G} are diagonal operators in momentum space

$$A(\vec{k}, \vec{k}', z) = V \delta_{\vec{k}, \vec{k}'} A(\vec{k}, z) \quad (7.47a)$$

$$G(\vec{k}, \vec{k}', z) = V \delta_{\vec{k}, \vec{k}'} G(\vec{k}, z) \quad (7.47b)$$

⁷This holds only for a homogenous, not disordered system

with

$$A(\vec{k}, z) = \int d^3r e^{-i\vec{k}\vec{r}} A(\vec{r}, z) \quad (7.48a)$$

$$G(\vec{k}, z) = \int d^3r e^{-i\vec{k}\vec{r}} G(\vec{r}, z) \quad (7.48b)$$

then the following is valid

$$\begin{aligned} & A(\vec{k}, z) G(\vec{k}, z) = \\ &= \langle \vec{k} | \hat{A}(z) | \vec{k} \rangle \langle \vec{k} | \hat{G}(z) | \vec{k} \rangle \\ &= \sum_{\vec{k}'} \langle \vec{k} | \hat{A}(\vec{k}, z) | \vec{k}' \rangle \langle \vec{k}' | \hat{G}(\vec{k}, z) | \vec{k} \rangle \\ &= \langle \vec{k} | \hat{A}(\vec{k}, z) \hat{G}(\vec{k}, z) | \vec{k} \rangle \\ &= \langle \vec{k} | \vec{k} \rangle = 1 \end{aligned} \quad (7.49)$$

where (7.29) and (7.43) have been used. If $A(\vec{k}, \omega)$ is a two-dimensional tensor, the previous equation can be written as

$$A_{ij}(\vec{k}, z) G_{jk}(\vec{k}, z) = \delta_{ik} \quad (7.50)$$

with the Kronecker delta δ_{ik} . Not disordered systems (which means we set $\Delta\bar{\mu}(\vec{r}) = 0$) are translationally invariant. If we set without loss of generality

$$\vec{k} = k \cdot \vec{e}_z \quad (7.51)$$

we obtain immediately from (7.15a) to (7.15c)

$$G_L(\vec{k}, z) := G_{zz}(\vec{k}, z) = \lim_{\varepsilon \rightarrow 0} \frac{1}{z + k^2 (\bar{\lambda}_0 + 2\bar{\mu}_0)} \quad (7.52)$$

and

$$G_T(\vec{k}, z) := G_{xx}(\vec{k}, z) = G_{yy}(\vec{k}, z) = \lim_{\varepsilon \rightarrow 0} \frac{1}{z + k^2 \bar{\mu}_0}. \quad (7.53)$$

The density of states is given by

$$g(\omega) = \frac{2\omega}{\pi} \text{Im Tr} \hat{G}^+(\omega) = \frac{2\omega}{\pi k_D^3} \text{Im} \int_0^{k_D} dk \vec{k}^2 \sum_i G_{ii}(\vec{k}, z_+) \quad (7.54)$$

7.3 Relation of the Green's function to the dynamic susceptibility

The response function is defined as follows: If a term $V(t)$ is added to the Hamilton function

$$H = H_0 + V(t) \quad (7.55)$$

with

$$V(t) = - \int d^3r B(\vec{r}) f(\vec{r}, t) \quad (7.56)$$

and the expectation value of the observable value A changes by the amount

$$\begin{aligned} \langle \delta A(\vec{r}, t) \rangle &\equiv \langle A(\vec{r}, t) \rangle - \langle A_0 \rangle \\ &= \int_{-\infty}^{\infty} dt' \int d^3r' \chi_{AB}(\vec{r}, \vec{r}', t, t') f(\vec{r}', t') \end{aligned} \quad (7.57)$$

then the function $\chi_{AB}(\vec{r}, \vec{r}', t, t')$ is the response function. Because of causality it has to be valid

$$\chi_{AB}(\vec{r}, \vec{r}', t, t') = 0 \text{ for } t < t'. \quad (7.58)$$

For systems where the original Hamilton operator is time independent and invariant under translations this equation can be Fourier transformed

$$\begin{aligned}
\delta A(\vec{k}, \omega) &= \\
&= \int_{-\infty}^{\infty} dt \int d^3r e^{-i\vec{k}\vec{r} + i\omega t} \langle \delta A(\vec{r}, t) \rangle \\
&= \int_{-\infty}^{\infty} dt \int d^3r e^{-i\vec{k}\vec{r} + i\omega t} \int_{-\infty}^{\infty} dt' \int d^3r' \chi_{AB}(\vec{r} - \vec{r}', t - t') f(r', t') \\
&= \chi_{AB}(\vec{k}, \omega) f(\vec{k}, \omega)
\end{aligned} \tag{7.59}$$

with

$$\chi_{AB}(\vec{k}, \omega) = \int d^3r dt e^{-i\vec{k}\vec{r} + i\omega t} \chi_{AB}(\vec{r}, t) \tag{7.60}$$

$\chi_{AB}(\vec{k}, \omega)$ is also known as dynamic susceptibility. It will become important in the theory of light scattering. In the following sections we evaluate the dynamic susceptibilities for displacements and for strain of an elastic medium.

7.3.1 Dynamic susceptibility for displacements

If we want to calculate the dynamic susceptibility for the displacement field of an elastic medium, then we have to set

$$A = u_i(\vec{r}) \tag{7.61a}$$

$$B = u_j(\vec{r}). \tag{7.61b}$$

Now we add

$$V(t) = - \int d^3r u_j(\vec{r}) f_j(\vec{r}, t) \tag{7.62}$$

to the Hamilton function. This is equivalent to replacing the Lagrange density \mathcal{L}_0 by

$$\mathcal{L}(\vec{r}, t) = \mathcal{L}_0(\vec{r}, t) + u_j(\vec{r}) f_j(\vec{r}, t). \tag{7.63}$$

So the original equations of motion

$$A_{ij}(\vec{k}, \omega) u_j(\vec{k}, \omega) = 0 \tag{7.64}$$

are replaced by

$$A_{ij}(\vec{k}, \omega) u_j(\vec{k}, \omega) = f_i(\vec{k}, \omega). \tag{7.65}$$

This means that $u_j(\vec{k}, \omega)$, which fulfils the original equations of motion, has to be replaced by

$$u_j(\vec{k}, \omega) + \delta u_j(\vec{k}, \omega) \tag{7.66}$$

with

$$A_{ij}(\vec{k}, \omega) \delta u_j(\vec{k}, \omega) = f_i(\vec{k}, \omega). \tag{7.67}$$

Setting

$$\delta u_j(\vec{k}, \omega) = G_{jk}^+(\vec{k}, \omega) f_k(\vec{k}, \omega) \tag{7.68}$$

leads to

$$\begin{aligned}
&A_{ij}(\vec{k}, \omega) \delta u_j(\vec{k}, \omega) = \\
&= A_{ij}(\vec{k}, \omega) G_{jk}^+(\vec{k}, \omega) f_k(\vec{k}, \omega) \\
&= \delta_{ik} f_k(\vec{k}, \omega) \\
&= f_i(\vec{k}, \omega)
\end{aligned} \tag{7.69}$$

where the property of the Green's function

$$A_{ij}(\vec{k}, \omega) G_{jk}^+(\vec{k}, \omega) = \delta_{ik} \quad (7.70)$$

was used. This proves that (7.68) fulfils the equations of motion (7.65). Comparing (7.59) with (7.68) this leads to

$$\boxed{\chi_{u_j u_k}(\vec{k}, \omega) = G_{jk}^+(\vec{k}, \omega)}. \quad (7.71)$$

So the dynamic susceptibility for displacements is just the retarded Green's function.

