Phonons II: Thermal properties

• Heat capacity of a crystal
  • density of state
  • Einstein mode
  • Debye model
• anharmonic effect
  • thermal conduction

A technician holding a silica fiber thermal insulation tile at 1300 Celsius

See www.youtube.com/watch?time_continue=3&v=Pp9Yax8UNoM
Heat capacity: experiment

Heat capacity drops to zero at low temperature

Heat capacity approaches $3R$ ($\sim 25 \text{ J/K}$) at high temperature (Dulong-Petit law, 1819)

After rescaling the temperature by $\theta$ (Debye temperature), which differs from material to material, a universal behavior emerges:
Debye temperature

<table>
<thead>
<tr>
<th>Li</th>
<th>Be</th>
<th>344</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na</td>
<td>Mg</td>
<td>158</td>
</tr>
<tr>
<td>K</td>
<td>Ca</td>
<td>91</td>
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<tr>
<td>Rb</td>
<td>Sr</td>
<td>56</td>
</tr>
<tr>
<td>Cs</td>
<td>Ba</td>
<td>38</td>
</tr>
<tr>
<td>Fr</td>
<td>Ra</td>
<td>163</td>
</tr>
</tbody>
</table>

| Table 1  Debye temperature and thermal conductivity$^a$ |
|----------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| B        | C               | N               | O               | F               | Ne              |
| 2230     | 1.29            | 75              |
| Al       | Si              | P               | S               | Cl              | Ar              |
| 428      | 645             | 92              |
| K        | Ca              | Sc              | Ti              | V               | Cr              | Mn              | Fe              | Co              | Ni              | Cu              | Zn              |
| 360      | 0.16            | 1400            | 2.00            |
| Nb       | Mo              | 380             | 0.31            | 0.94            | 0.08            | 1.00            | 0.91            | 4.01            | 1.16            |
| Rb       | Sr              | 280             | 0.17            | 0.23            | 2.75            | 4.50            | 6.00            | 4.80            | 2.74            | 2.25            | 209             |
| Cs       | Ba              | La $\beta$      | Hf              | Ta              | W               | Re              | Os              | Ir              | Pt              | Au              | Hg              |
| 110      | 142             | 252             | 0.14            | 0.23            | 0.58            | 1.74            | 0.48            | 0.88            | 1.47            | 0.72            | 3.17            |
| Fr       | Ra              | Ac              | Ce              | Pr              | Nd              | Pm              | Sm              | Eu              | Gd              | Tb              | Dy              |
| 0.11     | 0.12            | 0.16            | 0.13            | 200             | 0.11            | 1.11            | 210             | 0.11            | 0.16            | 0.14            | 0.17            |
| Th       | Pa              | U               | Np              | Pu              | Am              | Cm              | Bk              | Cf              | Es              | Fm              | Md              |
| 163      | 207             | 0.28            | 0.06            | 0.07            | 120             | 0.35            | 0.16            |

In general, a harder material has a higher Debye temperature.
• Dulong-Petit’s law is a result of the **equipartition of energy**.

• Early 1900’s, theory fails at low temperature (for diamond at *room temperature*, only 1/5 of expected value!)

• The classical theory of heat capacity is in trouble, just like the classical theory of thermal radiation.

**Planck:** Quantization of energy is a mathematical trick.

**Einstein:** Quantization of energy is real. It appears not only in thermal radiation, photoelectric effect, but also in crystal vibration.
Heat capacity: Quantum theory

- **Heat capacity** is nothing but the change of $U(T)$ w.r.t. to $T$:

$$C_V = \left( \frac{\partial U}{\partial T} \right)_V$$

- **Internal energy** $U$ of a crystal is the summation of vibrational energies (consider an insulator so there’s no electronic energies)

$$U(T) = \sum_{k,s} (n_{k,s} + 1/2)\hbar \omega_{k,s}$$

where $s$ sums over different phonon branches (L/T, A/O).

