Theory of condensed matter

Prof. Dr. Walter Schirmacher, WS 2008/9

Universität Mainz

Contents

4 Phonons in crystals and in noncrystalline materials

4.1 General models for quantized vibrational excitations

4.1.1 Einstein model

Just one year after the four famous papers by Einstein, namely in 1906, he published a paper on the specific heat of solids, which layed the foundation of modern solid state theory. He modelled the solid as a set of harmonic oscillators with eigenfrequency $\omega_E = 2\pi\nu_E$.

The total energy of N atoms vibrating with this frequency in the three spatial directions is

$$E_E = 3\underbrace{\sum_{i=1}^{N}}_{3N} \hbar\omega_E \frac{1}{e^{\hbar\omega_E/k_B T} - 1}$$

$$\longrightarrow\ 3Nk_B T \qquad T \to \infty$$

(4.1)

The high temperature limit is in accord with the equipartition theorem. From this we obtain the following formula for the specific heat

$$C_{N,E} = \frac{1}{N}\frac{\partial E_E}{\partial T} = 3k_B\, x_E^2 \frac{e^{x_E}}{\left(e^{x_E} - 1\right)^2} \qquad\qquad x_E = \frac{\hbar\omega_E}{k_B T}$$

(4.2)

Here Einstein applied the new quantum statistics introduced for electromagnetic radiation interacting with a black body by Max Planck.

While this formula explains the strong drop of the specific heat from the Dulong-Petit law $C_N = 3Nk_B$ towards zero as $T \to 0$ as a quantum phenomenon, the details *how* $C(T)$ behaves as $T \to 0$ are not adequately described by the Einstein model. In the Einstein model the specific heat vanishes exponentially with T as $T \to 0$, whereas one can prove from general considerations that the low-temperature behavior of the specific heat should be $C(T) \propto T^3$ as in the Debye model described below.

4.1.2 Elasticity theory and Debye model

186   *A. Einstein.*

spezifische Wärme stets den Wert 5,94 n besitze. Wir haben vielmehr zu setzen (7)
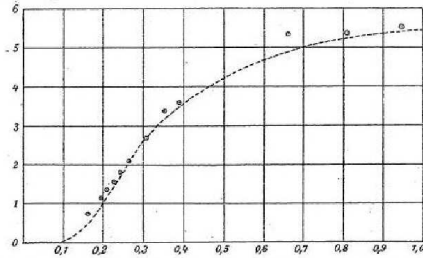
$$E = \frac{3R}{N} \frac{\beta\nu}{e^{\frac{\beta\nu}{T}} - 1}.$$

Die Energie von N solchen Elementargebilden, in Gramm-kalorien gemessen, hat daher den Wert

$$5,94 \frac{\beta\nu}{e^{\frac{\beta\nu}{T}} - 1},$$

so daß jedes derartige schwingende Elementargebilde zur spezifischen Wärme pro Grammäquivalent den Wert

(8) $$5,94 \frac{e^{\frac{\beta\nu}{T}} \cdot \left(\frac{\beta\nu}{T}\right)^2}{\left(e^{\frac{\beta\nu}{T}} - 1\right)^2},$$

beiträgt. Wir bekommen also, indem wir über alle Gattungen von schwingenden Elementargebilden summieren, welche in dem betreffenden festen Stoffe vorkommen, für die spezifische Wärme pro Grammäquivalent den Ausdruck[1]

(8a) $$c = 5,94 \sum \frac{e^{\frac{\beta\nu}{T}} \left(\frac{\beta\nu}{T}\right)^2}{\left(e^{\frac{\beta\nu}{T}} - 1\right)^2}.$$

Die vorstehende Figur[2] zeigt den Wert des Ausdruckes (8) in Funktion von $x = (T/\beta\nu)$. Wenn $(T/\beta\nu) > 0,9$, unterscheidet