7.4 Dynamic susceptibilities for strain

7.4.1 Dynamic susceptibilities for density fluctuations

If we want to calculate the susceptibility for the density fluctuations of an elastic medium, then we have to set

$$A = \partial_i u_i(\vec{r}) \quad (7.72a)$$

$$B = \partial_j u_j(\vec{r}) \quad (7.72b)$$

Now we have to add

$$V(t) = - \int d^3r \partial_j u_j(\vec{r}) f(\vec{r}, t) \quad (7.73)$$

to the Hamilton function. This is equivalent to replacing the Lagrange density \mathcal{L}_0 by

$$\mathcal{L}(\vec{r}, t) = \mathcal{L}_0(\vec{r}, t) + \partial_j u_j(\vec{r}) f(\vec{r}, t). \quad (7.74)$$

So the original equations of motion

$$A_{ij}(\vec{k}, \omega) u_j(\vec{k}, \omega) = 0 \quad (7.75)$$

are replaced by

$$A_{ij}(\vec{k}, \omega) u_j(\vec{k}, \omega) = -ik_i f(\vec{k}, \omega). \quad (7.76)$$

This means that $u_j(\vec{k}, \omega)$, which fulfils the original equations of motion, has to be replaced by

$$u_j(\vec{k}, \omega) + \delta u_j(\vec{k}, \omega) \quad (7.77)$$

with

$$A_{ij}(\vec{k}, \omega) \delta u_j(\vec{k}, \omega) = -ik_i f(\vec{k}, \omega). \quad (7.78)$$

Setting

$$\delta u_j(\vec{k}, \omega) = -iG_{jk}^+(\vec{k}, \omega) k_k f(\vec{k}, \omega) \quad (7.79)$$

or respectively

$$ik_j \delta u_j(\vec{k}, \omega) = k_j G_{jk}^+(\vec{k}, \omega) k_k f(\vec{k}, \omega) \quad (7.80)$$

leads to

$$\begin{aligned} A_{ij}(\vec{k}, \omega) \delta u_j(\vec{k}, \omega) &= \\ &= -iA_{ij}(\vec{k}, \omega) G_{jk}^+(\vec{k}, \omega) k_k f(\vec{k}, \omega) \\ &= -i\delta_{ik} k_k f(\vec{k}, \omega) \\ &= -ik_i f(\vec{k}, \omega) \end{aligned} \quad (7.81)$$

where the property of the Green's function

$$A_{ij}(\vec{k}, \omega) G_{jk}^+(\vec{k}, \omega) = \delta_{ik} \quad (7.82)$$

was used. This proves that (7.79) fulfils the equations of motion (7.65). Comparing (7.59) with (7.80) this leads to

$$\chi_L(\vec{k}, \omega) \equiv \chi_{\partial_j u_j, \partial_k u_k}(\vec{k}, \omega) = k_j G_{jk} k_k(\vec{k}, \omega) = (\vec{k})^2 G_L(\vec{k}, \omega) \quad (7.83)$$

where G_L is the longitudinal part of the Green's function. So the dynamic susceptibility for density fluctuations is just the product of the square of the wavenumber and the longitudinal part of the Green's function.

7.4.2 Dynamic susceptibilities for shear fluctuations

In order to calculate the susceptibility for the shear fluctuations of an elastic medium, we have to set

$$A_i = \varepsilon_{ikl} \partial_k u_l \quad (7.84a)$$

$$B_j = \varepsilon_{jmn} \partial_m u_n \quad (7.84b)$$

with the totally antisymmetric Levi-Civita tensor ε_{ijk} . Now we add

$$V(t) = - \int d^3r \varepsilon_{jmn} \partial_m u_n f_j(\vec{r}, t) \quad (7.85)$$

to the Hamilton function, which is equivalent to replacing the Lagrange density \mathcal{L}_0 by

$$\mathcal{L}(\vec{r}, t) = \mathcal{L}_0(\vec{r}, t) + \varepsilon_{jmn} \partial_m u_n f_j(\vec{r}, t). \quad (7.86)$$

So the original equations of motion

$$A_{ij}(\vec{k}, \omega) u_j(\vec{k}, \omega) = 0 \quad (7.87)$$

are replaced by

$$A_{ij}(\vec{k}, \omega) u_j(\vec{k}, \omega) = i \varepsilon_{imn} k_m f_n(\vec{k}, \omega). \quad (7.88)$$

This means that $u_j(\vec{k}, \omega)$, which fulfils the original equations of motion, has to be replaced by

$$u_j(\vec{k}, \omega) + \delta u_j(\vec{k}, \omega) \quad (7.89)$$

with

$$A_{ij}(\vec{k}, \omega) \delta u_j(\vec{k}, \omega) = i \varepsilon_{imn} k_m f_n(\vec{k}, \omega). \quad (7.90)$$

Setting

$$\delta u_j(\vec{k}, \omega) = i G_{jk}^+(\vec{k}, \omega) \varepsilon_{klm} k_l f_m(\vec{k}, \omega) \quad (7.91)$$

or respectively

$$i \varepsilon_{inj} k_n \delta u_j(\vec{k}, \omega) = -\varepsilon_{inj} k_n G_{jk}^+(\vec{k}, \omega) \varepsilon_{klm} k_l f_m(\vec{k}, \omega) \quad (7.92)$$

leads to

$$\begin{aligned} & A_{ij}(\vec{k}, \omega) \delta u_j(\vec{k}, \omega) = \\ & = i A_{ij}(\vec{k}, \omega) G_{jk}^+(\vec{k}, \omega) \varepsilon_{klm} k_l f_m(\vec{k}, \omega) \\ & = i \delta_{ik} \varepsilon_{klm} k_l f_m(\vec{k}, \omega) \\ & = i \varepsilon_{ilm} k_l f_m(\vec{k}, \omega) \end{aligned} \quad (7.93)$$

where the property of the Green's function

$$A_{ij}(\vec{k}, \omega) G_{jk}^+(\vec{k}, \omega) = \delta_{ik} \quad (7.94)$$

was used. This proves that (7.91) fulfils the equations of motion (7.90). Comparing (7.59) with (7.92) this leads to

$$\chi_{A_i B_j}(\vec{k}, \omega) = \varepsilon_{imn} k_m G_{nl}^+(\vec{k}, \omega) \varepsilon_{jkl} k_k. \quad (7.95)$$

Setting without loss of generality

$$\vec{k} = \begin{pmatrix} k \\ 0 \\ 0 \end{pmatrix} \quad (7.96)$$

leads to

$$\vec{G} = \begin{pmatrix} G_L & 0 & 0 \\ 0 & G_T & 0 \\ 0 & 0 & G_T \end{pmatrix} \quad (7.97)$$

where G_L is the longitudinal and G_T is the transverse part of the Green's function. From this the dynamic susceptibility for shear fluctuations can be seen to be

$$\boxed{\chi_T(\vec{k}, \omega) = \chi_{A_2 B_2}(\vec{k}, \omega) = \chi_{A_3 B_3}(\vec{k}, \omega) = \vec{k}^2 G_T(\vec{k}, \omega)}. \quad (7.98)$$

So the dynamic susceptibility for shear fluctuations is just equivalent to the product of the square of the wavenumber and the transverse part of the Green's function.