- For a crystal in thermal equilibrium, the average phonon number is (see Kittel, p.107)

$$\langle n_{k,s} \rangle = \frac{1}{e^{\hbar \omega_{k,s} / kT} - 1}, \quad \text{Bose-Einstein distribution}$$

- Therefore, we have

$$U(T) = \sum_{k,s} \left( \frac{\hbar \omega_{k,s}}{e^{\hbar \omega_{k,s} / kT} - 1} + \frac{\hbar \omega_{k,s}}{2} \right)$$
Connection between summation and integral

\[ \int_a^b dx f(x) = \lim_{\Delta x \to 0} \sum_i \Delta x \cdot f(x_i), \text{ or } \]

\[ \sum_i f(x_i) \equiv \int_a^b \frac{dx}{\Delta x} f(x). \]

Generalization to 3-dim:

\[ \sum_{\bar{x}} f(\bar{x}) \equiv \int \frac{d^3 x}{\Delta^3 x} f(\bar{x}) \]

or \[ \sum_{\bar{k}} f(\bar{k}) \equiv \int \frac{d^3 k}{\Delta^3 k} f(\bar{k}) \text{ in solid state} \]

\[ \Delta^3 k = \left( \frac{2\pi}{L} \right)^3 \]
Density of states $D(\omega)$ (DOS, 態密度)

- $D(\omega)d\omega$ is the number of states within the surfaces of constant $\omega$ and $\omega+d\omega$

$$D(\omega)d\omega = \int_{\Delta^3k} \frac{d^3k}{\Delta^3k}, \quad \Delta^3k = \left(\frac{2\pi}{L}\right)^3$$

$$\sum_k f(\omega_k) \equiv \int \frac{d^3k}{\Delta^3k} f(\omega_k) = \int d\omega D(\omega) f(\omega)$$

- For example, assume $N=16$, then there are $2\times2=4$ states within the interval $d\omega$

- Once we know the DOS, we can reduce the 3-dim $k$-integral to a 1-dim $\omega$ integral.

Alternative definition:

$$D(\omega) = \int \frac{d^3k}{\Delta^3k} \delta(\omega_k - \omega)$$

- Flatter $\omega(k)$ curve, higher DOS.
DOS: 1-dim

\[ D(\omega) d\omega = 2 \frac{dk}{\Delta k} = 2 \frac{dk / d\omega}{\Delta k} d\omega \]

\[ \therefore D(\omega) = \begin{cases} \frac{L}{\pi} \frac{1}{d\omega / dk} & \text{for } \omega \leq \omega_M \\ 0 & \text{otherwise} \end{cases} \]

Ex: Calculate \( D(\omega) \) for the 1-dim string with \( \omega(k) = \omega_M |\sin(ka/2)| \)  

Prob.1(a)

DOS: 3-dim (assume \( \omega(k) = \omega(k) \) is isotropic)

\[ D(\omega) d\omega = \int_{\text{shell}} \frac{d^3k}{\Delta^3k} = \frac{4\pi}{\Delta^3k} k^2 dk = \frac{L^3}{2\pi^2} \frac{k^2}{d\omega / dk} d\omega \]

for example, if \( \omega = \nu k \), then \( D(\omega) = V \omega^2 / 2\pi^2 \nu^3 \)

Non-dispersive

It’s not necessary to memorize the result, just remember the way of deriving it.
Einstein model (1907)

Assume that

1. each atom **vibrates independently** of each other, and
2. every atom has **the same vibration frequency** $\omega_0$

- The DOS can be written as

$$D(\omega) = 3N\delta(\omega - \omega_0)$$

- 3 dim $\times$
- number of atoms
Einstein model

\[ U = 3N \left( \langle n \rangle + \frac{1}{2} \right) \hbar \omega_0 = 3N \frac{\hbar \omega_0}{\exp(\hbar \omega_0 / kT) - 1} + 3N \frac{\hbar \omega_0}{2} \]

\[ C_V = (\partial U / \partial T)_V = 3Nk \left( \frac{\hbar \omega_0}{kT} \right)^2 \frac{e^{\hbar \omega_0 / kT}}{(e^{\hbar \omega_0 / kT} - 1)^2} \]

\[ \approx e^{-\hbar \omega_0 / kT} \text{ as } T \rightarrow 0 K \]

vibration is “frozen” at low T

Data of diamond from Einstein’s 1907 paper.
Debye model (1912)

Based on classical elasticity theory (continuous, prior to the classical theory of lattice dynamics).

