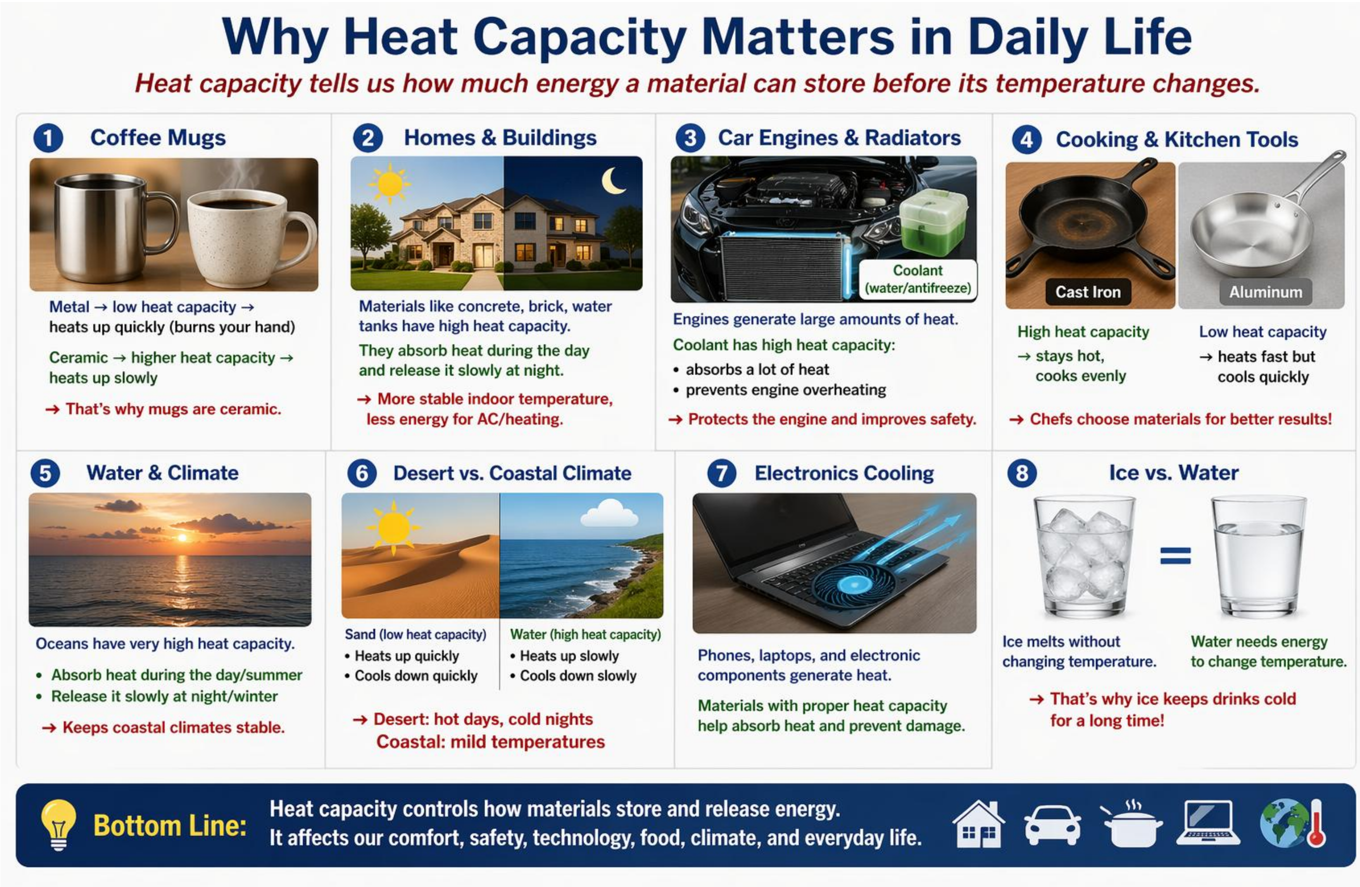
Chapter #5:
Thermal Properties of Insulators

Lecture 1: Heat Capacity of Solids: From Classical Theory to Einstein Model

5-1 Introduction



In this chapter, we will discuss the **phonon contribution to heat capacity (you can think about it now, what other particle(s) can also contribute to the heat capacity)**.

- **Phonons are quantized lattice vibrations that carry thermal energy in solids.**

Heat capacity is defined as the amount of heat required to raise the temperature of a system by one degree, as given by:

$$C = \frac{\Delta Q}{\Delta T} \qquad (1)$$

When we refer to heat capacity here, we mean the **heat capacity at constant volume**, which is usually determined experimentally.

From the laws of thermodynamics, the heat added equals the **internal energy** when no work is done. Therefore, heat capacity can also be written as:

$$C = \left(\frac{\partial E}{\partial T}\right)_V \qquad (2)$$

5-2 Classical Model of Heat Capacity

It was traditionally believed that heat capacity is constant:

C=3R

where R is the universal gas constant.

