Lecture XIV
Phonon II. Thermal Properties

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**Debye model**

\[ \omega = \nu K \]

\[ C_V = \frac{\partial U}{\partial T} = 9Nk_B \left( \frac{T}{\theta} \right)^3 \int_0^{x_D} dx \frac{x^4 e^x}{(e^x - 1)^2} \]

**Debye temperature**

**Einstein model**

\[ D(\omega) = N\delta(\omega - \omega_E) \]

\[ C_V = \frac{\partial U}{\partial T} = 3Nk_B \left( \frac{\hbar \omega}{k_B T} \right)^2 \frac{\exp(\hbar \omega / k_B T)}{[\exp(\hbar \omega / k_B T) - 1]^2} \]
<table>
<thead>
<tr>
<th>ELEMENT</th>
<th>$\Theta_D$ (K)</th>
<th>ELEMENT</th>
<th>$\Theta_D$ (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li</td>
<td>400</td>
<td>A</td>
<td>85</td>
</tr>
<tr>
<td>Na</td>
<td>150</td>
<td>Ne</td>
<td>63</td>
</tr>
<tr>
<td>K</td>
<td>100</td>
<td>Cu</td>
<td>315</td>
</tr>
<tr>
<td>Be</td>
<td>1000</td>
<td>Ag</td>
<td>215</td>
</tr>
<tr>
<td>Mg</td>
<td>318</td>
<td>Au</td>
<td>170</td>
</tr>
<tr>
<td>Ca</td>
<td>230</td>
<td>Zn</td>
<td>234</td>
</tr>
<tr>
<td>B</td>
<td>1250</td>
<td>Cd</td>
<td>120</td>
</tr>
<tr>
<td>Al</td>
<td>394</td>
<td>Hg</td>
<td>100</td>
</tr>
<tr>
<td>Ga</td>
<td>240</td>
<td></td>
<td></td>
</tr>
<tr>
<td>In</td>
<td>129</td>
<td>Cr</td>
<td>460</td>
</tr>
<tr>
<td>Tl</td>
<td>96</td>
<td>Mo</td>
<td>380</td>
</tr>
<tr>
<td>W</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C (diamond)</td>
<td>1860</td>
<td>Mn</td>
<td>400</td>
</tr>
<tr>
<td>Si</td>
<td>625</td>
<td>Fe</td>
<td>420</td>
</tr>
<tr>
<td>Ge</td>
<td>360</td>
<td>Co</td>
<td>385</td>
</tr>
<tr>
<td>Sn (grey)</td>
<td>260</td>
<td>Ni</td>
<td>375</td>
</tr>
<tr>
<td>Sn (white)</td>
<td>170</td>
<td>Pd</td>
<td>275</td>
</tr>
<tr>
<td>Pb</td>
<td>88</td>
<td>Pt</td>
<td>230</td>
</tr>
<tr>
<td>As</td>
<td>285</td>
<td>La</td>
<td>132</td>
</tr>
<tr>
<td>Sb</td>
<td>200</td>
<td>Gd</td>
<td>152</td>
</tr>
<tr>
<td>Bi</td>
<td>120</td>
<td>Pr</td>
<td>74</td>
</tr>
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</table>
General result for $D(\omega)$

For a given phonon dispersion relation $\omega(K)$, the number of allowed values of $K$ corresponding to the phonon frequency in the range of $\omega$ and $\omega + d\omega$ is

$$D(\omega)d\omega = \left(\frac{L}{2\pi}\right)^3 \int_{\text{shell}} d^3K$$

$$\int d^3K = \int dS_\omega dK_\perp$$

$$\therefore \left| \nabla_{\vec{K}} \omega \right| dK_\perp = d\omega$$

$$dK_\perp = \frac{d\omega}{\left| \nabla_{\vec{K}} \omega \right|} = \frac{d\omega}{v_g}$$

The element of area on the surface in K space of $\omega$. 
Then we have

\[ D(\omega) d\omega = \left( \frac{L}{2\pi} \right)^3 \int \frac{dS_\omega}{v_g} d\omega = \frac{V}{(2\pi)^3} \int \frac{dS_\omega}{v_g} d\omega \]

The density of states is

\[ D(\omega) = \frac{V}{(2\pi)^3} \int \frac{dS_\omega}{v_g} \]

The integral is taken over the area of the surface \( \omega = \text{constant} \), in \( \mathbf{K} \) space.