Vibration produces waves

\[ U(T) = \sum_{k,s} \left\langle n_{k,s} \right\rangle \hbar \omega_{k,s} \quad (\hbar \omega_{k,s}/2 \text{ neglected}) \]

\[ = \sum_{s=1}^{3} \int d\omega D_s(\omega) \frac{\hbar \omega}{e^{\hbar \omega/(kT)} - 1} \]

Debye assumed that
1. the wave is non-dispersive: \( \omega = \nu_s k \) (s=L, T1, T2).
2. Therefore, \( D_s(\omega) = V \omega^2 / 2 \pi^2 \nu_s^3 \) (quadratic)
3. (Iso-frequency surface is a sphere)
2. The 1st BZ is approximated by a sphere with the same total number of states.

High-frequency cut-off $\omega_D$:

- A simple estimate
  \[ \frac{4}{3} \pi k_D^3 \frac{\Delta^3 k}{\Lambda^3} = N \]
  \[ \rightarrow \quad \omega_D = \nu k_D = \nu (6\pi^2 n)^{1/3} \]

- or \[ \sum_{s=1}^{3} \int_{0}^{\omega_p} d\omega D_s(\omega) = 3N \]
  \[ \rightarrow \sum_{s=1}^{3} \frac{V \omega_D^3}{6\pi^2 \nu_s^3} = 3N \]
  \[ \frac{3}{\nu^3} \equiv \sum_{s=1}^{3} \frac{1}{\nu_s^3} \]
  \[ \rightarrow \omega_D = \nu (6\pi^2 n)^{1/3}, \quad n = N / V \]

Debye frequency
Internal energy and heat capacity

\[ U(T) = \sum_{s=1}^{3} \frac{V}{2\pi^2 v_s^3} \int_0^{\omega_D} d\omega \omega^2 \frac{\hbar \omega}{e^{\hbar \omega / k_B T} - 1} \]

\[ = \frac{3V}{2\pi^2 v^3} \hbar \left( \frac{k_B T}{\hbar} \right)^4 \int_0^{x_D} dx \frac{x^3}{e^x - 1}, \quad x_D = \frac{\hbar \omega_D}{k_B T} = \frac{\theta}{T}, \quad k_B \theta \equiv \hbar \omega_D \]

\[ = 9Nk_B T \left( \frac{T}{\theta} \right)^2 \int_0^{x_D} dx \frac{x^3}{e^x - 1} = \frac{\pi^4}{15} \text{ as } T \to 0 (x_D \to \infty) \]

\[ \therefore C_V = \frac{12\pi^4}{5} Nk_B \left( \frac{T}{\theta} \right)^3 \propto T^3 \text{ as } T \to 0 \]  

(Debye \text{ } T^3 \text{ law})

At low \( T \), Debye’s curve drops slowly because long wavelength vibration can still be excited.
A simple explanation of the $T^3$-dependence (at low $T$):

First, define $\hbar \nu k_T = k_B T$

Suppose that

1. All the phonons with wave vector $k < k_T$ are excited, while the modes between $k_T$ and $k_D$ are not excited.

2. Each excited mode roughly has thermal energy $k_B T$

\[ \frac{\hbar \nu}{k_D} = \frac{k_B T}{k_D} = \frac{T}{\theta} \]

- Then the fraction of excited modes
  \[ = \left( \frac{k_T}{k_D} \right)^3 = \left( \frac{T}{\theta} \right)^3. \]

- Thermal energy $U \sim k_B T \cdot 3N(T/\theta)^3$

- $\therefore$ Heat capacity $C \sim 12Nk_B(T/\theta)^3$
DOS for general dispersion relation