1) Die Betrachtung läßt sich leicht auf anisotrope Körper ausdehnen.
2) Vgl. deren gestrichelte Kurve.
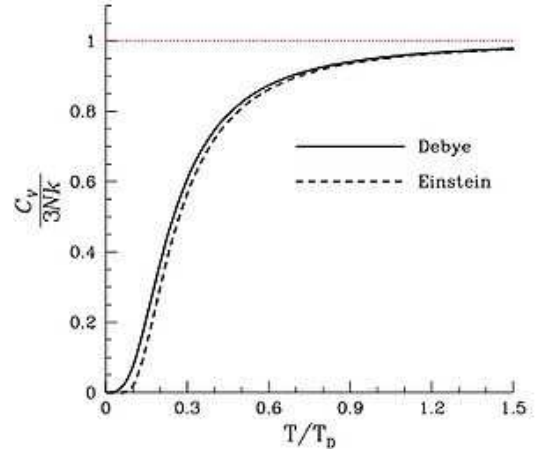
Left: original page from Einsteins article Ann Phys. 22, 180 (1907); comparison with experimental data of Weber on crystalline diamond.
Right: Comparison of the Einstein and Debye model for the specific heat

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* $\epsilon_{k\ell}$

$$\boxed{\sigma_{ij} = \sum_{k\ell} C_{ijk\ell}\epsilon_{k\ell}} \qquad i, j, k, \ell = 1, 2, 3 \tag{4.3}$$

The stress tensor is defined in terms of a force in i direction acting on a surface element $\mathrm{d}A_j$ with normal vector in j direction

$$\mathrm{d}F_i = \sum_j \sigma_{ij}\mathrm{d}A_j \tag{4.4}$$

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

$$\epsilon_{ij} = \frac{1}{2}\left(u_{i|j} + u_{j|i}\right) \qquad u_{i|j} = \frac{\partial u_j}{\partial x_i} \tag{4.5}$$

In an *isotropic* system the Hooke tensor $C_{ijk\ell}$ has only 2 independent entries and we have

$$C_{ijk\ell} = \lambda\,\delta_{ij}\delta_{k\ell} + \mu\left(\delta_{ik}\delta_{j\ell} + \delta_{i\ell}\delta_{jk}\right) \tag{4.6}$$

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

$$
\begin{aligned}
\mathcal{L}(\mathbf{r}, t) &= \frac{1}{2}\rho\,\dot{\mathbf{u}}\cdot\dot{\mathbf{u}} - \frac{1}{2}\sum_{ijk\ell} u_{i|j}C_{ijk\ell}u_{k|\ell} \\
&= \frac{1}{2}\rho\,\dot{\mathbf{u}}\cdot\dot{\mathbf{u}} - \frac{\lambda}{2}\left(\sum_i \epsilon_{ii}\right)^2 - \mu\sum_{ij}\epsilon_{ij}^2
\end{aligned}
\tag{4.7}
$$

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

$$
K = \lambda + \frac{2}{3}\mu = \frac{E}{2(1-2\nu)}
\tag{4.8}
$$

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

The equations of motion are

$$
\sum_{i=0}^{3} \frac{\partial}{\partial x_i}\frac{\partial\mathcal{L}}{\partial u_{k|i}} - \frac{\partial\mathcal{L}}{\partial u_k} = 0 \qquad x_0 = t \qquad k = 1, 2, 3
\tag{4.9}
$$

They can be refomulated as

$$
\begin{aligned}
\rho\ddot{u}_i &= \sum_{\ell=1}^{3} A_{i\ell}u_\ell \\
A_{i\ell} &= \lambda\partial_i\partial_\ell + \mu\left(\partial_\ell\partial_i + \nabla^2\delta_{i\ell}\right)
\end{aligned}
\tag{4.10}
$$

With the Ansatz

$$
\mathbf{u}(\mathbf{r}, t) = \mathbf{u}e^{i[\mathbf{kr}-\omega t]}
\tag{4.11}
$$

we obtain the matrix eigenproblem

$$
\begin{aligned}
\omega^2 u_i &= \sum_\ell D_{i\ell}u_\ell \\
D_{i\ell} &= \frac{1}{\rho}\left[(\lambda+\mu)k_i k_\ell + \mu k^2\delta_{i\ell}\right]
\end{aligned}
\tag{4.12}
$$

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

$$
D = \frac{1}{\rho}\begin{pmatrix} \mu k^2 & 0 & 0 \\ 0 & \mu k^2 & 0 \\ 0 & 0 & (\lambda+2\mu)k^2 \end{pmatrix}
\tag{4.13}
$$

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 ($\mathbf{u}||\mathbf{k}$) with sound velocity $c_L = \sqrt{(\lambda+2\mu)/\rho}$.