7.5 Determination of the configurationally averaged Green's function

We know now how useful the Green's function is in order to evaluate the properties of any solid. So we want to calculate the configurationally averaged Green's function for disordered solids. As we want to have an expression for both the retarded and advanced Green's function, the operator of the Green's function $\hat{G}(z)$ is defined by

$$\hat{A}(z) \hat{G}(z) = \hat{1} \quad (7.99)$$

$\hat{A}(z)$ is constructed to have the matrix elements given by (7.15a) - (7.15c) and describes therefore the equations of motion. The required Green's function is the matrix element of the inverse of this operator

$$\hat{G}(z) = \hat{A}(z)^{-1}. \quad (7.100)$$

This can formally be written as

$$\langle \vec{n}_1 | \hat{G}(z) | \vec{n}_2 \rangle = \frac{\partial^2}{\partial \langle \vec{n}_1 | \vec{J} \rangle \partial \langle \vec{n}_2 | \vec{J} \rangle} e^{\frac{1}{2} \langle \vec{J} | \hat{A}^{-1}(z) | \vec{J} \rangle} \Bigg|_{|\vec{J}\rangle=0}. \quad (7.101)$$

$|\vec{J}\rangle$ represents a real vector field, while $|\vec{n}_1\rangle$ and $|\vec{n}_2\rangle$ are elements of a full orthonormal system

$$\sum_{\vec{n}} |\vec{n}\rangle \langle \vec{n}| = \hat{1} \quad (7.102)$$

representing the real or momentum space variable and the Cartesian components, for example:

$$|\vec{n}\rangle = |\vec{r}, \vec{e}_i\rangle \quad (7.103)$$

with

$$\int d^3 r \sum_{i=1}^3 |\vec{r}, \vec{e}_i\rangle \langle \vec{r}, \vec{e}_i| = \hat{1} \quad (7.104)$$

and

$$\langle \vec{r}, \vec{e}_i | \hat{G}(z) | \vec{r}', \vec{e}_j \rangle = G_{ij}(z, \vec{r}, \vec{r}'). \quad (7.105)$$

Equation (7.101) can be proven easily by using (7.104) and by taking into account the symmetry

$$\langle \vec{n}_1 | \hat{A}^{-1}(z) | \vec{n}_2 \rangle = \langle \vec{n}_2 | \hat{A}^{-1}(z) | \vec{n}_1 \rangle. \quad (7.106)$$

The inverse of the operator $\hat{A}(z)$ is not known. So we have to transform the quantity

$$e^{\frac{1}{2} \langle \vec{J} | \hat{A}^{-1}(z) | \vec{J} \rangle} \quad (7.107)$$

that appears in (7.101) in a way that it contains not the inverse of the operator $\hat{A}(z)$, but the operator $\hat{A}(z)$ itself. This can be done with the help of (7.36). The result is

$$e^{\frac{1}{2}\langle \vec{J} | \hat{A}^{-1}(z) | \vec{J} \rangle} = \frac{\int \mathcal{D} |\vec{u}\rangle e^{-\frac{1}{2}\langle \vec{u} | \hat{A}(z) | \vec{u} \rangle} e^{\langle \vec{J} | \vec{u} \rangle}}{\int \mathcal{D} |\vec{u}\rangle e^{-\frac{1}{2}\langle \vec{u} | \hat{A}(z) | \vec{u} \rangle}}. \quad (7.108)$$

An averaging over different configurations cannot be performed in (7.108) as it contains $\hat{A}(z)$ both in the numerator and in the denominator. This problem can be solved by defining a generating functional $Z(|\vec{J}\rangle)$

$$Z(|\vec{J}\rangle) := \int \mathcal{D} |\vec{u}\rangle e^{-\frac{1}{2}\langle \vec{u} | \hat{A}(z) | \vec{u} \rangle} e^{\langle \vec{J} | \vec{u} \rangle}. \quad (7.109)$$

From (7.108) it can be seen that the term appearing in (7.101) is equivalent to

$$e^{\frac{1}{2}\langle \vec{J} | \hat{A}^{-1}(z) | \vec{J} \rangle} = \frac{Z(|\vec{J}\rangle)}{Z(|\vec{J}\rangle = 0)}. \quad (7.110)$$

(7.101) can therefore be written as

$$\langle \vec{n}_1 | \hat{G}(z) | \vec{n}_2 \rangle = \frac{\partial^2}{\partial \langle \vec{n}_1 | \vec{J} \rangle \partial \langle \vec{n}_2 | \vec{J} \rangle} \ln Z(|\vec{J}\rangle) \Big|_{|\vec{J}\rangle=0}. \quad (7.111)$$

We now introduce a different generating functional \tilde{Z} , where the relationship between this new generating functional and the Green's function is given by

$$\langle \vec{n}_1 | \hat{G}(z) | \vec{n}_2 \rangle = \frac{\partial}{\partial \langle \vec{n}_1 | \hat{J}(z) | \vec{n}_2 \rangle} \ln \tilde{Z}(\hat{J}) \Big|_{\hat{J}=0} \quad (7.112)$$

In order to obtain the same Green's function as given by (7.111) and (7.109), the new generating functional can be defined as

$$\tilde{Z}(\hat{J}) := \int \mathcal{D} |\vec{u}\rangle e^{-\frac{1}{2}\langle \vec{u} | \hat{A}(z) - 2\hat{J} | \vec{u} \rangle}. \quad (7.113)$$

As can be seen easily, both generating functionals lead to the same operator of the Green's function

$$\hat{G}(z) = \frac{\int \mathcal{D} |\vec{u}\rangle e^{-\frac{1}{2}\langle \vec{u} | \hat{A}(z) | \vec{u} \rangle} |\vec{u}\rangle \langle \vec{u}|}{\int \mathcal{D} |\vec{u}\rangle e^{-\frac{1}{2}\langle \vec{u} | \hat{A}(z) | \vec{u} \rangle}}. \quad (7.114)$$

We will have to perform a functional integral over the matrix elements of the Green's functions in order to obtain the configurationally averaged Green's function. However, we are not able to perform a functional integral over a logarithm. To evaluate the logarithm in (7.112) we use a trick known as *replica trick*. The replica trick is based on the fact that the logarithm of any variable Z can be written as

$$\ln Z = \lim_{n \rightarrow 0} \frac{1}{n} (Z^n - 1). \quad (7.115)$$

The analysis is carried out for finite and integer n , and in the end n is continued analytically. $\tilde{Z}(\hat{J})$ contains a functional integral over one field $|\vec{u}\rangle$. So $\tilde{Z}(\hat{J})^n$ contains the functional integrals over n fields $|\vec{u}^\alpha\rangle$, $\alpha = 1, \dots, n$. The newly introduced indices α have the name *replica indices*. Therefore the following relation is valid

$$\ln \tilde{Z}(\hat{J}) = \lim_{n \rightarrow 0} \frac{1}{n} \left(\int \prod_{\alpha=1}^n \mathcal{D} |u^\alpha\rangle e^{-\frac{1}{2}\langle \vec{u}^\alpha | \hat{A}(z) \delta_{\alpha\alpha'} - 2\hat{J}^{\alpha\alpha'} | \vec{u}^{\alpha'} \rangle} - 1 \right). \quad (7.116)$$

With this the Green's function is given by

$$\langle \vec{n}_1 | \hat{G}(z) | \vec{n}_2 \rangle = \lim_{n \rightarrow 0} \frac{\partial}{\partial \langle \vec{n}_1 | \hat{J}^{11}(z) | \vec{n}_2 \rangle} \tilde{Z}^n(\hat{J}^{\alpha\alpha'}) \Big|_{\hat{J}=0} \quad (7.117a)$$

$$= \lim_{n \rightarrow 0} \tilde{Z}^{n-1}(\hat{J}=0) \frac{\partial}{\partial \langle \vec{n}_1 | \hat{J}(z) | \vec{n}_2 \rangle} \tilde{Z}(\hat{J}) \Big|_{\hat{J}=0}. \quad (7.117b)$$

7.5.1 Configurational averaging

Now the configurational averaged Green's function may be evaluated, i.e.

$$\begin{aligned} \langle \langle \vec{n}_1 | \hat{G}(z) | \vec{n}_2 \rangle \rangle &\equiv \int \mathcal{D} |\Delta\bar{\mu}\rangle P(|\Delta\bar{\mu}\rangle) \langle \vec{n}_1 | \hat{G}(z, [\Delta\bar{\mu}]) | \vec{n}_2 \rangle \\ &= P_0 \int \mathcal{D} |\Delta\bar{\mu}\rangle \cdot e^{-\frac{1}{2}\langle \Delta\bar{\mu} | \hat{\gamma}^{-1} | \Delta\bar{\mu} \rangle} \langle \vec{n}_1 | \hat{G}(z, [\Delta\bar{\mu}]) | \vec{n}_2 \rangle. \end{aligned} \quad (7.118)$$

