Chapter 5

Thermodynamical Properties

So far, we developed a description of phonons in terms of classical waves. This follows the development of the physical understanding of lattice vibrations developed in the early 20ties century. But a principal limitation of this approach is derived from the failure to properly describe the specific heat $c_v = 1/V(\partial\text{inner energy})/\partial T$ of matter (see Fig. 5.1).

$$\text{Classical Physics (Dulong-Petit):} c_v = 5.96 \frac{cal}{mol \cdot K} \tag{5.1}$$

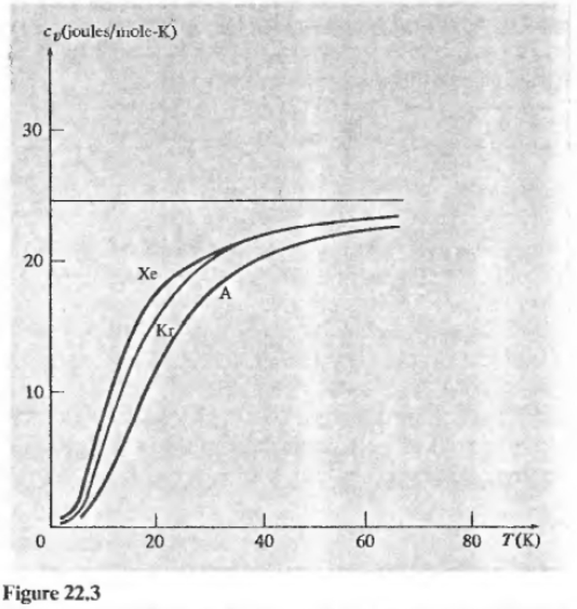

Figure 22.3
Measured specific heats of argon, xenon, and krypton. The horizontal line is the classical Dulong and Petit value. (Quoted in M. L. Klein, G. K. Horton, and J. L. Feldman, *Phys. Rev.* **184**, 68 (1969).)

Figure 5.1: from Ashcroft-Mermin

The law of Dulong-Petit, which is derived from Classical Physics, predicts a temperature independent specific heat. Figure 5.1 shows the experimentally determined specific heat for Argon, Krypton, and Xenon. For high temperatures, the specific heat approaches the value predicted by Dulong-Petit, whereas in the low temperature regime classical physics fails even to qualitatively describe the specific heat.

Experimental observation (at low temperatures):

- $c_v \propto T^3$ for insulators

- $c_v \propto aT + bT^3$ for metals

($\propto T$ is the contribution of the electrons, as discussed later and is only relevant at very low temperatures in the range of few K)

The observed discrepancy lead to a quantum mechanical interpretation of lattice vibrations.

- classical interpretation: the energy of a wave with ω, q can be changed by an infinitismal amount of energy. At temperature T: Boltzmann distribution for the amount of total energy: $\rightarrow E(\omega, q, T) = \int_0^\infty \hbar\omega e^{\hbar\omega/(k_BT)} d\omega$.
- quantum mechanical interpretation: waves are formed of quasi-particles, so called phonons - and the energy of phonons is quantized by $\hbar\omega$. A lattice wave of ω, q is formed of n phonons, each contributing $\hbar\omega$ energy:$\rightarrow E(\omega, q, T) = \sum_{n=0}^\infty (n + 1/2)\hbar\omega e^{(n+1/2)\hbar\omega/(k_BT)}$ (the term $1/2\hbar\omega$ is the vacuum energy).

In the following sections:

- Density of States for Phonons
- calculation of n and the thermal energy
- calculation of c_v

5.1 Density of States

- previous chapter: infinite systems, i.e. $N \rightarrow \infty, \omega(\vec{q})$ is continuous
- this chapter: finite crystals, i.e. $N \neq \infty$

Problem: finite crystals have surface effects (broken symmetry). To ease calculation: assume periodicity with crystal size ($N^{1/3}$ unit cells in every direction).

$$\begin{aligned} \texttt{periodicity condition} : e^{iN^{\frac{1}{3}}\vec{q}(\vec{a}_1+\vec{a}_2+\vec{a}_3)} &= 1 \\ \vec{G} = h\vec{g}_1 + k\vec{g}_2 + l\vec{g}_3; \vec{q} &= q_1\vec{g}_1 + q_2\vec{g}_2 + q_2\vec{g}_2 \\ q_i = \frac{n_i}{N^{\frac{1}{3}}}; n_i = 0, \pm1, \pm2 \cdots \texttt{ with } \vec{G}\cdot\vec{q} &\leq \frac{1}{2}G^2 \texttt{ , i.e. 1st Brillouin Zone} \end{aligned} \tag{5.2}$$

Within the 1st Brillouin Zone, we therefore have N lattice points at a density of N/V^*. $V^* = \vec{g}_1 \cdot (\vec{g}_2 \times \vec{g}_3)$. We get (using equation 3.16): $N/V^* = V/(2\pi)^3$. V is the volume of the crystal. Fig. 5.2 gives an illustration.

With the phonon dispersion relation $\omega(\vec{q})$ known, which is plotted as a line in Fig. 5.2, we can determine all points in the reciprocal space which represent the identical energy. Then, the number of reciprocal points, which match a given energy ω, is called Density-of-States ($Z(\omega)d\omega$).