Recall: $\langle E \rangle = 3NKT$

For one mole of atoms:

$$\langle E \rangle = 3N_A KT = 3RT$$

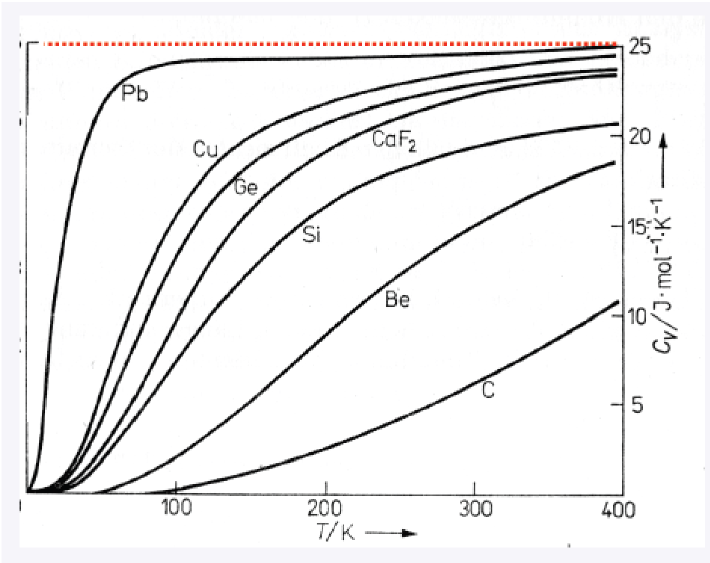
$$C = \frac{\partial \langle E \rangle}{\partial T} = 3R \qquad (3)$$

where N_A is Avogadro's number.

However, experimental results later showed that **heat capacity is not constant**.

- At **high temperatures** → heat capacity is approximately constant
- At **low temperatures** → heat capacity strongly depends on temperature

☞ As shown in the **figure**, different materials (Pb, Cu, Ge, Si, Be, C) exhibit this behavior. The red dot lines show the heat capacity for the classical model.



This contradiction motivated scientists to develop better models, most notably:

- **Einstein Model**
- **Debye Model**

5-3 Einstein Model for Specific Heat

To resolve this failure, Einstein proposed quantizing lattice vibrations.

Einstein assumed:

1. Each atom behaves as an **independent harmonic oscillator** (single frequency).
2. Energy is **quantized** according to Planck's theory:

$$E_n = (n + \tfrac{1}{2})\hbar\omega \qquad (4)$$

Average Energy

The average energy of an oscillator at thermal equilibrium is:

$$\langle E \rangle = \frac{\hbar\omega}{e^{\hbar\omega/kT} - 1} \qquad (5)$$

where k is Boltzmann constant.

Total Energy

Since each atom has **3 degrees of freedom**, for N atoms:

$$E_{total} = 3N\langle E \rangle = 3N\frac{\hbar\omega_E}{e^{\hbar\omega_E/kT} - 1} \qquad (6)$$

See the appendix below to see how this equation derived.

Define Einstein temperature: $\theta_E = \frac{\hbar\omega_E}{k}$

Where, ω_E is called Einstein frequency.

Then for one mole:

$$E_{total} = 3N_A k\frac{\theta_E}{e^{\theta_E/T} - 1} \qquad (7)$$

Heat Capacity (Einstein Model):

By differentiating the total energy with respect to temperature, we obtain the heat capacity as follows:

$$C = 3R\left(\frac{\theta_E}{T}\right)^2 \frac{e^{\theta_E/T}}{(e^{\theta_E/T} - 1)^2} \qquad (8)$$

It is clear from this relation that the heat capacity depends on temperature according to the Einstein model. We will now examine how this dependence behaves in two regimes:

Temperature Limits

1. High Temperature ($T >> \theta_E$)

$$e^{\theta_E / T} \approx 1 + \frac{\theta_E}{T}$$

Thus:

$$C \approx 3R$$

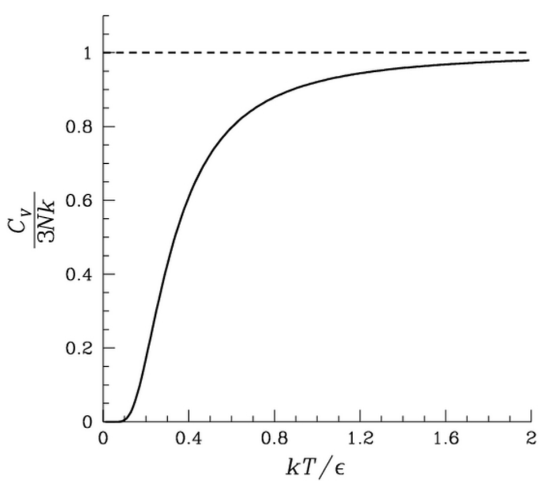
✔ Matches **classical theory** and experiments.