We return now to the ideas of *Debye*. Her 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):

$$
N = \sum_{\substack{\mathbf{k} \\ |\mathbf{k}|<k_D}} = \frac{V}{(2\pi)^3}\int_{|\mathbf{k}|<k_D} d^3\mathbf{k} = \frac{V}{2\pi^2}\int_0^{k_D} dk\,k^2 = \frac{V}{6\pi^2}k_D^3
\tag{4.14}
$$

$$
\Rightarrow \boxed{k_D = \sqrt[3]{6\pi^2 N/V}}
\tag{4.15}
$$

46
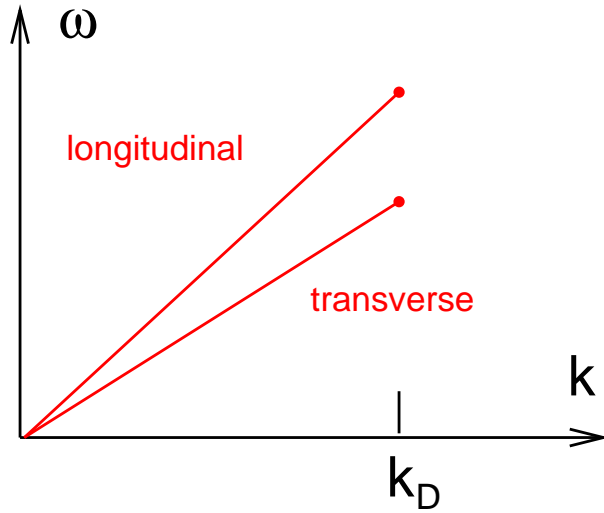
Dispersion of the Debye model

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

$$
\begin{aligned}
E &= \sum_{\lambda=1}^{2} \sum_{\mathbf{k}} \frac{\hbar \omega_{k\lambda}}{e^x - 1} \qquad\qquad \omega_{k\lambda} = c_\lambda k \\
&= \sum_\lambda c_\lambda \frac{V}{2\pi^2} \int_0^{k_D} dk \frac{k^3}{e^x - 1} \qquad x = \hbar c_\lambda k / k_B T \equiv \Theta_D / T \\
&= \sum_\lambda \frac{(k_B T)^4}{(\hbar c_\lambda)^3} \frac{V}{2\pi^2} \int_0^{\Theta_D/T} dx \frac{x^3}{e^x - 1}
\end{aligned}
$$
(4.16)

Θ_D is called the *Debye temperature*.

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

$$
\begin{aligned}
\frac{E}{N} &= \frac{V}{N} \frac{I}{2\pi^2} \frac{1}{\hbar^3} \left(\frac{1}{c_L^3} + \frac{2}{c_T^3} \right) (k_B T)^4 \\
&= \frac{3I}{(\hbar k_D)^3} \left(\frac{1}{c_L^3} + \frac{2}{c_T^3} \right) (k_B T)^4
\end{aligned}
$$
(4.17)

$$
\Rightarrow \qquad \boxed{C_N = \frac{3I k_B}{(\hbar k_D)^3} \left(\frac{1}{c_L^3} + \frac{2}{c_T^3} \right) (k_B T)^3}
$$
(4.18)

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. In metals there is an additional contribution proportional to T. In *disordered* i.e. noncrystalline or strongly distorted crystals there is an *approximate* linear contribution to the temperature dependent specific heat, i.e. the Debye law is no more valid.

For the whole temperature ramge the Debye formula serves as an interpolation formula between the exact Debye T^3 law and the exact Dulong-Petit law, which does lead to very good agreement with experimental specific heat data. The formula for the specific heat per atom C_N is

$$
C_N = 9 k_B \left(\frac{T}{\Theta_C} \right) \int_0^{\Theta_D/T} dx \frac{x^4 e^x}{(e^x - 1)^2}
$$
(4.19)

4.2 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 ist 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)

47

– 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

$$E = E_0 + \frac{1}{2} \sum_{\substack{i,j=1 \\ i \neq j}}^{N} \phi(r_{ij}) \tag{4.20}$$

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

$$E = E_0 + \frac{1}{2} \sum_{\substack{i,j=1 \\ i \neq j}}^{N} \phi(R_{ij}) + \frac{1}{4} \sum_{ij} \left[(\mathbf{u}_i - \mathbf{u}_j) \cdot \nabla \right]^2 \phi(r_{ij}) \Big|_{r_{ij}=R_{ij}} \tag{4.21}$$