Van Hove singularities: the points which the group velocity is zero.

![Figure 14](image) Density of states as a function of frequency for (a) the Debye solid and (b) an actual crystal structure. The spectrum for the crystal starts as \( \omega^2 \) for small \( \omega \), but discontinuities develop at singular points.
The harmonic theory

The potential energy has been limited to terms quadratic in the interatomic displacements.

\[ U = \frac{1}{2} \sum C u^2 \]

- Two lattice waves do not interact; a single wave does not decay or change form with time.
- There is no thermal expansion.
- Adiabatic and isothermal elastic constants are equal.
- The elastic constants are independent of pressure and temperature.
- The heat capacity becomes constant at high temperature \( T > \theta \).
Anharmonic crystal interactions

In real crystal the harmonic theory is not satisfied accurately. The deviations may be attributed to the neglect of anharmonic (higher than quadratic) terms in the interatomic displacements.

Three-phonon processes

Experiments: the interaction of two phonons to produce a third phonon at frequency $\omega_3 = \omega_1 + \omega_2$.

Theory: due to the third-order terms in the lattice potential energy, e.g. $U_3 = A e_{xx} e_{yy} e_{zz}$.

The presence of one phonon causes a periodic elastic stain (through the anharmonic interaction) which modulates the elastic constant. A second phonon perceives the modulation of the elastic constant and thereupon is scattered to produce a third phonon.
Thermal expansion

Take the higher order terms of the potential energy into account.

\[ U(x) = cx^2 - gx^3 - fx^4 \]

The average displacement at finite temperature in classical statistics

\[
\langle x \rangle = \frac{\int_{-\infty}^{\infty} dx \, x \exp[\beta U(x)]}{\int_{-\infty}^{\infty} dx \, \exp[\beta U(x)]} \\
\approx \frac{\int_{-\infty}^{\infty} dx \, x[\exp(-\beta cx^2) \exp(\beta gx^3 + \beta fx^4)]]}{\int_{-\infty}^{\infty} dx \, \exp[\beta cx^2 (1 - gx/c - fx^2/c)]} \\
\approx \frac{\int_{-\infty}^{\infty} dx \, x(1 + \beta gx^3 + \beta fx^4) \exp(-\beta cx^2)}{\int_{-\infty}^{\infty} dx \, \exp(-\beta cx^2)} \\
= \frac{(3\pi^{1/2}/4)(g/c^{5/2})\beta^{-3/2}}{(\pi/\beta c)^{1/2}} = \frac{3gk_B}{4c^2} T
\]
Thermal expansion

<table>
<thead>
<tr>
<th>METAL</th>
<th>COEFFICIENT \textsuperscript{a}</th>
<th>METAL</th>
<th>COEFFICIENT \textsuperscript{a}</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li</td>
<td>45</td>
<td>Ca</td>
<td>22.5</td>
</tr>
<tr>
<td>Na</td>
<td>71</td>
<td>Ba</td>
<td>18</td>
</tr>
<tr>
<td>K</td>
<td>83</td>
<td>Nb</td>
<td>7.1</td>
</tr>
<tr>
<td>Rb</td>
<td>66</td>
<td>Fe</td>
<td>11.7</td>
</tr>
<tr>
<td>Cs</td>
<td>97</td>
<td>Zn</td>
<td>14 (⊥)</td>
</tr>
<tr>
<td>Cu</td>
<td>17.0</td>
<td>Al</td>
<td>23.6</td>
</tr>
<tr>
<td>Ag</td>
<td>18.9</td>
<td>In</td>
<td>−7.5 (∥)</td>
</tr>
<tr>
<td>Au</td>
<td>13.9</td>
<td>Pb</td>
<td>50 (⊥)</td>
</tr>
<tr>
<td>Bc</td>
<td>9.4 (∥)</td>
<td>Ir</td>
<td>6.5</td>
</tr>
<tr>
<td></td>
<td>11.7 (⊥)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mg</td>
<td>25.7 (∥)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>24.3 (⊥)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\textsuperscript{a} The units are 10^{-6} K^{-1}. In the noncubic cases separate coefficients are listed for expansion parallel and perpendicular to the axis of highest symmetry. Source: W. B. Pearson, *A Handbook of Lattice Spacings and Structures of Metals and Alloys*, Pergamon, New York, 1958.
Thermal conductivity