The Density-of-States becomes the volume integral:

$$Z(\omega)d\omega = \frac{V}{(2\pi)3}\int_\omega^{\omega+d\omega} d\vec{q} \tag{5.3}$$

and with

$$d\vec{q} = df_\omega d\vec{q}_\perp \texttt{ and } d\omega = |\vec{\nabla}_{\vec{q}}\omega| d\vec{q}\perp \tag{5.4}$$

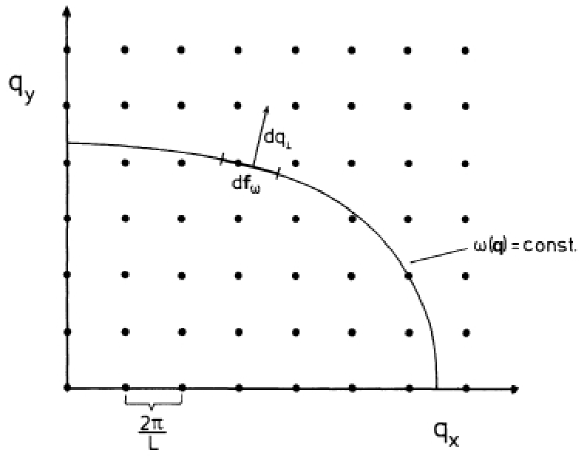

Figure 5.2: allowed values for the q-space. The spacing between q-points is $2\pi/L$ with L the size of the crystal. With N units cells in the crystal, we get $N^{1/3}$ q-points in very direction which form the 1st Brillouin zone. The line indicates all points of identical energy

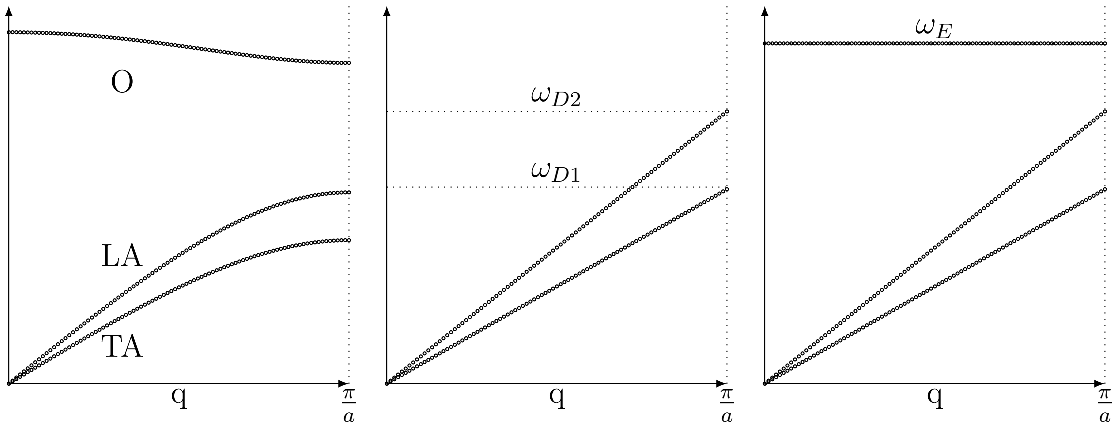
(a) Dispersion (b) Debeye Model (c) Einstein Model

Figure 5.3: Schematic presentation of phonon modes for three different cases

is transformed into a line (in 2D) / surface (in 3D) integral:

$$Z(\omega)d\omega = \frac{V}{(2\pi)^3} d\omega \int_{\omega=const} \frac{df_\omega}{|\vec{\nabla}_{\vec{q}}\omega|} \tag{5.5}$$

Note 1: if $\frac{df_\omega}{|\vec{\nabla}_{\vec{q}}\omega|=0}$, we get a singularity in the Density-of-States. This singularity is called van-Hove-singularity, and is always given when we have standing waves, i.e. $\partial\omega/\partial q = 0$.

Note 2: Density-of-states is NOT the consequence of the periodicity. Periodicity just simplifies the calculation. For all materials, including amorphous materials, the density-of-states is given.

Eq. 5.5 is the general definition of the density-of-states and can be applied to every system.

Simplification for a crystal with r atoms per unit cell:

- elastic approximation (Debye-Model): Instead of $\omega(q) \to \omega = qc_x$. $x = T$ speed of sound for transversal modes, and $x = L$ speed of sound for longitudinal modes.

- isotropic crystal: one longitudinal mode with c_L and two degenerate transversal modes with c_T equal in all three space directions.
- Debye-Model: elastic approximation plus a maximum $\omega_{Debey} = \omega_D$ to compensate for the wrong description of ω (see later)
- Einstein-Model: Debye-model to describe acoustic modes plus a fixed frequency $\omega_{Einstein} = \omega_E$ to describe $3(r-1)$ optical modes

We get:

- $\omega(\vec{q}) = \vec{q}c_x \rightarrow |\vec{\nabla}_{\vec{q}}\omega| = c_x$ (elastic) - and independent of the surface integral !
- $\int_{surface} df_\omega = 4\pi q^2$ (isotropic medium).