By using (7.117a) and (7.118) it can be seen that evaluating the configurationally averaged Green's function means evaluating the generating functional to the n , averaged over all configurations. So we first have to calculate the configurational average of the generating functional to the n

$$\begin{aligned} &\langle \tilde{Z}^n(\hat{J}^{\alpha\alpha'}) \rangle = \\ &= P_0 \int \mathcal{D} |\Delta\bar{\mu}\rangle e^{-\frac{1}{2}\langle \Delta\bar{\mu} | \hat{\gamma}^{-1} | \Delta\bar{\mu} \rangle} \tilde{Z}^n(\hat{J}^{\alpha\alpha'}, [\Delta\bar{\mu}]) \\ &= P_0 \int \mathcal{D} |\Delta\bar{\mu}\rangle \int \prod_{\alpha=1}^n \mathcal{D} |\vec{u}^\alpha\rangle e^{-\frac{1}{2}\langle \Delta\bar{\mu} | \hat{\gamma}^{-1} | \Delta\bar{\mu} \rangle} e^{-\frac{1}{2}\langle \vec{u}^\alpha | \hat{A}(z, [\Delta\bar{\mu}]) \delta_{\alpha\alpha'} - 2\hat{J}^{\alpha\alpha'} | \vec{u}^{\alpha'} \rangle} \end{aligned} \quad (7.119)$$

The operator $\hat{A}(z, [\Delta\bar{\mu}])$ can now be split up into a part $\hat{A}_0(z)$, independent of $\Delta\bar{\mu}$, and a part $\hat{A}_1(z, [\Delta\bar{\mu}])$ depending on the configuration $\Delta\bar{\mu}$ (see also (7.15a)).

$$\begin{aligned} \langle \tilde{Z}^n(\hat{J}^{\alpha\alpha'}) \rangle &= \int \prod_{\alpha=1}^n \mathcal{D} |\vec{u}^\alpha\rangle e^{-\frac{1}{2}\langle \vec{u}^\alpha | \hat{A}_0(z) \delta_{\alpha\alpha'} - 2\hat{J}^{\alpha\alpha'} | \vec{u}^{\alpha'} \rangle} \\ &\cdot P_0 \int \mathcal{D} |\Delta\bar{\mu}\rangle e^{-\frac{1}{2}\langle \Delta\bar{\mu} | \hat{\gamma}^{-1} | \Delta\bar{\mu} \rangle} e^{-\frac{1}{2}\langle \vec{u}^\alpha | \hat{A}_1(z, [\Delta\bar{\mu}]) | \vec{u}^\alpha \rangle}. \end{aligned} \quad (7.120)$$

For further evaluation we perform an integration by parts

$$\begin{aligned} &\langle \vec{u}^\alpha | \hat{A}_1(z, [\Delta\bar{\mu}]) | \vec{u}^\alpha \rangle = \\ &= - \int d^3r u_i^\alpha(\vec{r}) (\partial_j \Delta\bar{\mu}(\vec{r}) \partial_i + \delta_{ij} \partial_l \Delta\bar{\mu}(\vec{r}) \partial_l) u_j^\alpha(\vec{r}) \\ &= \int d^3r \Delta\bar{\mu}(\vec{r}) ((\partial_j u_i^\alpha(\vec{r})) (\partial_i u_j^\alpha(\vec{r})) + (\partial_l u_j^\alpha(\vec{r})) (\partial_l u_i^\alpha(\vec{r}))) \\ &\equiv \langle \Delta\bar{\mu} | ((\partial_l u_i^\alpha) (\partial_i u_l^\alpha) + (\partial_l u_i^\alpha) (\partial_l u_i^\alpha)) \rangle. \end{aligned} \quad (7.121)$$

To make sure the surface terms vanish it has to be presumed that the solutions of the equations of motion are either periodical or vanish at the surface. The term in the second line of (7.120), named F in the following, can therefore be rewritten as

$$F = P_0 \int \mathcal{D} |\Delta\bar{\mu}\rangle e^{-\frac{1}{2}\langle \Delta\bar{\mu} | \hat{\gamma}^{-1} | \Delta\bar{\mu} \rangle} e^{-\frac{1}{2}\langle \vec{u}^\alpha | \hat{A}_1(z, [\Delta\bar{\mu}]) | \vec{u}^\alpha \rangle} \quad (7.122a)$$

$$= P_0 \int \mathcal{D} |\Delta\bar{\mu}\rangle e^{-\frac{1}{2}\langle \Delta\bar{\mu} | \hat{\gamma}^{-1} | \Delta\bar{\mu} \rangle} e^{-\langle \Delta\bar{\mu} | \frac{1}{2}((\partial_l u_i^\alpha) (\partial_i u_l^\alpha) + (\partial_l u_i^\alpha) (\partial_l u_i^\alpha)) \rangle} \quad (7.122b)$$

$$= P_0 \left(\int \mathcal{D} |\Delta\bar{\mu}\rangle e^{-\frac{1}{2}\langle \Delta\bar{\mu} | \hat{\gamma}^{-1} | \Delta\bar{\mu} \rangle} \right) \cdot \quad (7.122c)$$

$$\cdot e^{\frac{1}{8} \langle (\partial_l u_i^\alpha) (\partial_i u_l^\alpha) + (\partial_l u_i^\alpha) (\partial_l u_i^\alpha) | \hat{\gamma} | (\partial_m u_j^{\alpha'}) (\partial_j u_m^{\alpha'}) + (\partial_m u_j^{\alpha'}) (\partial_m u_j^{\alpha'}) \rangle} \quad (7.122d)$$

$$\begin{aligned} &= e^{\frac{1}{8} \int d^3r d^3r' \gamma(\vec{r}-\vec{r}') [(\partial_l u_i^\alpha(\vec{r})) (\partial_i u_l^\alpha(\vec{r})) + (\partial_l u_i^\alpha(\vec{r})) (\partial_l u_i^\alpha(\vec{r}))] \cdot} \\ &\quad \cdot [(\partial_m u_j^{\alpha'}(\vec{r}')) (\partial_j u_m^{\alpha'}(\vec{r}')) + (\partial_m u_j^{\alpha'}(\vec{r}')) (\partial_m u_j^{\alpha'}(\vec{r}'))] \\ &= e^{\frac{1}{8} \int d^3r d^3r' \gamma(\vec{r}-\vec{r}') \left[\frac{1}{2} (\partial_l u_i^\alpha(\vec{r})) (\partial_m u_j^{\alpha'}(\vec{r}')) + \frac{1}{2} (\partial_l u_i^\alpha(\vec{r})) (\partial_j u_m^{\alpha'}(\vec{r}')) + \right.} \\ &\quad \left. + \frac{1}{2} (\partial_i u_l^\alpha(\vec{r})) (\partial_m u_j^{\alpha'}(\vec{r}')) + \frac{1}{2} (\partial_l u_i^\alpha(\vec{r})) (\partial_j u_m^{\alpha'}(\vec{r}')) \right]^2} \end{aligned} \quad (7.122e)$$

where in the step from (7.122b) to (7.122d) again equation (7.36) was used. The equivalence of (7.122d) and (7.122e) can be shown by expanding the occurring products explicitly and renaming of the indices.