An energy shell

Surface $\omega = \text{const}$

$\omega + d\omega = \text{const}$

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

$d^3k = dS_\omega dk_\perp$

$d\omega = \nabla_\vec{k} \omega \cdot dk = \left| \nabla_{\vec{k}} \omega \right| dk_\perp$

$\therefore d^3k = dS_\omega \frac{d\omega}{\left| \nabla_{\vec{k}} \omega \right|}$

$\Rightarrow D(\omega) = \left(\frac{L}{2\pi}\right)^3 \int dS_\omega \frac{d\omega}{\left| \nabla_{\vec{k}} \omega \right|}$

If $\nu_g = \left| \nabla_{\vec{k}} \omega \right| = 0$, then there is "van Hove singularity" (1953)

An energy shell

Group velocity

Heat capacity, DOS

Einstein model, Debye model

Anharmonic effect

Silicon

Density of states $Z(\nu)$

Debye approximation

Frequency $\nu$ ($10^{12}$ s$^{-1}$)
Dispersion relation and DOS

Giannozzi et al, PRB 43, 7231 (1991)
• Heat capacity of a crystal
  • density of states
  • Einstein model
  • Debye model
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  • thermal conduction
Aharmonic effect in crystals

If there is no aharmonic effect, then

- No thermal expansion
- No phonon-phonon interaction
- Thermal conductivity would be infinite (for a pure crystal)
- Heat capacity becomes constant at high T
- …
Thermal conductivity

- **Thermal current density** (Fourier’s law, 1807)
  \[ \mathbf{J}_U = -K \nabla T \quad \sim \quad \mathbf{J} = -\sigma \nabla \phi \]

- In **metals**, thermal current is carried by both electrons and phonons. In **insulators**, only phonons can be carriers.

- The collection of phonons is similar to an ideal gas

<table>
<thead>
<tr>
<th>THE CLASSICAL GAS vs. THE PHONON GAS</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>CLASSICAL GAS OF MOLECULES</strong></td>
</tr>
<tr>
<td>Container</td>
</tr>
<tr>
<td>Collisions</td>
</tr>
<tr>
<td>Energy conserved in collisions</td>
</tr>
<tr>
<td>(Crystal) momentum conserved in collisions</td>
</tr>
<tr>
<td>Number conserved in collisions</td>
</tr>
</tbody>
</table>

Ashcroft and Mermin, Chaps 23, 24
• Thermal conductivity

\[ K = \frac{1}{3} c v \ell \]

- \( c \): specific heat
- \( v \): phonon velocity
- \( \ell \): mean free path

 Dimensional analysis:

Assume \([K] = [c]^a [v]^b [\ell]^c\)

\[ \rightarrow a = b = c = 1 \]

• The mean free path of a phonon can be affected by defects, boundary, and other phonons.
Phonon-phonon scattering

A result of the anharmonic vibration

Modulation of elastic const.
(\sim \text{ acoustic grating})

\[ F = -kx + k'x^2 \]
\[ = -(k - k'x)x \]
\[ \therefore k_{\text{eff}}(x) = k - k'x \]

- Total momentum of the 2 phonons remains the same during the scattering. \textbf{No resistance to thermal current?}
Phonon-phonon scattering

- Normal process:

- Umklapp process (轉向過程, Peierls 1929):

Figs from wiki
◆ **$T$-dependence of the phonon mean free path $\ell$**

- **Low $T$:** For a crystal with few defects, the mean free path is limited mainly by the boundary of the sample.

- **High $T$:** The number of phonons are proportional to $T$. The mean free path $\sim 1/T^x$ ($x=1\sim2$).

◆ **$T$-dependence of the lattice thermal conductivity $K (\sim cv\ell)$**

- **Low $T$:** $K \sim c \sim T^3$

- **High $T$:** $K \sim \ell \sim 1/T$

Boer and Pohl, Semiconductor Physics 2018
Boundary scattering

LiF

Isotope scattering

LiF with various Li-6 isotopes (0.02% to 50%)

www.ucl.ac.uk/~ucapahh/teaching/3C25/Lecture12s.pdf

Berman and Brock PRS London 1965