Therefore, the density-of-states for an elastic, isotropic medium in the Debye-model is:

$$Z(\omega)d\omega = \frac{V}{(2\pi)^3}d\omega\frac{4\pi q^2}{c_x} = \frac{V\omega^2}{2\pi^2 c_x^3}d\omega \texttt{ for each mode} \tag{5.6}$$

$$Z(\omega)d\omega = \frac{V}{2\pi^2}(\frac{1}{c_L^3} + \frac{2}{c_T^3})\omega^2 d\omega \texttt{ for all modes together} \tag{5.7}$$

Note: In this description, $Z(\omega)$ is growing to infinity with increasing ω. This is the consequence of the elastic approximation.

5.2 thermal energy of an harmonic oscillator

Mathematical equations used in the following:

$$\begin{aligned} (I)\sum_{n=0}^{\infty} x^n &= \frac{1}{1-x} \\ \frac{\partial}{\partial x}\sum_{n=0}^{\infty} x^n &= \frac{\partial}{\partial x}\frac{1}{1-x} \\ \rightarrow (II)\sum_{n=0}^{\infty} n x^n &= \frac{x}{(1-x)^2} \end{aligned} \tag{5.8}$$

As earlier mentioned, lattice waves are quantized and for one point of the reciprocal space as defined by $\omega, \vec{q}$, the energy is

$$E_n = (n + 1/2)\hbar\omega. \tag{5.9}$$

$1/2\hbar\omega$ is the vacuum energy, and n the occupation number of a specific lattice wave, with n being an integer.

$P_n^{\omega(q)}$ is the probability, to find n excited phonons of that specific energy. At a temperature T the occupation is determined by the Boltzmann distribution:

$$P_n = const \cdot e^{E_n/k_B T} \tag{5.10}$$

with the normalization condition

$$\sum_{n=0}^{\infty} P_n = 1 \tag{5.11}$$

which states that the system is always in exactly one defined state.

Introducing eq. 5.9 into eq. 5.10 and fulfilling the normalization condition (eq. 5.8), we get:

$$\begin{aligned} P_n &= \frac{e^{-n\hbar\omega/k_BT}}{1-e^{-\hbar\omega/k_BT}} \\ \texttt{with } const &= \frac{1-e^{-\hbar\omega/k_BT}}{e^{-\hbar\omega/k_BT}} \end{aligned} \tag{5.12}$$

To determine the const, we used the solution of the geometrical series eq. 5.8I.

The average energy $\epsilon(\omega, T)$ which is stored by phonons of the mode $\omega(q)$ can now be calculated:

$$\begin{aligned} \epsilon(\omega, T) &= \sum_{n=0}^{\infty} E_n P_n \\ &= (1-e^{-\hbar\omega/k_BT})\hbar\omega \sum_{n=0}^{\infty}(n+\frac{1}{2})(e^{-\hbar\omega/k_BT})^n \\ &\texttt{using eq. 5.8I for the term 1/2 and eq. 5.8II for the term with n} \\ &= \frac{\hbar\omega e^{-\hbar\omega/k_BT}}{1-e^{-\hbar\omega/k_BT}} + \frac{1}{2}\hbar\omega \end{aligned} \tag{5.13}$$

Summary:

$$\epsilon(\omega, T) = \hbar\omega(\frac{1}{2} + \frac{1}{e^{\hbar\omega/k_BT}-1}) = \hbar\omega(\frac{1}{2} + <n>_T) \tag{5.14}$$

is the average energy at temperature T for an oscillator at ω and follows the Bose-statistic for non-interacting particles. $<n>_T$ is the expectation value for the oscillator in thermal equilibrium with n the number of quasi particles (phonons).

$q, \omega, <n>_T$ define the state.

P_n follows the Boltzmann distribution, i.e. the probability of one particle in state n.

$<n>_T$ follows Bose statistics and describes the average number of particles and n is not limited.

5.3 specific heat

Mathematical equations used in the following:

$$\int_0^\infty \frac{x^3}{e^x-1}dx = \frac{\pi^4}{15} \tag{5.15}$$

$$\begin{aligned} c_v &= 1/V(\partial\texttt{inner energy })/\partial T \\ \epsilon(\omega, T) &: \texttt{ thermal energy of one oscillator} \\ Z(\omega) &: \texttt{ density of oscillators per energy} \end{aligned} \tag{5.16}$$

We can now calculate the specific heat c_v:

$$\begin{aligned} c_v(T) &= \frac{1}{V}\frac{\partial}{\partial T}\int_0^\infty Z(\omega)\epsilon(\omega, T)d\omega \\ &= \frac{1}{V}\frac{V}{(2\pi)^3}(\frac{1}{c_L^3}+\frac{2}{c_T^3})\int_0^\infty \omega^2\frac{\partial}{\partial T}\epsilon(\omega, T)d\omega \end{aligned} \tag{5.17}$$

Note:

$$\int_0^\infty Z(\omega)d\omega \tag{5.18}$$

would give an infinite value. This is a consequence of the elastic model. To compensate for the wrong description of the dispersion relation at large q-values, we introduce the Debye-frequency ω_D. ω_D (and the Debye Temperature is $\Theta = \hbar\omega_D/k$) is chosen so that the integral gives the correct number of oscillators:

$$\int_0^{\omega_D} Z(\omega)d\omega = 3rN \tag{5.19}$$

Substituting the Debye frequency into the equation of the specific heat results in:

$$c_v = \frac{9rN}{V}\frac{1}{\omega_D^3}\frac{\partial}{\partial T}\int_0^{\omega_D}\frac{\hbar\omega^3 d\omega}{e^{\hbar\omega/k_B\Theta}-1} \tag{5.20}$$

Notes:

- High-Temperature Approximation ($k_B T > \hbar\omega_D$):

  $$(e^y = 1 + y \texttt{ for small y})\ c_v \to 1/V3rNkB. \tag{5.21}$$

  We get the Dulong-Petit equation !