The thermal conductivity coefficient $K$ of a solid is defined with respect to the steady-state flow of heat down a long rod with a temperature gradient, 

$$j_u = -K \frac{dT}{dx}$$

where $j_u$ is the flux of thermal energy.

• The process of thermal energy transfer is a random process.
• The energy diffuses through the specimen, suffering frequent collisions.
• The random nature of the conductivity process brings the temperature gradient.
• The mean free path of a particle between collisions.
The kinetic theory of gases

Consider a system with temperature gradient along the $x$ direction. The energy transfer is due to the collisions between particles.

The flux of the particles in the $x$ direction is

$$n\langle v_x \rangle$$

where $n$ is the concentration of the particles, and $\langle v_x \rangle$ is the average velocity along the $x$ direction.

If $c$ is the heat capacity of a particle, then in moving from a region at local temperature $T + \Delta T$ to a region at local temperature $T$ a particle will give up energy

$$U = c \Delta T$$

$\Delta T$ between the ends of a free path of the particle is

$$\Delta T = \frac{dT}{dx} l_x = \frac{dT}{dx} v_x \tau$$
the flux of thermal energy

\[ j_U = -n < v_x > U = -n < v_x > c \frac{dT}{dx} v_x \tau \]

\[ = -n < v_x^2 > c \tau \frac{dT}{dx} = -\frac{1}{3} n < v^2 > c \tau \frac{dT}{dx} \]

If \( v \) is constant as for phonon

\[ j_U = -\frac{1}{3} Cvl \frac{dT}{dx} \]

where \( l \equiv v \tau \) is the mean free path of the particle between collisions and \( C \equiv nc \) is the heat capacity of the particles.

Thus the thermal conductivity coefficient

\[ K = \frac{1}{3} Cvl \]
Thermal resistivity of phonon gas

The phonon mean free path $l$ is determined by

- geometrical scattering (scattering with crystal boundary)
- scattering with lattice imperfections
- scattering with other phonons

For harmonic interaction, $l$ is limited only by collision of a phonon with the crystal boundary, and by lattice imperfections.

For anharmonic interaction, the coupling between different phonons limits $l$. 
At high temperature ($T \gg \theta_D$)

$$< n > = \frac{1}{\exp(\hbar \omega / k_B T) - 1} \approx \frac{k_B T}{\hbar \omega}$$

The collision frequency 

$$1 / \tau \propto < n >$$

$$l = \nu \tau \propto 1 / T$$

thus 

$$K \propto 1 / T$$
### The Classical Gas vs. The Phonon Gas

<table>
<thead>
<tr>
<th></th>
<th>Classical Gas of Molecules</th>
<th>Phonon Gas</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Container</strong></td>
<td>A vessel with impenetrable walls</td>
<td>A crystal, which is the medium that sustains the phonons</td>
</tr>
<tr>
<td><strong>Collisions</strong></td>
<td>Molecules collide with each other and with walls of vessel</td>
<td>Phonons collide with each other with surface of crystal, and with impurities</td>
</tr>
<tr>
<td><strong>Energy conserved in collisions</strong></td>
<td>Yes</td>
<td>Yes</td>
</tr>
<tr>
<td><strong>(Crystal) momentum conserved in collisions</strong></td>
<td>Yes (except at walls)</td>
<td>Yes (except at surfaces and in collisions with impurities), provided that $T&lt;&lt;\theta_D$, so that umklapp processes are frozen out</td>
</tr>
<tr>
<td><strong>Number conserved in collisions</strong></td>
<td>Yes</td>
<td>No</td>
</tr>
</tbody>
</table>
To define a thermal conductivity there must exist mechanisms in the crystal whereby the distribution of phonons may be brought locally into thermal equilibrium.

