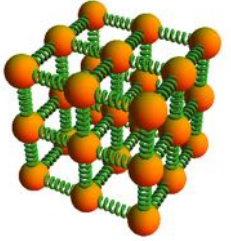# Lecture 19

14.11.2018

Phonon gas & Einstein solid

Eistein model for a Solid

Each atom in 3D has 3 one dimensional harmonic oscillators.

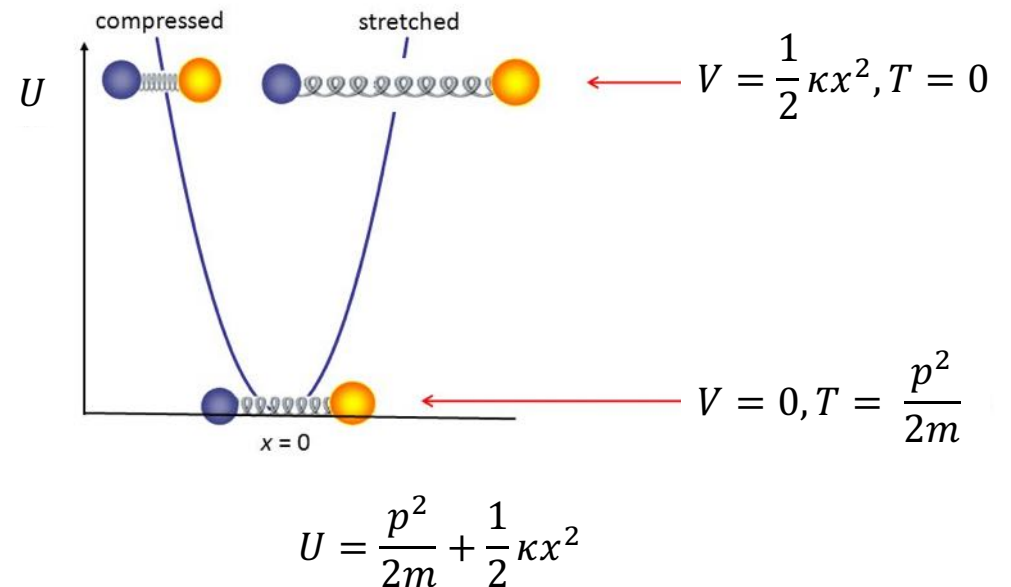- A solid is a a collection of identical harmonic oscillators.

$$U_1 = \frac{p^2}{2m} + \frac{1}{2}m\omega^2(x - x_0)^2$$

- Classical oscillator:

- Frequency:

$$\omega = \sqrt{\frac{\kappa}{m}}$$

Classical Harmonic Oscillator

compressed   stretched

U

$V = \frac{1}{2}\kappa x^2, T = 0$

$x = 0$

$V = 0, T = \frac{p^2}{2m}$

$$U = \frac{p^2}{2m} + \frac{1}{2}\kappa x^2$$

Eistein model for a Solid

One quantum harmonic oscillator

$$\hat{H} = \frac{\hat{p}^2}{2m} + \frac{1}{2}\kappa\hat{x}^2 = \frac{\hat{p}^2}{2m} + \frac{1}{2}m\omega^2\hat{x}^2$$