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

$$
\begin{aligned}
E_{\text{harm}} &= \frac{1}{4} \sum_{\substack{ij \\ \mu\nu}} (u_{i\mu} - u_{j\mu}) \phi_{\mu\nu}^{ij} (u_{i\nu} - u_{j\nu}) \\
\phi_{\mu\nu}^{ij} &= \frac{\partial}{\partial x_\mu} \frac{\partial}{\partial x_\nu} \phi(r_{ij}) \Big|_{r_{ij}=R_{ij}}
\end{aligned}
\tag{4.22}
$$

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

$$
\begin{aligned}
E_{\text{harm}} &= \frac{1}{2} \sum_{\substack{ij \\ \mu\nu}} u_{i\mu} D_{\mu\nu}^{ij} u_{j\nu} \\
\text{with} \quad D_{\mu\nu}^{ii} &= \sum_\ell \phi_{\mu\nu}^{i\ell} \\
D_{\mu\nu}^{ij} &= -\phi_{\mu\nu}^{ij} \qquad i \neq j \, .
\end{aligned}
\tag{4.23}
$$

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

$$M \ddot{u}_{i\mu} = -\sum_j D_{\mu\nu}^{ij} u_{j\nu} \tag{4.24}$$

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

4.3 Phonon dispersions in crystals

The task is, of course, to *diagonalize* $D_{\mu\nu}^{ij}$. The eigenvectors are called *normal modes* of the lattice. We shall now consider
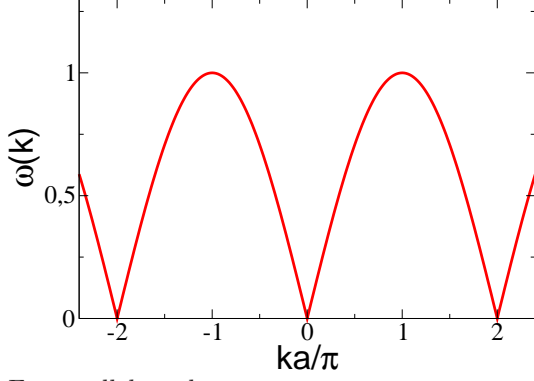
– Normal modes of a one-dimensional lattice;

– normal modes of a one-dimensional lattice with basis;

– normal modes of a three-dimensional lattice.

The *eigenvalues* in reciprocal space are the squares of the characteristic frequencies $\omega_\alpha(\mathbf{k})$, which are called *phonon dispersions*.

48

4.3.1 Normal modes of a one-dimensional lattice

Let u_ℓ be the *longitudinal* displacements (i.e. in chain direction) of a one-dimensional chain of atoms with lattice constant a and periodic boundary condition $\mathbf{u}(\mathbf{r}_0) = \mathbf{u}(\mathbf{r}_N)$. We further assume that there are only nearest-neighbor force constants $K = \phi_{xx}^{\ell m}$. Then we have the equation of motion

$$\ell+1 + u_{\ell-1} - 2u_\ell) \tag{4.25}$$

We make the ansatz

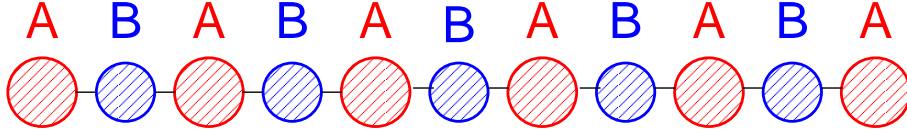$$u_i(t) = u_k(\omega)e^{i(k\ell a - \omega t)} \tag{4.26}$$

from which we obtain

$$
\begin{aligned}
M\omega^2 &= 2K\left(1 - \cos ka\right) = 4K\sin\frac{ka}{2} \\
\omega(k) &= 2\sqrt{\frac{K}{M}}\sin\frac{ka}{2} = 2\sqrt{\frac{K}{M}}\left|\sin\frac{ka}{2}\right|
\end{aligned}
\tag{4.27}
$$

For small k we have

$$\omega(k) = \sqrt{\frac{K}{M}}ka = ck \tag{4.28}$$

This corresponds to a continuous one-dimensional wave with sound velocity $c = a\sqrt{K/M}$.