- Low-Temperature Limit:

  $$(\texttt{use } \int_0^{\text{inf}} \frac{x^3}{e^x-1}dx = \frac{\pi^4}{15})\ c_v = \frac{1}{V}3rNk_B\frac{4\pi^4}{5}(\frac{T}{\Theta})^3 \tag{5.22}$$

- Debye Temperature is a good guidance but not precise
  - elastic approximation
  - only acoustic modes
- correction by Einstein model:
  - optical modes: constant energy ω_E
  - Z(ω) = 0 for $\omega \neq \omega_E$
  - Z(ω) = $3(r-1)N$ for $\omega = \omega_E$
  - specific heat $c_v^{opticalmode}$

$$c_v^O = pnk_B\frac{(\hbar\omega_E/k_BT)^2 e^{\hbar\omega_E/k_BT}}{(e^{\hbar\omega_E/k_BT}-1)^2} \tag{5.23}$$

5.4 anharmonic effects

Reading: Ashcroft and Mermin, Chapter 25

Harmonic approximation:

$$\Phi(x+\Delta x) = \Phi(x) + \frac{1}{2}\Phi''(x)\Delta x^2 \tag{5.24}$$

explains:

- phonon dispersion
- phonons are quantum mechanical eigenstates
- mechanical properties
- sound propagation
- specific heat

fails to explain (among others)

- thermal expansion (here)
- heat dissipation (here)
- phonon decay (here)
- temperature dependence of elasticity (not discussed)
- the increase of c_v above Θ (not discussed)

These are properties due to anharmonic ($+\frac{1}{6}\Phi'''(x)\Delta x^3$) or higher order terms. The anharmonic term adds an asymmetric component, i.e. $< \Delta x > \neq 0$.

5.4.1 Thermal Expansion

Every material shows temperature dependent changes of volume and dimension (technologically relevant).

$$\texttt{expansion coefficient} : \alpha = \frac{1}{x}\frac{dx}{dT} \tag{5.25}$$

for cubic or isotropic materials also:

$$\texttt{expansion coefficient} : \alpha_V = 3\alpha = \frac{1}{V}\frac{dV}{dT} \tag{5.26}$$

typically: $\alpha \approx 10^{-5} K^{-1}$.

harmonic oscillator

In the harmonic case, an increase of the temperature will lead to an oscillation of the atoms around their ground state position x_0. However, for the harmonic oscillator, the average position $< x >$ is independent of the excitation level, i.e. $< x >= x_0$ (see Figure 5.4a) and the therefore, no expansion of the material can be expected in this case.

anharmonic approach - classical

The expansion of materials with temperature is related to higher order terms of the potential. This is qualitatively demonstrated in Figure 5.4. In the harmonic case (see section 4.1), the (1d) potential $\Phi(x)$ is described by $\Phi(x) = a + c(x - x_0)^2$, which is symmetric around the origin x_0. For a higher order development of the potential, we get additional terms: $\Phi(x) = a + c(x - x_0)^2 - d(x - x_0)^3 - e(x - x_0)^4$. d describes the asymmetry of the potential. As we can see in Figure 5.4b, the average position $< x >$

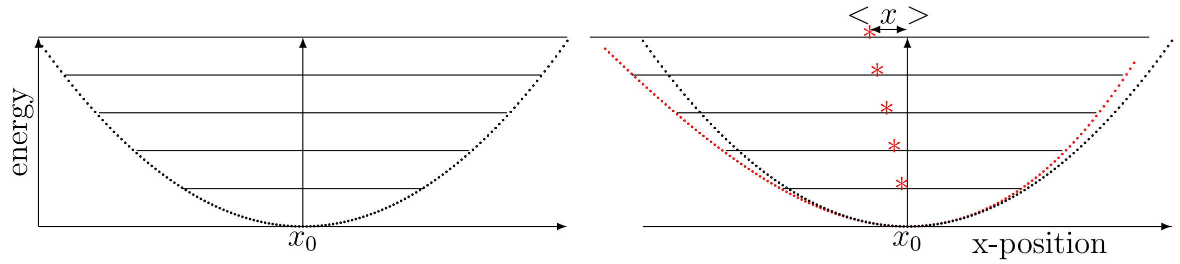

Figure 5.4: $< x >$ versus energy for a) a harmonic and b) anharmonic oscillator. In classical physics, every energy can be obtained. However, as we previously learned, the oscillation is quantized (respective states are indicated).

for the oscillator in an excited state deviates from x_0. Therefore, the entire crystal will change its size.