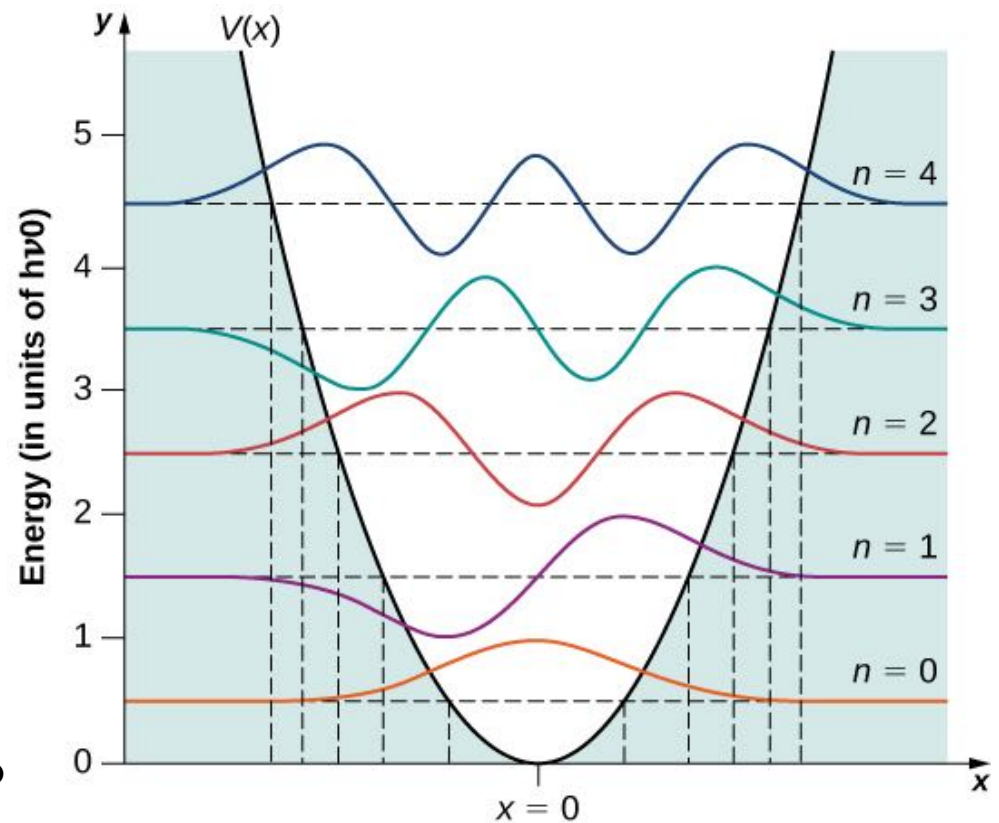Quantized energy levels $\epsilon = \left(n + \frac{1}{2}\right)\hbar\omega$

Energy level relative to the ground state

$$\Delta\epsilon = n\hbar\omega$$

Total energy of N harmonic oscillators

$$U_N = \sum_{i=1}^{N}\epsilon_i = \sum_{i=1}^{N} n_i\,\hbar\omega + \frac{N}{2}\hbar\omega$$

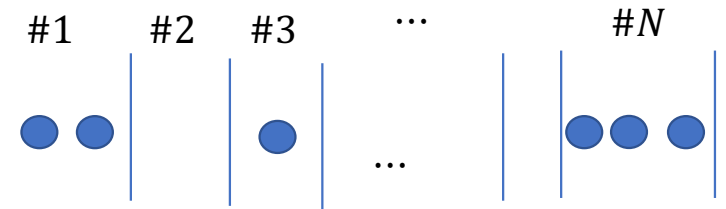**Energy units for N quantum harmonic oscillators at frequency ω**

$$\mathbf{q} = \frac{U_N - \dfrac{N}{2}\hbar\omega}{\hbar\omega}$$

Fys2160, 2018

Multiciplity of a macrostate with *N* oscillators and *q* units of energy distributed between them

#1   #2   #3   ⋯   #N

q energy units $\sim q$ identical balls

N oscillators $\sim$ N identical boxes

Number of ways of distributing q balls between N boxed is the same as the number of combinations with q balls and (N-1)-walls between the lined up boxes

Number of ways of combining *(N-1)-walls* and q balls

$$\Omega(q, N) = \frac{(N - 1 + q)!}{q!\,(N - 1)!}$$

Heat capacity

It can be shown with the Einstein model that, with $\varepsilon=hf$:

$$C_V = 3Nk\frac{(\epsilon/kT)^2 e^{\epsilon/kT}}{\left(e^{\epsilon/kT} - 1\right)^2}$$

For large kT, C_V -> $3Nk$, which is consistent with the equipartition theorem.