So now we have successfully eliminated the function $\Delta\bar{\mu}(\vec{r})$ by integrating over all possible configurations. The problem with (7.122e) is now that it contains terms that are quartic in the field $\vec{u}^\alpha(\vec{r})$. So the integral over the field, which is needed for (7.120), is not of the Gaussian type any more. The solution to this problem is a *Hubbard-Stratonovich transformation*. This means using (7.36) again, where

$$\begin{aligned} & \frac{1}{2}(\partial_l u_i^\alpha(\vec{r}))(\partial_m u_j^{\alpha'}(\vec{r}')) + \frac{1}{2}(\partial_l u_i^\alpha(\vec{r}))(\partial_j u_m^{\alpha'}(\vec{r}')) + \\ & + \frac{1}{2}(\partial_i u_l^\alpha(\vec{r}))(\partial_m u_j^{\alpha'}(\vec{r}')) + \frac{1}{2}(\partial_l u_i^\alpha(\vec{r}))(\partial_j u_m^{\alpha'}(\vec{r}')) \end{aligned} \quad (7.123)$$

takes the role of $|j\rangle$. Some special care has to be taken as (7.123) is a representation of an element of a product space of the original Hilbert space with the elements $\partial_l u_i^\alpha(\vec{r})$. To avoid misunderstandings the bra and ket notation is not used in this case any more. The newly introduced integrational variable, which is an element of the same product space, will be named

$$\Lambda_{ilmj}^{\alpha\alpha'}(\vec{r}, \vec{r}', z). \quad (7.124)$$

The functional integration over all of these $\Lambda_{ilmj}^{\alpha\alpha'}(\vec{r}, \vec{r}', z)$ will be abbreviated by $\mathcal{D}\Lambda$. The result for this transformation of (7.122e) is

$$\begin{aligned} F &= C^{n^2} \int \mathcal{D}\Lambda e^{-\frac{1}{2} \int d^3r d^3r' (\gamma(\vec{r}-\vec{r}'))^{-1} (\Lambda_{ilmj}^{\alpha\alpha'}(\vec{r}, \vec{r}', z))^2} \\ & \cdot e^{\frac{1}{2} \int d^3r d^3r' \Lambda_{ilmj}^{\alpha\alpha'}(\vec{r}, \vec{r}', z) \left(\frac{1}{2}(\partial_l u_i^\alpha(\vec{r}))(\partial_m u_j^{\alpha'}(\vec{r}')) + \frac{1}{2}(\partial_l u_i^\alpha(\vec{r}))(\partial_j u_m^{\alpha'}(\vec{r}')) \right) +} \\ & + \frac{1}{2}(\partial_i u_l^\alpha(\vec{r}))(\partial_m u_j^{\alpha'}(\vec{r}')) + \frac{1}{2}(\partial_l u_i^\alpha(\vec{r}))(\partial_j u_m^{\alpha'}(\vec{r}'))} \\ &= C^{n^2} \int \mathcal{D}\Lambda e^{-\frac{1}{2} \int d^3r d^3r' (\gamma(\vec{r}-\vec{r}'))^{-1} (\Lambda_{ilmj}^{\alpha\alpha'}(\vec{r}, \vec{r}', z))^2} \\ & \cdot e^{\frac{1}{2} \int d^3r d^3r' \left(\frac{1}{2}\Lambda_{ilmj}^{\alpha\alpha'}(\vec{r}, \vec{r}', z) + \frac{1}{2}\Lambda_{iljm}^{\alpha\alpha'}(\vec{r}, \vec{r}', z) + \frac{1}{2}\Lambda_{limj}^{\alpha\alpha'}(\vec{r}, \vec{r}', z) + \frac{1}{2}\Lambda_{lijm}^{\alpha\alpha'}(\vec{r}, \vec{r}', z) \right) (\partial_l u_i^\alpha(\vec{r}))(\partial_m u_j^{\alpha'}(\vec{r}'))} \\ &= C^{n^2} \int \mathcal{D}\Lambda e^{-\frac{1}{2} \int d^3r d^3r' (\gamma(\vec{r}-\vec{r}'))^{-1} (\Lambda_{ilmj}^{\alpha\alpha'}(\vec{r}, \vec{r}', z))^2} \\ & \cdot e^{-\frac{1}{2} \langle u_i^\alpha | \partial_l \left(\frac{1}{2}\Lambda_{ilmj}^{\alpha\alpha'} + \frac{1}{2}\Lambda_{iljm}^{\alpha\alpha'} + \frac{1}{2}\Lambda_{limj}^{\alpha\alpha'} + \frac{1}{2}\Lambda_{lijm}^{\alpha\alpha'} \right) \partial_m | u_j^{\alpha'} \rangle}. \end{aligned} \quad (7.125)$$

The emerging constants, which are equal to 1 for $n \rightarrow 0$, are combined in the constant C^{n^2} . After defining

$$\begin{aligned} A_{ij}^{\alpha\alpha'}(z, \Lambda) &:= z\delta_{ij}\delta_{\alpha\alpha'} - \delta_{\alpha\alpha'}((\bar{\lambda}_0 + \bar{\mu}_0)\partial_i\partial_j + \bar{\mu}_0\delta_{ij}\partial_l\partial_l) - \\ & - \partial_l \left(\frac{1}{2}\Lambda_{ilmj}^{\alpha\alpha'}(\vec{r}, z) + \frac{1}{2}\Lambda_{iljm}^{\alpha\alpha'}(\vec{r}, z) + \frac{1}{2}\Lambda_{limj}^{\alpha\alpha'}(\vec{r}, z) + \frac{1}{2}\Lambda_{lijm}^{\alpha\alpha'}(\vec{r}, z) \right) \partial_m \end{aligned} \quad (7.126)$$

we obtain for equation (7.120)

$$\begin{aligned} \langle \tilde{Z}^n(\hat{j}^{\alpha\alpha'}) \rangle &= C^{n^2} \int \mathcal{D}\Lambda e^{-\frac{1}{2} \int d^3r d^3r' (\gamma(\vec{r}-\vec{r}'))^{-1} (\Lambda_{ilmj}^{\alpha\alpha'}(\vec{r}, \vec{r}', z))^2} \\ & \cdot \int \prod_{\alpha=1}^n \mathcal{D}|\vec{u}^\alpha\rangle e^{-\frac{1}{2} \langle \vec{u}^\alpha | \hat{A}(z, \Lambda)^{\alpha\alpha'} - 2\hat{j}^{\alpha\alpha'} | \vec{u}^\alpha \rangle}. \end{aligned} \quad (7.127)$$

The integration over \vec{u}^α can now be done with the help of (7.35):

$$\begin{aligned} & \langle \tilde{Z}^n(\hat{j}^{\alpha\alpha'}) \rangle = \\ &= C^{n^2} \tilde{C}^n \int \mathcal{D}\Lambda e^{-\frac{1}{2} \int d^3r d^3r' (\gamma(\vec{r}-\vec{r}'))^{-1} (\Lambda_{ilmj}^{\alpha\alpha'}(\vec{r}, \vec{r}', z))^2} e^{-\frac{1}{2} \text{Tr} \ln(\hat{A}^{\alpha\alpha'}(z, \Lambda) - 2\hat{j}^{\alpha\alpha'})} \\ &= C^{n^2} \tilde{C}^n \int \mathcal{D}\Lambda e^{S_{eff}(\Lambda, \hat{j})} \end{aligned} \quad (7.128)$$

with

$$\begin{aligned}
S_{eff}(\Lambda, \hat{J}) &= \\
&= -\frac{1}{2} \int d^3r d^3r' \frac{1}{\gamma(\vec{r}-\vec{r}')} \left(\Lambda_{ilmj}^{\alpha\alpha'}(\vec{r}, \vec{r}', z) \right)^2 - \frac{1}{2} \text{Tr} \ln \left(\hat{A}^{\alpha\alpha'}(z, \Lambda) - 2\hat{J}^{\alpha\alpha'} \right) \\
&\equiv - \sum_{i,l,m,j=1}^3 \sum_{\alpha,\alpha'=1}^n \frac{1}{2} \int d^3r \int d^3r' \frac{1}{\gamma(\vec{r}-\vec{r}')} \left(\Lambda_{ilmj}^{\alpha\alpha'}(\vec{r}, \vec{r}', z) \right)^2 \\
&\quad - \frac{1}{2} \sum_{\vec{k}} \sum_{i=1}^3 \sum_{\alpha=1}^n \left\langle \vec{k}, \vec{e}_i \left| \ln \left(\hat{A}^{\alpha\alpha'}(z, \Lambda) - 2\hat{J}^{\alpha\alpha'} \right) \right| \vec{k}, \vec{e}_i \right\rangle
\end{aligned} \tag{7.129}$$