Let us calculate the average distance $< x >$ between two atoms (for simplicity, we set $x_0 = 0$)! We now have to consider the probability of an atom to be in an excited state at temperature T using the Boltzmann distribution:

$$< x >= \frac{\int_{-\infty}^{+\infty} x e^{\frac{-\Phi(x)}{k_B T}} dx}{\int_{-\infty}^{+\infty} e^{\frac{-\Phi(x)}{k_B T}} dx} \tag{5.27}$$

In the case of small dislocations of the atoms, we can further approximate the deduced expression:

$$\int_{-\infty}^{+\infty} x e^{\frac{-\Phi(x)}{k_B T}} dx \approx \int_{-\infty}^{+\infty} e^{\frac{-cx^2}{k_B T}} (x + \frac{dx^4}{k_B T} + \frac{ex^5}{k_B T}) dx = \frac{3g}{4} \sqrt{\frac{\pi (k_B T)^3}{c^5}} \tag{5.28}$$

$$\text{we use: } e^{\frac{dx^3}{k_B T} + \frac{ex^4}{k_B T}} \approx 1 + \frac{dx^3}{k_B T} + \frac{ex^4}{k_B T} \tag{5.29}$$

$$\int_{-\infty}^{+\infty} e^{\frac{-\Phi(x)}{k_B T}} dx \approx \int_{-\infty}^{+\infty} e^{\frac{-cx^2}{k_B T}} dx = \sqrt{\frac{\pi (k_B T)}{c}} \tag{5.30}$$

We finally get as solution of the thermal expansion the following expression in the classical case:

$$< x >= \frac{3d}{4c^2} k_B T \tag{5.31}$$

For illustration, Figure 5.5 shows the lattice constant of solid Argon versus Temperature. We can see that at higher temperatures the expansion of solid Argon follows approximately the result of the chosen classical approach. But explicitly when we go to lower temperatures, we can clearly see a deviation from the T proportionality.

quasi harmonic approach - quantized

To qualitatively understand the expansion of solid matter with temperature, we therefore have to include (a) the quantization of possible energy levels and (b) the inharmonic terms of the potential. This is generally described by the statistical physics of quantized systems.

$$-\frac{\partial F}{\partial V}_T = p = 0 \quad \texttt{F} \; = \; \texttt{Helmholtz Free Energy} \tag{5.32}$$

If we know how F depends on V we can deduce the expansion parameter !

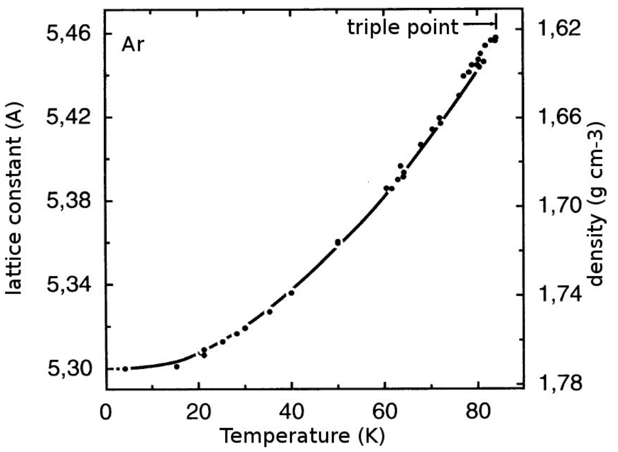

Figure 5.5: Lattice constant of solid Argon versus Temperature.

Approach: (I) determine F for one free oscillator and (II) extension to a lattice.

$$F = \phi - ST = \phi - kT\ln(Z) \texttt{ with } Z = \sum_i e^{E_i/kT} \tag{5.33}$$

and i the sum over all quantum mechanical states. For an harmonic oscillator, we get:

$$Z = \sum_n e^{\frac{\hbar\omega(n+1/2)}{kT}} = \frac{e^{-\hbar\omega/2kT}}{1 - e^{-\hbar\omega/kT}} \tag{5.34}$$

We get:

$$F = \phi + \frac{1}{2}\hbar\omega + kT\ln(1 - e^{-\hbar\omega/kT}) \tag{5.35}$$

The potential energy was (1 dimensional case):

$$\phi(x + \Delta x) = \phi(x) + \frac{\partial^2\phi}{\partial x^2}\Delta x^2 = \phi^{x_0} + \frac{1}{2}(\overline{x} - x_0)^2 C \tag{5.36}$$

In the case of an anharmonic potential, the average position ($\overline{x}$) of an excited phonon state is unequal to the average position of the phonon in the ground state (x_0). The system is therefore loosing potential energy (C is a spring constant)!