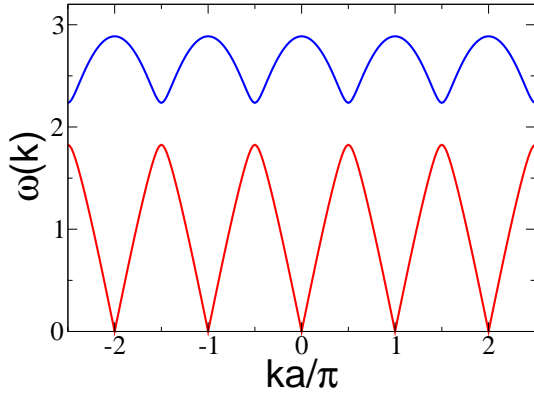### 4.3.2 Normal modes of a one-dimensional lattice with basis

Qe now consider a chain of atoms who have different masses, i.e. alternating m_A and m_B. The set of equations of motion is

$$
\begin{aligned}
\ddot{u}_i^A &= -\frac{1}{m_A}K\sum_\ell\left(u_i^A - u_\ell^B\right) \\
\ddot{u}_\ell^B &= -\frac{1}{m_B}K\sum_i\left(u_\ell^B - u_i^A\right)
\end{aligned}
\tag{4.29}
$$

leading to the set of eigenvalue equations

$$
\begin{aligned}
-\omega^2 u^A &= -2Ku^A + 2K\cos(ka)u^B \\
-\omega^2 u^B &= -2Ku^B + 2K\cos(ka)u^A
\end{aligned}
\tag{4.30}
$$

From this we obtain the characteristic equations

$$\left(\omega^2 - \frac{2K}{m_A}\right)\left(\omega^2 - \frac{2K}{m_B}\right) - \frac{4K^2}{m_A m_B}\cos^2 ka = 0 \tag{4.31}$$

with the solutions

$$\omega_{1,2} = \left[\frac{K}{\mu}\left(1 \pm \sqrt{1 - \frac{4\mu}{m_A + m_B}\left(1 - \cos^2 ka\right)}\right)\right]^{\frac{1}{2}} \tag{4.32}$$

where $mu = m_A m_B/(m_A + m_B)$ is the reduced mass.

Looking at the dispersion we see two new features in comparison with the mono-atomic chain: (*i*) the reciprocal lattice has doubled; (*ii*) there are now two branches of the dispersion. The first feature is due to the overstructure (*Überstruktur*) introduced by the different masses: The new lattice constant is not a but $2a$, and we have a one-dimensional lattice with basis, which leads to the second branch of the phonon dispersion. The bottom branch is called *acoustical*, because it includes acoustic waves near the Γ point: near $k = 0$ the dispersion is linear. The top branch is called *optical*, because it is observed by optical (in particular Raman) spectroscopy.

4.3.3 Normal modes of a monatomic three-dimensional lattice

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

$$E_{\mathrm{harm}} = \frac{1}{2}\sum_{\substack{ij \\ \mu\nu}} u_{i\mu} D_{\mu\nu}^{ij} u_{j\nu} \tag{4.33}$$

which corresponds to the set of equations of motion

$$m\ddot{u}_{i\mu}(t) = -\sum_{j\nu} D_{\mu\nu}^{ij} u_{j\nu} \tag{4.34}$$

The dynamical matrix has the symmerties

$$
\begin{aligned}
D_{\mu\nu}^{ij} &= D_{\nu\mu}^{ji} \\
D_{\mu\nu}^{ij} &= D_{\mu\nu}^{ji} \\
\sum_i D_{\mu\nu}^{ij} &= \sum_j D_{\mu\nu}^{ij} = 0
\end{aligned}
\tag{4.35}
$$

We seek solutions of the form

$$u_{i\mu}(t) = u_\mu e^{i(\mathbf{k}\cdot\mathbf{R}_i - \omega t)} \tag{4.36}$$

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

$$\mathbf{k} = \frac{n_1}{N_1}\mathbf{b}_1 + \frac{n_2}{N_2}\mathbf{b}_2 + \frac{n_3}{N_3}\mathbf{b}_3 \tag{4.37}$$