7.5.2 Saddle point approximation

Now $\langle \tilde{Z}^n(\hat{J}^{\alpha\alpha'}) \rangle$ is approximated by

$$\langle \tilde{Z}^n(\hat{J}^{\alpha\alpha'}) \rangle \approx C^{n^2} \tilde{C}^n \int \mathcal{D}\Lambda e^{S_{eff}(\Lambda_0, \hat{J})} \tag{7.130}$$

where Λ_0 is the point at which $S_{eff}(\Lambda, \hat{J}=0)$ has a saddle point. For the saddle point we make an ansatz of the form

$$\Lambda_{ilmj}^{\alpha\alpha'}(\vec{r}, \vec{r}', z) = -\frac{1}{2} \Sigma(\vec{r}-\vec{r}', z) \delta_{\alpha\alpha'} (\delta_{im}\delta_{lj} + \delta_{ij}\delta_{lm}). \tag{7.131}$$

This ansatz is motivated by the fact that the self-energy should be translationally invariant. Additionally it should be diagonal in replica space and may have the same symmetry as the fluctuating part of the elasticity tensor. With the Fourier transform

$$\Sigma(\vec{k}, z) = \int d^3r e^{-i\vec{k}\vec{r}} \Sigma(\vec{r}, z) \tag{7.132}$$

this leads to

$$\begin{aligned}
A_{ij}^{\alpha\alpha'}(\vec{k}, z) &= \\
&= z\delta_{ij}\delta_{\alpha\alpha'} + \delta_{\alpha\alpha'} ((\bar{\lambda}_0 + \bar{\mu}_0)k_i k_j + \bar{\mu}_0\delta_{ij}k_l k_l) \\
&\quad - \delta_{\alpha\alpha'} \Sigma(\vec{k}, z) (\delta_{im}\delta_{lj} + \delta_{ij}\delta_{lm}) k_l k_m \\
&= \delta_{\alpha\alpha'} \left(z\delta_{ij} + (\bar{\lambda}_0 + \bar{\mu}_0 - \Sigma(\vec{k}, z))k_i k_j + (\bar{\mu}_0 - \Sigma(\vec{k}, z))\delta_{ij}k_l k_l \right)
\end{aligned} \tag{7.133}$$

and

$$\begin{aligned}
S_{eff}(\Lambda, \hat{J}=0) &= \\
&= -\frac{1}{2} 6 \cdot n \cdot V \cdot \int d^3r \frac{1}{\gamma(\vec{r})} \Sigma(\vec{r}, z) \Sigma(\vec{r}, z) \\
&\quad - \frac{1}{2} \cdot n \cdot \frac{V}{(2\pi)^3} \int d^3k \ln \left(z + \vec{k}^2 (\bar{\lambda}_0 + \bar{\mu}_0 - \Sigma(\vec{k}, z)) + \vec{k}^2 (\bar{\mu}_0 - \Sigma(\vec{k}, z)) \right) \\
&\quad - \frac{1}{2} \cdot 2 \cdot n \cdot \frac{V}{(2\pi)^3} \int d^3k \ln \left(z + \vec{k}^2 (\bar{\mu}_0 - \Sigma(\vec{k}, z)) \right).
\end{aligned} \tag{7.134}$$

Hereby it is used that $k_i k_j$ has the single eigenvalue \vec{k}^2 and the double eigenvalue 0. The saddle point satisfies the relationship

$$\left. \frac{\partial S_{eff}(\Sigma(\vec{r}-\vec{r}', z), \hat{J}=0)}{\partial \Sigma(\vec{r}-\vec{r}', z)} \right|_{\Sigma(z)=\Sigma_0(z)} = 0 \tag{7.135}$$

which leads to

$$\begin{aligned}
& \Sigma_0(\vec{r}, z) = \\
&= \frac{\gamma(\vec{r})}{6} \cdot \frac{1}{(2\pi)^3} \int d^3k \left(\frac{\vec{k}^2}{z + \vec{k}^2(\bar{\lambda}_0 + 2\bar{\mu}_0 - 2\Sigma_0(\vec{k}, z))} + \frac{\vec{k}^2}{z + \vec{k}^2(\bar{\mu}_0 - \Sigma_0(\vec{k}, z))} \right) e^{-i\vec{k}\vec{r}} \\
&= \frac{\gamma(\vec{r})}{6} \cdot \frac{1}{(2\pi)^3} \int d^3k \left(\chi_L(\vec{k}, z) + \chi_T(\vec{k}, z) \right) e^{-i\vec{k}\vec{r}} \\
&= \frac{1}{6} \gamma(\vec{r}) (\chi_L(\vec{r}, z) + \chi_T(\vec{r}, z))
\end{aligned} \tag{7.136}$$

where

$$\frac{\partial \Sigma(\vec{k}, z)}{\partial \Sigma(\vec{r}, z)} = e^{-i\vec{k}\vec{r}} \tag{7.137}$$

and

$$\chi_L(\vec{k}, z) := \frac{\vec{k}^2}{z + \vec{k}^2(\bar{\lambda}_0 + 2\bar{\mu}_0 - 2\Sigma_0(\vec{k}, z))} \tag{7.138}$$

$$\chi_T(\vec{k}, z) := \frac{\vec{k}^2}{z + \vec{k}^2(\bar{\mu}_0 - \Sigma_0(\vec{k}, z))} \tag{7.139}$$

was used. The Fourier transform of (7.136) is

$$\begin{aligned}
\Sigma_0(\vec{k}, z) &= \int d^3r e^{-i\vec{k}\vec{r}} \Sigma_0(\vec{r}, z) \\
&= \frac{1}{6} \frac{1}{(2\pi)^3} \int d^3k' \gamma(\vec{k} - \vec{k}') (\chi_L(\vec{k}', z) + \chi_T(\vec{k}', z))
\end{aligned} \tag{7.140}$$

with

$$\gamma(\vec{k}) = \int d^3r e^{-i\vec{k}\vec{r}} \gamma(\vec{r}). \tag{7.141}$$

When evaluating (7.128), (7.129) and (7.133) in saddle point approximation it becomes clear that the resulting generating functional is just the one of a system where the matrix elements of the operator that describes the equations of motion is given by (7.133). This operator is diagonal in momentum space. So we obtain from (7.117b) within the saddle point approximation for the Fourier transform of the configurationally averaged Green's function

$$\langle G_L(\vec{k}, z) \rangle := \langle G_{11}(k \cdot \vec{e}_1, z) \rangle = \frac{1}{z + k^2(\bar{\lambda}_0 + 2\bar{\mu}_0 - 2\Sigma_0(\vec{k}, z))} \tag{7.142}$$

$$\langle G_T(\vec{k}, z) \rangle := \langle G_{22}(k \cdot \vec{e}_1, z) \rangle = \langle G_{33}(k \cdot \vec{e}_1, z) \rangle = \frac{1}{z + k^2(\bar{\mu}_0 - \Sigma_0(\vec{k}, z))} \tag{7.143}$$

where $G_L(\vec{k}, z)$ is the longitudinal and $G_T(\vec{k}, z)$ is the transverse part of the Green's function. The influence of the disorder (as compared to the unperturbed Green's function (7.52), (7.53)) is represented by the self-energy $\Sigma_0(\vec{k}, z)$, which has to be evaluated self-consistently as

$$\Sigma_0(\vec{k}, z) = \frac{1}{6} \frac{1}{(2\pi)^3} \int d^3k' \gamma(\vec{k} - \vec{k}') (\chi_L(\vec{k}', z) + \chi_T(\vec{k}', z)) \tag{7.144}$$

with

$$\chi_L(\vec{k}, z) = \vec{k}^2 G_L(\vec{k}, z) \tag{7.145a}$$

$$\chi_T(\vec{k}, z) = \vec{k}^2 G_T(\vec{k}, z). \tag{7.145b}$$

A similar result has been obtained by John et al. for a spatially correlated fluctuation of the mass density [?]. It has to be noted that (7.145a) and (7.145b) are not the real dynamic susceptibilities. We have

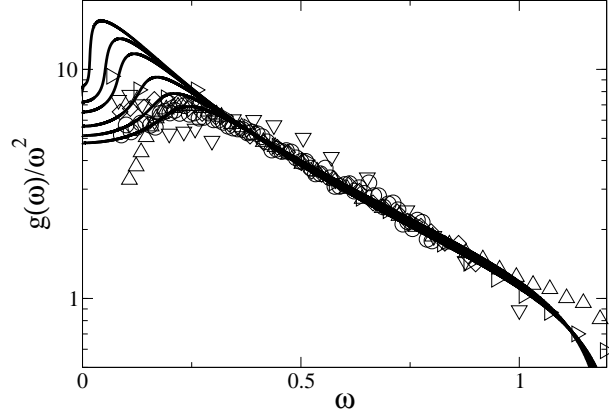


Figure 1: Lines: Reduced DOS as calculated in SCBA for the disorder parameters (from bottom to top) $\tilde{\gamma}_\mu = 0.13, 0.14, 0.15, 0.16, 0.164, 0.1664$. In all calculations we use units in which $c_T = 1$, $k_D = 1$, $\Theta_D = 1$ (transverse sound velocity, Debye wave number, Debye temperature). The longitudinal sound velocity is set $c_L = \sqrt{2}c_T$. For this choice we have $\tilde{\gamma}_\mu^c = 1/6$.