We get:

$$F = \phi^{x_0} + \frac{1}{2}(\overline{x} - x_0)^2 C + \frac{1}{2}\hbar\omega + kT\ln(1 - e^{-\hbar\omega/kT}) \tag{5.37}$$

With the side condition equation 5.32, this ends to:

$$\begin{aligned} 0 = \left(\frac{\partial F}{\partial x}\right)\bigg|_{x=x_0} &= C(x - x_0) + \frac{1}{2}\hbar\frac{\partial\omega}{\partial x} + kT\frac{\partial}{\partial x}\ln(1 - e^{-\hbar\omega/kT}) \\ &= C(x - x_0) + \frac{\partial\omega}{\partial x}\left[\frac{\hbar}{2} + \frac{\hbar}{e^{\hbar\omega/kT} - 1}\right] \\ &= C(x - x_0) + \frac{1}{\omega}\frac{\partial\omega}{\partial x}\epsilon(\omega, T) \end{aligned} \tag{5.38}$$

The gained solution is now applied to the coefficient of thermal expansion (see eq. 5.25):

$$\begin{aligned} dx = -\frac{1}{\omega C}\frac{\partial\omega}{\partial x}\epsilon(\omega, T) &= -\frac{x}{x\omega C}\frac{\partial\omega}{\partial x}\epsilon(\omega, T) = -\frac{1}{xC}\frac{\partial(\ln\omega)}{\partial(\ln x)}\epsilon(\omega, T) \\ \Rightarrow \alpha = \frac{1}{x}\frac{dx}{dT} &= -\frac{1}{x^2 C}\frac{\partial(\ln\omega)}{\partial(\ln x)}\frac{\partial}{\partial T}\epsilon(\omega, T) \end{aligned} \tag{5.39}$$

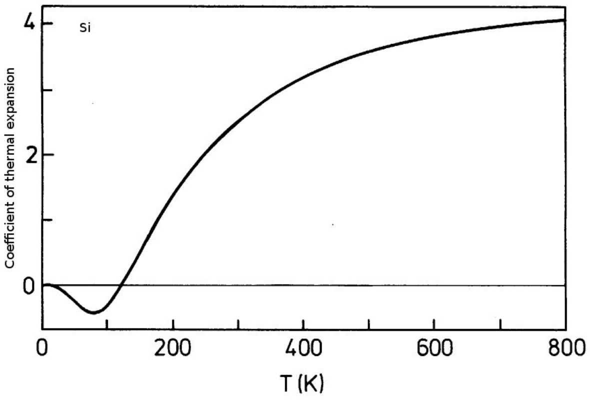

Figure 5.6: Coefficient of thermal expansion versus Temperature here for the tetragonal structure of Si. Note the negative value of α_V at $\sim$ 100 K.

Extension to the 3-Dimensional case:

$$\frac{1}{x}\frac{dx}{dT} \Rightarrow \frac{1}{V}\frac{dV}{dT} \tag{5.40}$$

and integration over all q-values and all phonon modes.

$$\texttt{instead of } x^2C \Rightarrow V\kappa \texttt{ with } \kappa = V\left(\frac{\partial p}{\partial V}\right) \texttt{ the compression module} \tag{5.41}$$

We get:

$$\frac{1}{V}\frac{\partial V(T)}{\partial T} = \alpha_V = \frac{1}{V\kappa}\sum_{j,q}(-1)\frac{\partial(\ln(\omega(q,j)))}{\partial(\ln(V))}\frac{\partial}{\partial T}\epsilon(\omega(q,j),T) \tag{5.42}$$

The term $-\frac{\partial(\ln(\omega(q,j)))}{\partial(\ln(V))}$ is called Grüneisen-Parameter γ
Notes:

a) Often, depending on the specific grid type, γ is only weakly dependent on ω and typically in the range of $\gamma \sim 2$.

b) The proportionality of $\alpha_V \sim c_v$ is not valid for all crystal classes

For tetragonal structures, α_V even changes sign (see Figure 5.6).
For hexagonal structures: $\alpha_c \neq \alpha_a, \alpha_b$, a, b, c for the three space directions.
Tellur (Te): extension in $c_\perp$ and contraction in $c_{||}$ direction with increasing temperature.

5.4.2 Thermal Conductivity

Thermal transport: electrons (see later chapter) and phonons !

- metals: mainly electrons (always good conductors)
- insulators: phonons - can be good (but need not) thermal conductors

For example, at low temperature crystalline Al_2O_3 or SiO_2 are better thermal conductors than copper !
Thermal conductivity = property of thermal non-equilibrium:

$$Q = -\lambda \nabla T \tag{5.43}$$

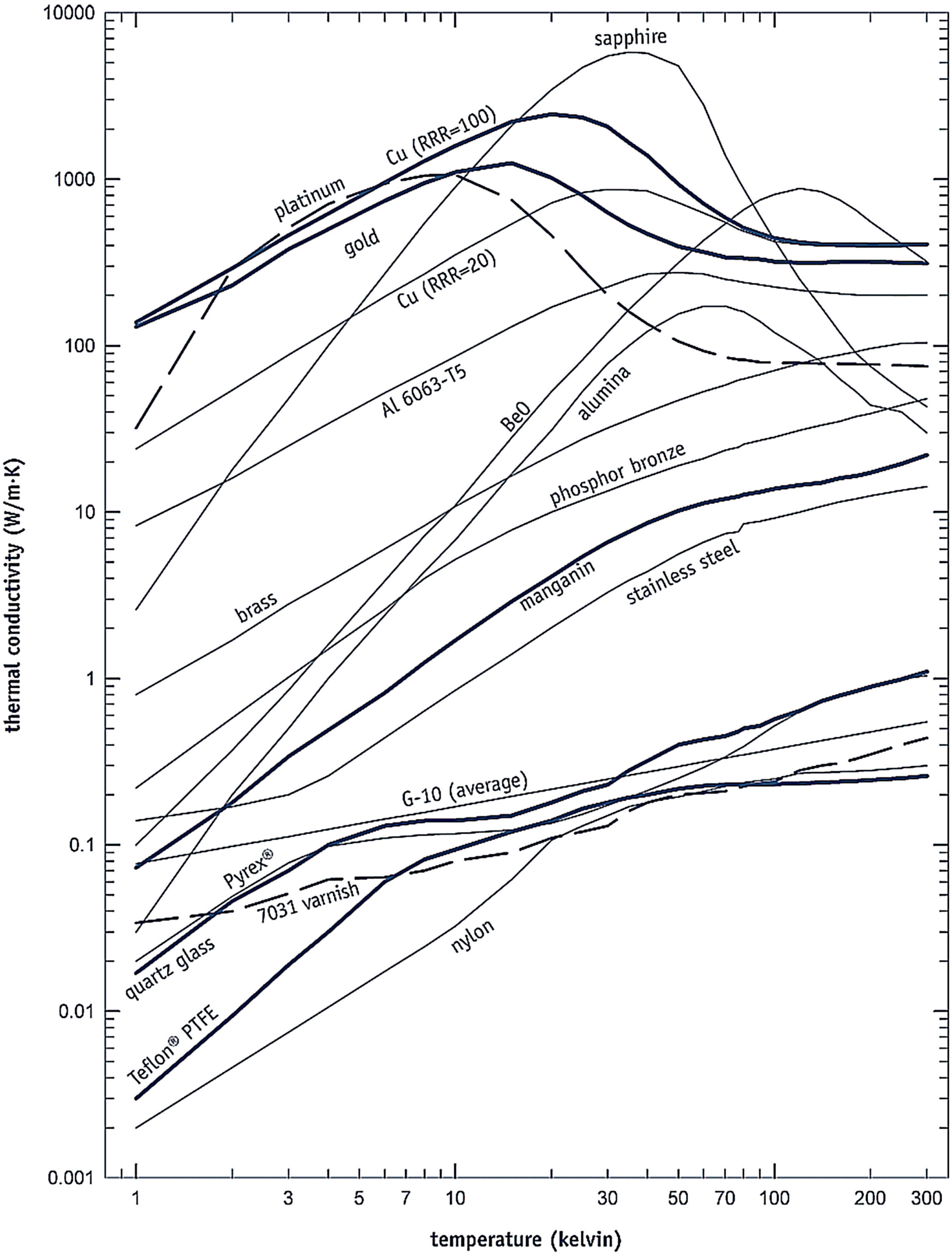

Figure 5.7: Thermal Conductivity of varios materials versus temperature (Taken from Lake Shore, Temperature Measurement and Control Catalogue

- Q = thermal current density
- λ = coefficient of thermal conductivity
- ∇T = temperature gradient

Problem: inner energy $\epsilon(\omega, T)$ and phonon number $<n>$ are defined for homogeneous temperature. $\Rightarrow$ assume a temperature gradient, which is small on the atomic scall, $\Rightarrow$ $<n>$ becomes a function of position.

We have to express λ in terms of phonon properties.

$$Q_x = \frac{1}{V}\sum_{q,j} \hbar\omega <n> v_x \tag{5.44}$$

- Q_x = amount of energy transport
- $\frac{1}{V}$ per volum
- $\sum_{q,j}$ all phonons contribute to the transport
- $\hbar\omega$ energy carried by the phonon
- $<n>$ number of photons with identical properties
- $v_x = \frac{\partial\omega}{\partial q_x}$ speed of phonon propagation

In thermal equilibrium, we have $Q_x = 0$ ($<n>^0$ is the equilibrium distribution).

$$Q_x = \frac{1}{V}\sum_{q,j} \hbar\omega(<n> - <n>^0)v_x \tag{5.45}$$

We have to find an expression for $<n>$ with position !
Boltzmann equation for transport phenomena:

$$\frac{d<n>}{dt} = \left.\frac{\partial <n>}{\partial t}\right|_{diffusion} + \left.\frac{\partial <n>}{\partial t}\right|_{decay}. \tag{5.46}$$

Stationary case: $\frac{d<n>}{dt} = 0$
Decay:

$$\left.\frac{\partial <n>}{\partial t}\right|_{decay} = -\frac{<n> - <n>^0}{\tau} \tag{5.47}$$

τ is the relaxation time and the time dependent rate of decay is proportional to the time dependent imbalance.

$$\begin{aligned}\left.\frac{\partial <n>}{\partial t}\right|_{diffusion} &= \lim_{\Delta t\to 0}\frac{1}{\Delta t}\left[<n(x - v_x\Delta t)> - <n(x)>\right] \\ &= -v_x\frac{\partial <n>}{\partial x} = -v_x\frac{\partial <n>^0}{\partial T}\frac{\partial T}{\partial x}\end{aligned} \tag{5.48}$$

Introducing all equations into equation 5.45, we get:

$$Q = \frac{1}{V}\sum_{q,j}\hbar\omega(q,j)\tau(q,j)v_x^2(q,j)\frac{\partial <n(q,j)>}{\partial T}\frac{\partial T}{\partial x}. \tag{5.49}$$

Thereby, Λ is often introduced ($\tau(q,j)v_x(q,j) = \Lambda$) which is called the 'mean free path'. Λ is actually the average distance a phonon is traveling before an interaction with other phonons or lattice defects occurs.