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 obrain the characteristic equations

$$m\omega^2 u_\mu = \sum_\nu D_{\mu\nu}(\mathbf{k}) u_\nu D_{\mu\nu} \tag{4.38}$$
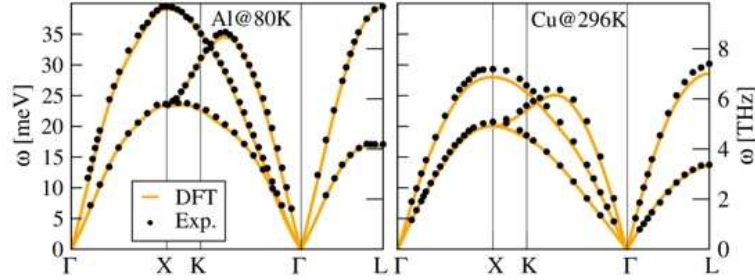
$$D_{\mu\nu}(\mathbf{k}) = \sum_{\substack{\ell \\ \mathrm{lattice}}} e^{i\mathbf{k}\mathbf{R}_\ell} D_{\mu\nu}(\mathbf{R}_i - \mathbf{R}_j)\Big|_{\mathbf{R}_\ell = \mathbf{R}_i - \mathbf{R}_j} \tag{4.39}$$

Taking advantage of the symmetries (4.35) of the dynamical matrix we re-write (4.39) as follows

$$D_{\mu\nu}(\mathbf{k}) = \frac{1}{2} \sum_\ell e^{i\mathbf{k}\mathbf{R}_\ell} \left[D_{\mu\nu}(\mathbf{R}_\ell) + D_{\mu\nu}(-\mathbf{R}_e ll) \right] - \underbrace{\sum_\ell D_{\mu\nu}(\mathbf{R}_\ell)}_{=0}$$

$$= \frac{1}{2} \sum_\ell D_{\mu\nu}(\mathbf{R}_\ell) \left[\cos \mathbf{k}\mathbf{R}_\ell - 1 \right] = \sum_\ell D_{\mu\nu}(\mathbf{R}_\ell) \sin^2 \left(\frac{1}{2} \mathbf{k}\mathbf{R}_\ell \right)$$

(4.40)

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

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

(4.41)

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).

4.3.4 Vibrational density of states

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

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

(4.42)

For the Debye model

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

(4.43)

This gives

$$g(\omega) = \frac{V}{6\pi^2 N}$$
$$\sum_s \int_0^{k_D} \delta(\omega - kc_s) = \sum_s \frac{V}{6\pi^2 N c_s^3} \omega^2$$
$$= 3\frac{\omega^2}{\omega_D^3}$$

(4.44)

where we have introduced the *Debye frequency*

$$\omega_D = k_D \left[\frac{1}{c_L^3} + frac2c_L^3 \right]^{-1/3} \equiv k_D c_D$$

(4.45)

Instead the dynamical matrix $\overset{\leftrightarrow}{D}$ we can also introduce a modified dynamical matrix

$$K^{ij}_{\mu\nu} = \frac{1}{m_i} D^{ij}_{\mu\nu} \tag{4.46}$$

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

$$\lambda \mathbf{u} = \overset{\leftrightarrow}{K} \mathbf{u} \tag{4.47}$$

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

$$\tilde{g}(\lambda) = \frac{1}{3N} \sum_s \sum_{\mathbf{k}} \delta\big(\lambda - \lambda_s(\mathbf{k})\big) \tag{4.48}$$

and we have

$$g(\omega) = \frac{\mathrm{d}\lambda}{\mathrm{d}\omega}\tilde{g}(\lambda) = 2\omega\tilde{g}(\lambda) \tag{4.49}$$

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

$$
\begin{aligned}
E_N &= \frac{1}{N} \sum_{s=1}^{3} \sum_{\mathbf{k}} \hbar\omega_s(\mathbf{k}) \frac{1}{e^{\hbar\omega_s(\mathbf{k})/k_B T} - 1} \\
&= 3 \int \mathrm{d}\omega \frac{1}{3N} \sum_{s\mathbf{k}} \delta\big(\omega - \omega_s(\mathbf{k})\big) \frac{\hbar\omega_s(\mathbf{k})}{e^{\hbar\omega_s(\mathbf{k})/k_B T} - 1} \\
&= 3 \int \mathrm{d}\omega g(\omega) \frac{\hbar\omega}{e^{\hbar\omega/k_B T} - 1} \\
\Rightarrow \quad C_N &= 3 \int \mathrm{d}\omega g(\omega)\hbar\omega \frac{\partial}{\partial T} \left(\frac{1}{e^{\hbar\omega/k_B T} - 1} \right)
\end{aligned}
\tag{4.50}
$$

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 $\mathbf{k}$.