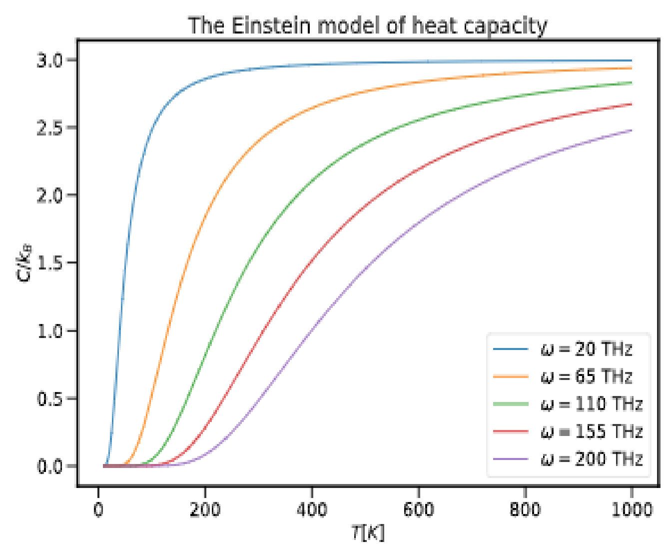
2. Low Temperature ($T << \theta_E$)

$$C \approx 3R \left(\frac{\theta_E}{T}\right)^2 \frac{e^{\theta_E/T}}{(e^{\theta_E/T})^2} \approx 3R \left(\frac{\theta_E}{T}\right)^2 e^{-\theta_E/T} \qquad (9)$$

➡ Heat capacity **decreases exponentially** ($e^{-\theta_E/T}$) and approaches zero as $T \rightarrow 0K$.

This behavior is illustrated in the following **graph** , where C_V approaches zero at low temperature.





☞ The key limitation:

- Assumes **single frequency**.

- Cannot explain C∝T^3 at low temperatures.

 At low T, phonons are not excited → fewer energy modes → lower heat capacity.
 Classical model assumes continuous energy → overestimates modes.

Recap:

 Why does classical theory fail?
 What assumption is wrong?
 What would happen if frequencies are not identical?

Appendix: Average Energy Derivation

The average energy is defined as:

$$\langle E \rangle = \frac{E}{N}$$

$$E = \sum_{i}^{m} N(E_i) E_i$$

$$\langle E \rangle = \frac{\sum_{i}^{m} N(E_i) E_i}{\sum_{i}^{m} N(E_i)}$$

In the case of continuous energy states:

$$\langle E \rangle = \frac{\int_0^\infty N(E) E \, dE}{\int_0^\infty N(E) \, dE}$$

According to the Boltzmann statistical distribution:

$$\langle E \rangle = \frac{\sum_{n=0}^\infty E_n \, e^{-\frac{E_n}{kT}}}{\sum_{n=0}^\infty e^{-\frac{E_n}{kT}}}$$

$$\langle E\rangle = \frac{\sum_{n=0}^{\infty} n\hbar\omega\, e^{-\frac{n\hbar\omega}{kT}}}{\sum_{n=0}^{\infty} e^{-\frac{n\hbar\omega}{kT}}}$$

Note:
Zero-point energy is neglected since it does not affect heat capacity.

$$\langle E\rangle = \frac{\sum_{n=0}^{\infty} n\hbar\omega\, e^{-\frac{n\hbar\omega}{kT}}}{\sum_{n=0}^{\infty} e^{-\frac{n\hbar\omega}{kT}}}$$

$$\langle E\rangle = \frac{0 + \hbar\omega\, e^{-\frac{\hbar\omega}{kT}} + 2\hbar\omega\, e^{-\frac{2\hbar\omega}{kT}} + \ldots\ldots\ldots\ldots}{1 + e^{-\frac{\hbar\omega}{kT}} + e^{-\frac{2\hbar\omega}{kT}} + \ldots\ldots\ldots\ldots}$$

$$= \frac{\hbar\omega\, e^{x}(1 + 2e^{x} + 3e^{2x} + \ldots\ldots\ldots\ldots)}{1 + e^{x} + e^{2x} + \ldots\ldots\ldots\ldots}$$

Where, $x = -\frac{\hbar\omega}{k}$

Since, $\frac{1}{(1-e^{x})^2} = 1 + 2e^{x} + 3e^{2x} + \ldots$

$$\frac{1}{(1-e^{x})} = 1 + e^{x} + e^{2x} + \ldots$$

Then, $\langle E\rangle = \frac{\hbar\omega\, e^{x}}{(1-e^{x})} = \frac{\hbar\omega}{(e^{-x}-1)} = \frac{\hbar\omega}{(e^{\hbar\omega/kT}-1)} = \langle n\rangle\hbar\omega$

$$\langle n\rangle = \frac{1}{(e^{-x}-1)}$$

$$\langle E\rangle = \frac{\hbar\omega}{(e^{\hbar\omega/kT}-1)}$$