Symbols: measured reduced density of states $g(\omega)/\omega^2$ for some glasses. The frequency has been scaled with a characteristic frequency, and the DOS has been multiplied with a scaling factor to obtain a "universal plot". \triangleright : simulated Lennard-Jones glass [1]; \circ : metallic glass [2]; \triangle : PMMA [3]; \diamond : OTP [4]; ∇ : SiO₂ [5].

divided the equations of motions (7.10) by the mass density. So the real dynamic susceptibilities have an additional factor $1/m_0$ where m_0 is the mass density. We now apply the approximation

$$\Sigma_0(\vec{k}, z) \approx \Sigma_0(\vec{k} = 0, z) \equiv \Sigma_0(z). \quad (7.146)$$

The assumption (7.146) is based on the fact that we expect the renormalized velocities of sound

$$c_L^2(\vec{k}, z) = \bar{\lambda}_0 + 2\bar{\mu}_0 - 2\Sigma_0(\vec{k}, z) \quad (7.147a)$$

$$c_T^2(\vec{k}, z) = \bar{\mu}_0 - \Sigma_0(\vec{k}, z) \quad (7.147b)$$

to be only weakly \vec{k} -dependent in the relevant \vec{k} -range. This leads to

$$\Sigma_0(z) = \frac{1}{6} \frac{1}{(2\pi)^3} \int d^3\mathbf{k} \gamma(\vec{k}) \left(\chi_L(\vec{k}, z) + \chi_T(\vec{k}, z) \right) \quad (7.148)$$

These equations establish the vector form of the self-consistent Born approximation (SCBA) for the disordered elasticity problem. For a short correlation length ξ_C the correlation function can be replaced by a single parameter $\tilde{\gamma}_\mu$, which is proportional to the variance of $\delta\mu\xi_C^3$. The SCBA then takes the form

$$\begin{aligned} \Sigma(z) &= \tilde{\gamma}_\mu \sum_{k < k_D} [\chi_L(k, z) + \chi_T(k, z)]; \\ \chi_L(k, z) &= k^2 G_L(k, z) = k^2 [-z^2 + k^2(c_L^2 - 2\Sigma(z))]^{-1}; \\ \chi_T(k, z) &= k^2 G_T(k, z) = k^2 [-z^2 + k^2(c_T^2 - \Sigma(z))]^{-1}. \end{aligned} \quad (7.149)$$

It is easily seen that Eqs. (7.149) describes longitudinal and transverse sound-like excitations with dispersions $\Omega_L(q)^2 = [c_L^2 - \text{Re}\{2\Sigma(\omega)\}]q^2$, $\Omega_T(q)^2 = [c_T^2 - \text{Re}\{\Sigma(\omega)\}]q^2$, and a linewidth $\Gamma(q) \propto q^2 \text{Im}\{\Sigma(\omega)\}/\omega$. This is in qualitative agreement with the recent experimental and simulational findings. However the present theory is only valid in the low (ω, q) range, in which the detailed microscopic structure of the material is not important.

As in the scalar model the system becomes unstable if $\tilde{\gamma}_\mu$ exceeds a critical value $\tilde{\gamma}_\mu^c$. For $\tilde{\gamma}_\mu < \tilde{\gamma}_\mu^c$ the reduced DOS $g(\omega)/\omega^2$ exhibits a BP that is enhanced and shifted towards lower frequencies as $\tilde{\gamma}_\mu \rightarrow \tilde{\gamma}_\mu^c$ (see Fig. 1). This critical value ($\tilde{\gamma}_\mu^c = 1/6$ for $c_L^2 = 2c_T^2$) is much smaller than in the scalar version of the theory ($\tilde{\gamma}^c = 1/2$), which shows that the transverse excitations are much more sensitive to disorder than the longitudinal ones.

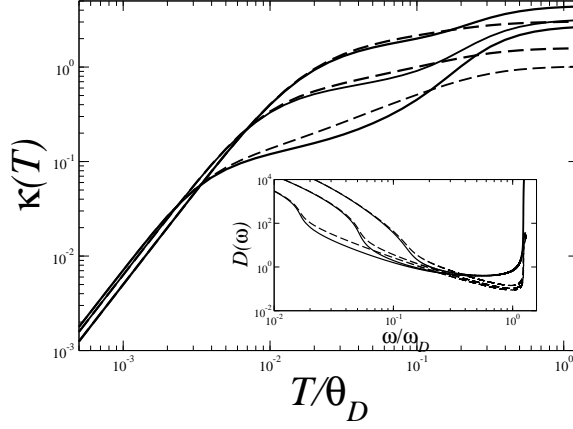


Figure 2: Inset: Frequency-dependent diffusivity according to the kinetic formula $D(\omega) \propto \ell_0(\omega) \propto 1/[\omega\Sigma''(\omega)]$ (dashed lines) and according to the present theory $D(\omega) \propto \ell_0(\omega)\omega^2/g(\omega)$ (full lines) for the disorder parameters (from right to left) $\tilde{\gamma}_\mu = 0.15, 0.164$, and 0.1664 . Main body: Thermal conductivity $\kappa(T)$ as calculated from Eqs. (7.149), (7.150), (7.153) and (7.154) using the same $D(\omega)$ as in the insert. The bottom curves correspond to $\tilde{\gamma}_\mu = 0.1664$. For the inelastic scattering parameter we used $C_{in} = 0.02$ in our units. (Taking smaller values of C_{in} results in a shift of the T^2 branch to lower frequencies.)

It is emphasized that the BP marks the position where the mean free path (see below) starts to become comparable to the wavelength of the excitations, and where $\Omega(q)$ and $\Gamma(q)$ are of the same order of magnitude.

Why does the BP appear at such a low frequency, although the elastic constants have a symmetric distribution around their mean? As noted already in the literature, the disorder affects the vibrational states in such a way that their eigenvalues become distributed like those of a random matrix. The random hybridization of the states leads to level repulsion so that the states "need more space" in the frequency domain than they would without the disorder. So they are both shifted up and down as compared to a Debye spectrum. This effect becomes stronger with increasing $\tilde{\gamma}_\mu$. The BP marks the low-frequency border of this effect and appears as a shoulder in $g(\omega)$. Only in the $g(\omega)/\omega^2$ representation it appears as a peak.

It has been noted recently that in most of the experimental DOS data $g(\omega)/\omega^2$ exhibits an exponential decrease over a large frequency range. As can be seen from the semilogarithmic representation of Fig. 1 the SCBA is compatible with these findings.