4.4 Harmonic vibrational dynamics in disordered Solids

4.4.1 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

$$\frac{\mathrm{d}^2}{\mathrm{d}t^2} u_i(t) = -\sum_j K_{ij}\big(u_i(t) - u_j(t)\big) \tag{4.51}$$

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

$$\frac{\mathrm{d}^2}{\mathrm{d}t^2}\mathcal{G}_{ij}(t,t') + \sum_\ell K_{i\ell}(\mathcal{G}_{ij} - \mathcal{G}_{\ell j}) = \delta_{ij}\delta(t - t') \tag{4.52}$$

Defining a "Hamiltonian Matrix"

$$\mathcal{H}_{ij} = \begin{cases} -\sum_j K_{ij} & i = j \\ \\ K_{ij} & i \neq j \end{cases} \tag{4.53}$$

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

$$\big(\tilde{z} - \mathcal{H}\big)\mathcal{G} = \big(-\omega^2 + i\tilde{\epsilon} - \mathcal{H}\big)\mathcal{G} = 1 \tag{4.54}$$

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:

$$K_{ij}^{eff}(\tilde{z}) = \Gamma(\tilde{z}). \tag{4.55}$$

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

$$H_{ij} = \begin{cases} -\sum_j K_{ij}^{eff}(\tilde{z}) - Z\Gamma(\tilde{z}) & i = j \\ K_{ij}^{eff}(\tilde{z}) = \Gamma(\tilde{z}) & i \neq j \end{cases} \tag{4.56}$$

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

$$\tilde{z}G_{ij} - \delta_{ij} = Z\Gamma(\tilde{z})(G_{\ell j} - G_{ij}) \qquad \ell \text{ arbitrary neighboring site} \tag{4.57}$$

As in the Lorentz theory of dielectric polarizability[1] 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

$$V = \begin{pmatrix} -v_{i_0 j_0}(\tilde{z}) & v_{i_0 j_0}(\tilde{z}) \\ v_{i_0 j_0}(\tilde{z}) & -v_{i_0 j_0}(\tilde{z}) \end{pmatrix} \tag{4.58}$$

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

$$\langle T \rangle = \langle \frac{V}{1 - VG} \rangle \tag{4.59}$$

should vanish. Working out the 2×2 inverse and using (4.57) with $i = j$ we obtain the following CPA self-consistent equation for $\Gamma(\tilde{z})$

$$\langle \frac{K - \Gamma(\tilde{z})}{1 + (K - \Gamma(\tilde{z}))\frac{2}{Z\Gamma(\tilde{z})}(1 - \tilde{z}G_{ii}(\tilde{z}))} \rangle = 0 \tag{4.60}$$

which can be reformulated as

$$\Gamma(\tilde{z}) = \langle \frac{K}{1 + (K - \Gamma(\tilde{z}))\frac{2}{Z\Gamma(\tilde{z})}(1 - \tilde{z}G_{ii}(\tilde{z}))} \rangle \tag{4.61}$$

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

$$G_{ii}^{(0)}(\tilde{z}) = \sum_{\mathbf{k} \in BZ} \frac{1}{\tilde{z} + 6 - E(\mathbf{k})} \tag{4.62}$$

with the simple-cubic band structure

$$E(\mathbf{k}) = 2[\cos(k_x a) + \cos(k_y a) + \cos(k_z a)] \tag{4.63}$$

---

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

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

$$G_{ii}(\tilde{z}) = \frac{1}{\Gamma(\tilde{z})} G_{ii}^{(0)}\left(\frac{\tilde{z}}{\Gamma(\tilde{z})}\right) \qquad (4.64)$$

(4.61) and (4.64) now establish a self-consistent set of equations which can (and have to be) solved on a computer.
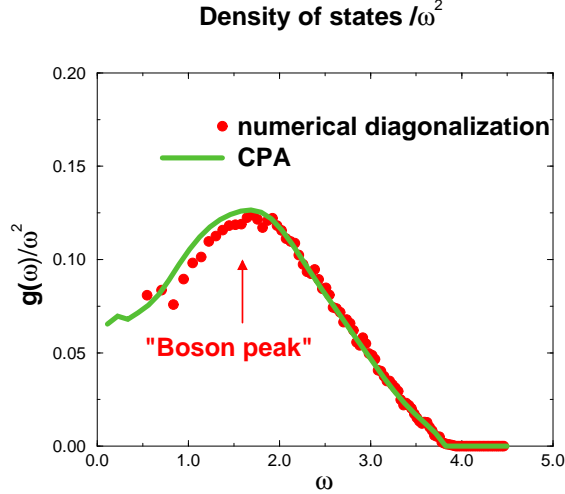