Flow of gas molecules in a state of drifting equilibrium. Elastic collision processes do not change the momentum and energy flux of the gas. The energy is transported by mass flow without being driven by a temperature gradient. The thermal resistivity is zero and the thermal conductivity is infinite.

The usual definition of thermal conductivity in gas refers to a situation where no mass flow is permitted. With a temperature gradient, the colliding pairs with above-average center mass velocities will tend to be directed to the right. A slight concentration gradient, high on the right, will be set up to allow a net energy transport without net mass transport.
To establish a mechanism

It is not sufficient to have only a way of limiting the mean free path, but there must also be a way of establishing a local thermal equilibrium distribution of phonons.

Phonon collisions with a static imperfection or a crystal boundary will not by themselves establish thermal equilibrium, because such collisions do not change the energy of individual phonons.

A three-phonon collision process $\mathbf{K}_1 + \mathbf{K}_2 = \mathbf{K}_3$ will also not establish thermal equilibrium, because the total momentum of the phonon gas is not changed by such a collision. Similar like the gas flow in a state of drifting equilibrium.
Umklapp processes (倒逆过程)

Normal (N) processes: \( K_1 + K_2 = K_3 \)

Umklapp (U) processes: \( K_1 + K_2 = K_3 + G \)

In N processes, \( K \) is conserved. However, due to the periodic lattices U processes are possible which changes the momentum of phonons in collisions. For all processes, N or U, energy must be conserved, so that \( \omega_1 + \omega_2 = \omega_3 \).
In N processes, the phonon flux is unchanged in momentum on collision and some phonon flux will persist down the length of the crystal. The thermal resistivity is zero.

In U processes there is a large net change in phonon momentum in each collision event. An initial net phonon flow will rapidly decay as we move to the right. Net energy transport under a temperature gradient occurs.
At high temperature ($T \gg \theta_D$), all phonon modes are excited because $k_B T > \hbar \omega_{max}$. A substantial proportion of all phonon collisions will be U processes. A lattice thermal resistivity $\propto T$. 
• If both phonons have low $K$, there is no way to have an $U$ process. The energy of phonons $K_1, K_2$ suitable for umklapp is of the order of $k_B \theta/2$. At low temperature the number of suitable phonons of the high energy $k_B \theta/2$ required may be expected to vary roughly as $\exp(-\theta/2T)$. Therefore the thermal resistivity is roughly proportional to $\exp(-\theta/2T)$.

• Note the phonon mean free path for thermal conductivity is the mean free path for umklapp collisions between phonons and not for all collisions between phonons.

$K_1 + K_2 = K_3 + G$
Imperfections

Geometrical effects may also be important in limiting the mean free path.

The size effect:
When at low temperatures the mean free path $l$ becomes comparable with the width of the specimen, the value of $l$ is limited by the width, and the thermal conductivity becomes a function of the dimensions of the specimen. The abrupt decrease in thermal conductivity of pure crystals at low temperatures is caused by the size effect.
At low temperatures the umklapp process becomes ineffective in limiting the thermal conductivity, and the size effect becomes dominant.

$l$ is limited by the width of the specimen.

\[ l \approx D \]

\[ K \approx Cvl \approx CvD \propto T^3 \]

NB: \( \nu \) and \( D \) do not depend on \( T \).
Dielectric crystals may have thermal conductivities as high as metals.

The distribution of isotopes of the chemical elements often provides an important mechanism for phonon scattering.
1. Problem 5.3 of textbook.

2. Problem 5.4 of textbook.

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