Let us now study the impact of the boson peak on the energy diffusivity $D(\omega)$ and the thermal conductivity $\kappa(T)$. The latter can be calculated from the former via

$$\kappa(T) \propto \int d\omega g(\omega) D(\omega) (\omega/T)^2 \frac{e^{\hbar\omega/k_B T}}{[\exp\{\hbar\omega/k_B T\} - 1]^2}. \quad (7.150)$$

The energy diffusivity $D(\omega)$ can be treated as a classical quantity as long as we do not consider anharmonic interactions. It can be calculated from the Kubo-type formula

$$D(\omega) \propto \lim_{\eta \rightarrow 0} 2\eta \frac{\int d^3\mathbf{r} d^3\mathbf{r}' \langle (x-x')^2 \Delta E(\mathbf{r}, \omega, \eta)^* \Delta E(\mathbf{r}', \omega, \eta) \rangle}{\int d^3\mathbf{r} d^3\mathbf{r}' \langle \Delta E(\mathbf{r}, \omega, \eta)^* \Delta E(\mathbf{r}', \omega, \eta) \rangle}, \quad (7.151)$$

where $\Delta E(\mathbf{r}', \omega, \eta) \propto \sum_{ij} \epsilon_{ij}(\mathbf{r}, z_-)^* \epsilon_{ij}(\mathbf{r}, z_+)$ is the fluctuating part of the energy density with strain tensor $\epsilon_{ij}(\mathbf{r}, z) = \frac{1}{2}[\nabla_i u_j(\mathbf{r}, z) + \nabla_j u_i(\mathbf{r}, z)]$.

In order to be able to evaluate configurational averages of fourfold products of $u_j(\mathbf{r}, z_\xi)$ appearing in Eq. (7.151) we have to go beyond the saddle-point approximation. Defining the sums $\Lambda_{\alpha\alpha'}^{\xi\xi'} \equiv \sum_{ij} \Lambda_{ijij}^{\xi\xi'\alpha\alpha'}$ we put $\Lambda_{\alpha\alpha'}^{\xi\xi'}(\mathbf{r}, \omega) = \Lambda_{sp} + \Delta\Lambda_{\alpha\alpha'}^{\xi\xi'}(\mathbf{r}, \omega)$ and $S_{eff} = S_{eff}^{sp} + \Delta S_{eff}$.

In terms of the spatial Fourier transforms $\Delta\Lambda_{\alpha\alpha'}^{\xi\xi'}(\mathbf{q}, \omega)$ of $\Delta\Lambda_{\alpha\alpha'}^{\xi\xi'}(\mathbf{r}, \omega)$ this yields a correction to the effective action of the form $\Delta S_{eff} = \sum_{\alpha\alpha'} \sum_{\xi\xi'} \sum_{\mathbf{q}} [\Delta\Lambda_{\alpha\alpha'}^{\xi\xi'}(\mathbf{q})]^* C^{\xi\xi'}(\mathbf{q}, \omega) \Delta\Lambda_{\alpha\alpha'}^{\xi\xi'}(\mathbf{q})$ with $C^{\xi\xi'}(\mathbf{q}, \omega) = \varphi_L^{\xi\xi'}(\mathbf{q}, \omega) + \frac{1}{2}\varphi_T^{\xi\xi'}(\mathbf{q}, \omega) - \frac{1}{2\tilde{\gamma}_\mu}$ and $\varphi_{L,T}^{\xi\xi'}(\mathbf{q}, \omega) = \sum_{\mathbf{k}} \chi_{L,T}(\mathbf{k} + \frac{\mathbf{q}}{2}, z_\xi) \chi_{L,T}(\mathbf{k} - \frac{\mathbf{q}}{2}, z_{\xi'})$, where the functions

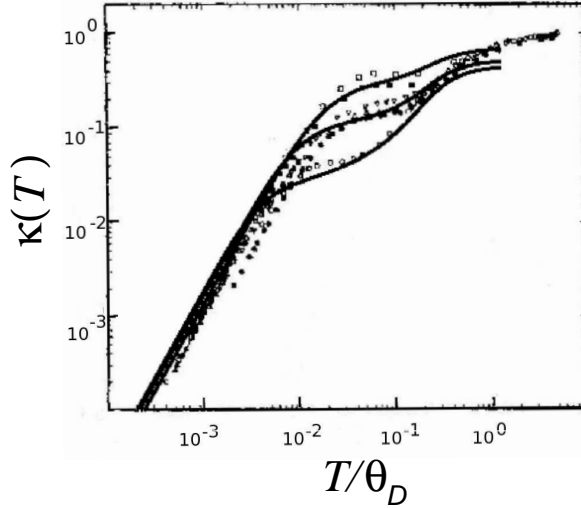


Figure 3: Scaled thermal conductivity data of several glasses (from top to bottom): PB, PMMA, PET, B₂O₃, PS, SiO₂, as compiled by Freeman and Anderson [6] together with the full-line calculations of Fig. 2.

$\chi_{L,T}(\mathbf{k}, z_\xi)$ have to be evaluated in SCBA. By inserting a suitable source field into the effective action we can convince ourselves that $C^{+-}(\mathbf{q}, \omega)$ is just the inverse of the Fourier transform of the energy correlation function that appears in Eq. (7.151) so that we have

$$D(\omega) \propto -\lim_{\eta \rightarrow 0} \eta \frac{1}{C^{+-}(0, \omega)} \left(\frac{\partial}{\partial q_x} \right)^2 C^{+-}(\mathbf{q}, \omega)|_{\mathbf{q}=0}. \quad (7.152)$$

Evaluating the numerator and denominator explicitly by means of the SCBA expressions, Eqs. (7.149), of χ_L and χ_T we find

$$D(\omega) \propto \ell_0(\omega) \omega^2 / g(\omega) \equiv \tilde{D}(\omega), \quad (7.153)$$

where $\ell_0(\omega) \propto [\omega \Sigma''(\omega)]^{-1}$ is an effective scattering mean free path and $\Sigma''(\omega) \equiv \text{Im}\{\Sigma(z_+)\}$. Equation (7.153) is the main result of the present paper. It states that the expression for $D(\omega)$ that corresponds to the SCBA is not equivalent to the kinetic expression $D(\omega) \propto \ell_0(\omega)$ used so far in the literature but contains an “inverse boson peak factor” $\omega^2/g(\omega)$ which reduces the diffusivity in the BP regime in a much stronger way than obtained from the kinetic expression. This is demonstrated in the insert of Fig. 2, where we have compared the frequency dependence of the two formulae. Also the behavior above the BP is quite different in our theory than as obtained from the kinetic formula.

In order to calculate the thermal conductivity by summing over frequency with the proper quantum weight factor (Eq. (7.150)), we have to overcome a problem common to all harmonic theories of thermal conductivity, namely the fact that for small frequencies $D(\omega)$ diverges as $D(\omega) \propto \omega^{-4}$ (Rayleigh law). In reality this divergence is cut off by inelastic scattering for which one usually takes the scattering from two-level systems. As we do not deal with anharmonic phenomena in the present paper we use for simplicity

$$\tilde{D}_{eff}(\omega) = [\tilde{D}(\omega)^{-1} + \tilde{D}_{in}(\omega)^{-1}]^{-1} \quad (7.154)$$

with $\tilde{D}_{in}(\omega)^{-1} = C_{in}\omega$, where C_{in} is a constant which should not vary very much from material to material [?].

In Fig. 2 we compare the results for the thermal conductivity using the kinetic formula and the new theory (Eq. (7.153)). It is clear that the latter describes the experimentally observed structure much better than the kinetic formula. In Fig. 3 we compare the theory with the experimental results for several glasses as compiled by Freeman and Anderson [6]. It should be mentioned that there is no adjustment or rescaling of the T/θ_D axis. It is clearly seen how the BP is related to the plateau: As the disorder increases the plateau is more pronounced and shifted to lower temperatures. It is interesting to note that obviously SiO₂ is the material with the strongest disorder and that the Freeman-Anderson scaling may serve as a means to classify glassy materials with respect to their degree of disorder.

In conclusion we have achieved to obtain a mean-field description of the boson peak in terms of transverse elastic degrees of freedom which are affected by the frozen-in disorder. The high-temperature structure

of the temperature dependence of the thermal conductivity can be explained by means of this theory as a result of the strong elastic scattering in the frequency regime of the BP and above.

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