Density of states /ω^2

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 (4.61) and (4.64)), 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

$$g(\omega) = 2\omega g(\omega^2) = -\frac{2\omega}{\pi}\Im m\{G(\tilde{z})\} \qquad (4.65)$$

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 exixtence 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
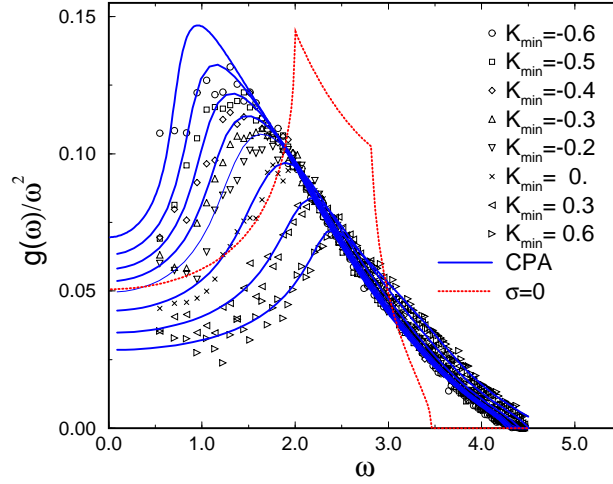
Fig. 9: Density of states, divided by ω^2 of a simple-cubic lattice with a varying lower cutoff K_{min} and width parameter $\sigma/K_0 = 1$. The full line is a CPA calculation (solution of (4.61) and (4.64)), the points are the result of numerical diagonalizations of systems with periodic boundary conditions, 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.

4.4.2 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

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

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

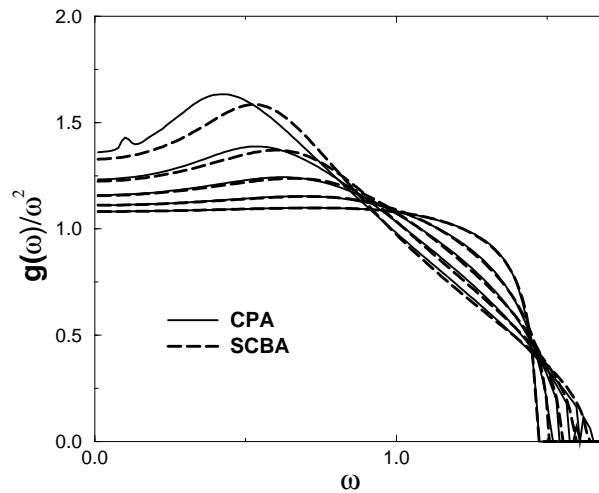Fig. 10: Density of states, divided by ω^2 for a generalized Debye model with fluctuating elastic constants $\tilde{K} \equiv c^2$ calculated for different disorder parameters $\gamma \propto \langle \delta \tilde{K}^2 \rangle / \langle \tilde{K} \rangle^2$, calculated in SCBA and CPA

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

$$\delta\Gamma(\tilde{z}) = -\gamma \sum_{|\mathbf{k}|<k_D} \frac{k^2}{\tilde{z} + k^2[c_0^2 + \delta\Gamma(\tilde{z})]} \qquad (4.66)$$

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 use safely 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 (4.66) 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

$$\delta\Gamma(\tilde{z}) = \Gamma(\tilde{z}) - 1 = -\gamma \frac{1}{\tilde{z} + \Gamma(\tilde{z})} \qquad (4.67)$$

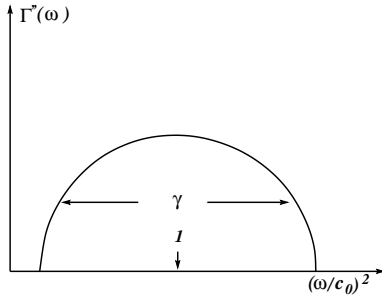which is a quadratic equation for $\Gamma(\tilde{z})$

Fig. 11: Imaginary part of the "self energy" $\Gamma(\tilde{z}$ for the simplified SCBA equation (4.67). 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 occurrance 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.