Decay of Phonons (from n incoming phonons into m outgoing phonons):

Not possible in an infinite crystal with only a harmonic potential. Decays of phonons are due to () lattice defects - altered potential, () surface - reduced symmetry, () anharmonic potential.

Follows conservation rules:

$$\begin{aligned} \sum_{i=incoming} q_i &= \sum_{o=outgoing} q_o + G \; (\texttt{momentum conservation}) \\ \sum_{i=incoming} \hbar\omega_i &= \sum_{o=outgoing} \hbar\omega_o \; (\texttt{energy conservation}) \end{aligned} \tag{5.50}$$

Note: Momentum conservation includes multiplicities of the reciprocal lattice vector G !

The involvement of $k = n + m$ phonons is a process of k-order - and is physically described by the interaction of the phonons with the k-order development of the anharmonic potential.

$k = 2$, i.e. $n = m = 1$ is an elastic scattering event. We will briefly describe process of the 3rd-order:

- 1 phonon decays into 2 phonons (due to time reversal also the opposite process is possible).
- 1 phonon decays into 2 phonons but the momentum is changed by one reciprocal lattice vector G. This process is called 'Umklapp' process and is only possible if $G \leq q$. That means, at low temperatures, when q is small, such effects are not possible.

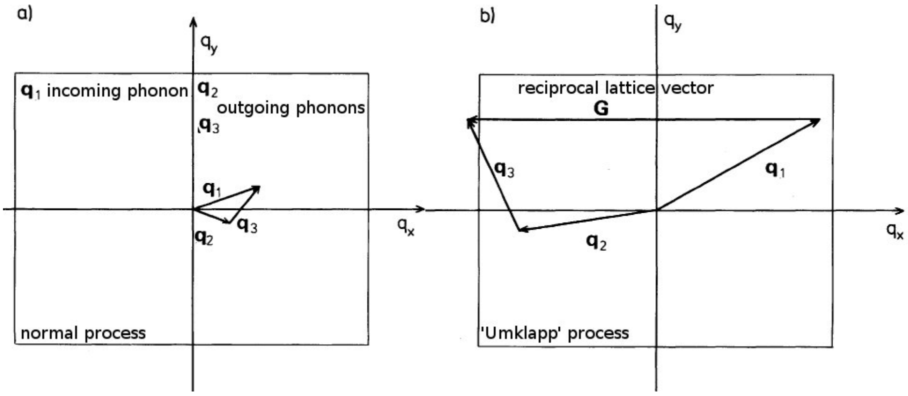

Figure 5.8: (a) normal process with one phonon decaying into two phonons at lower energies (opposite process is possible as well). (b) Umklapp-process. One phonon decays into two phonons under the involvement of the reciprocal lattice vector G. The two newly emerging phonons travel into the opposite direction.

Notes:

- acoustic phonons at $q \sim \pi/a$ give only a very minor contribution to the thermal conductivity via phonons. Close to the Brillouin Zone and due to the dispersion relation, $\partial\omega/\partial q = v_x$, i.e. the propagation speed of such phonons is low.

- the Umklapp process creates phonons which are traveling into the opposite direction of the starting phonon. As the Umklapp process is only present at larger temperatures, a decrease in thermal conductivity at larger energies can be observed

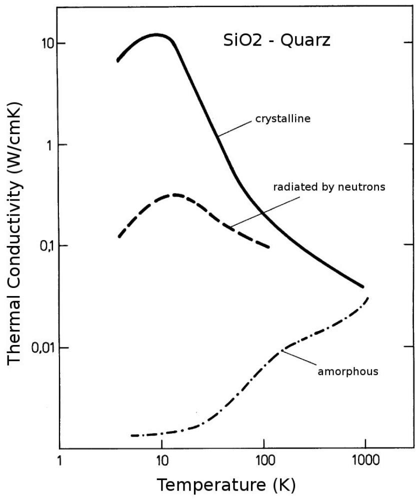

Figure 5.9: Thermal conductivity with temperature for SiO_2 (quartz)in three different states - for crystalline quartz, quartz after neutron radiation, and amorphous quartz.

Figure 5.9 shows a representative experimental result for SiO_2.

- at low temperatures ($< 10K$) the conductivity increases. This is because more phonons are thermally excited - and more phonons can transport thermal energy.
- at around $10K$ the conductivity reaches its maximum. And higher temperatures, the Umklapp process becomes possible and generates by phonon decays phonons which are also propagating against the thermal gradient. Therefore, the thermal conductivity is reduced by this process.
- highest conductivity can be observed for highly periodic systems like quartz in a crystalline phase. Local crystalline defects induced by neutron radiation or with the whole material being in an amorphous state, the conductivity gradually reduces.