However, for low kT (when $kT<\varepsilon$), there is a discrepancy with experiments. Instead of going towards zero, we should reach C_v~T^3 as observed experimentally.

Problem – atoms are coupled

The potential energy of an atom depends on its neighbours and in particular distance.
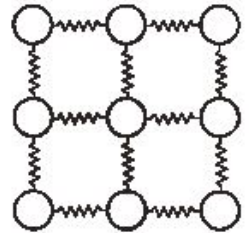
Atoms do not vibrate independently, and their motion depends on the oscillations in the lattice.

Low frequency large scale modes – large domains moving together.

High frequencies modes - atoms are moving opposite to each other.

Oscillation modes are similar to the EM waves in vacuum.

Debye theory for solids

Debye: start from continuum point of view (1912). Consider it similarly to EM radiation.

Vibrational modes at low frequencies within the field.

The normal modes are sound waves – mechanical oscillations. Sound speed cs depends on the material properties (stiffness and density). Smaller by factor 10^5 than the speed of light.

Sound waves can have 3 polarisations: longitudinal and transversal.

The shortest wavelengts are limited by the interatomic distance.

$n=1$

$n=2$

$n=3$

$n=N^{1/3}$
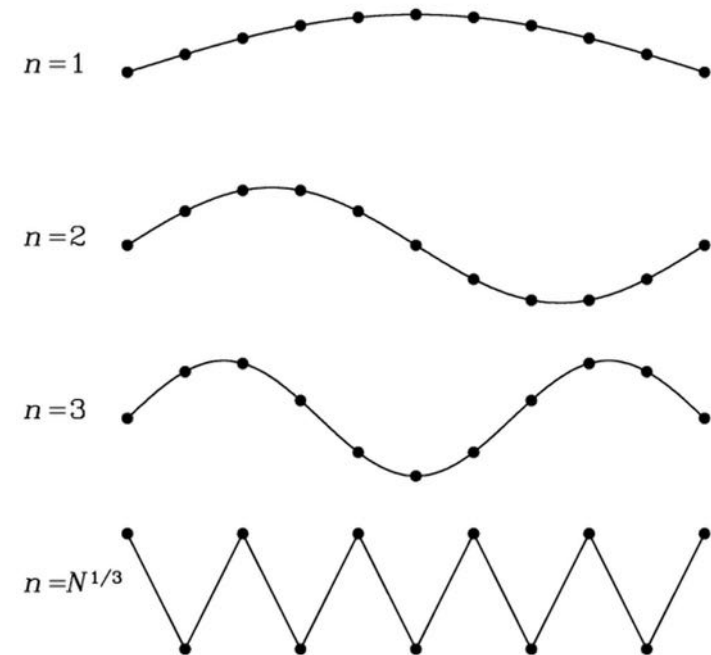
Phonons

Introduce phonons: quanta of the elastic field of the solid body.

Their energies: $\epsilon = hf = \dfrac{hc_s}{\lambda} = \dfrac{hc_s n}{2L}$

L – length of the crystal, n magnitude of the vector in the n space defining the shape of the wave.

When the mode is in equilibrium at temperature T, the number of units of energy it contains on average is given by the Planck distribution:

$$\bar{n}_P = \frac{1}{e^{\beta hf} - 1}$$
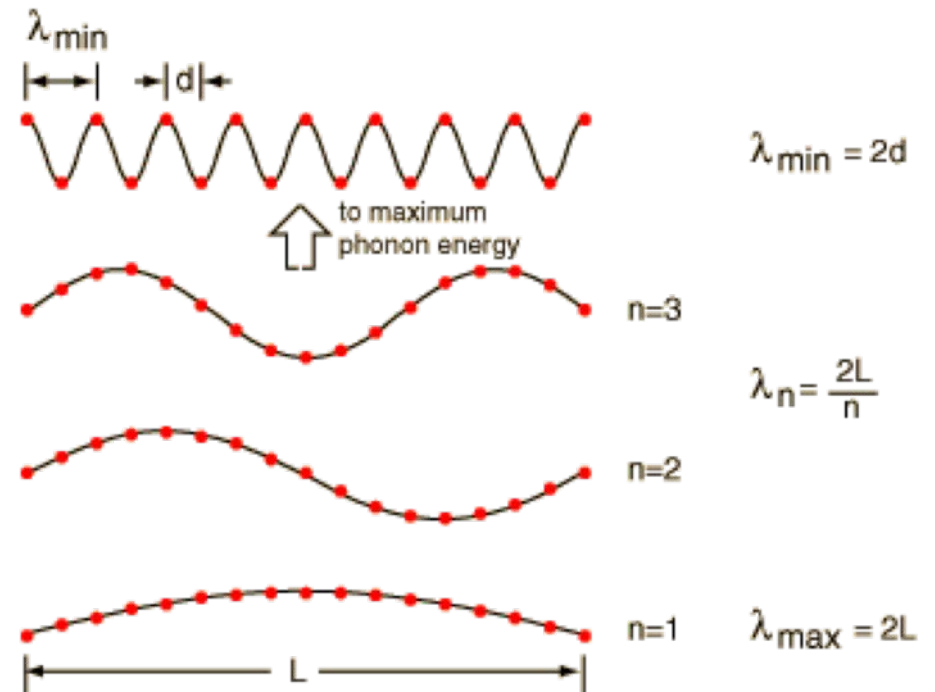
.

$n=1$

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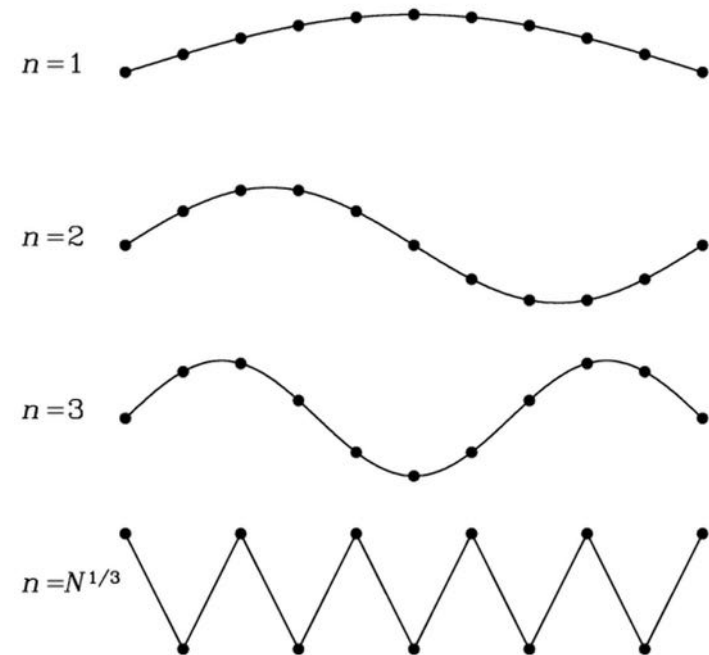
The total thermal energy

It will be a summation over all allowed modes:

$$U = 3 \sum_{n_x, n_y, n_z} \epsilon \bar{n}_P(\epsilon)$$

3 accounts for 3 polarisations. We want to move to integral. But need to find the maximum *n*.

Modes limited by the number of atoms in the crystal. $N^{1/3}$ in each direction.
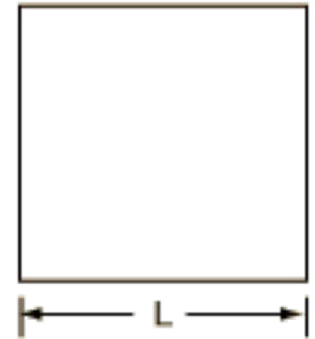
.

The total thermal energy

If we approximate with a 1/8 of a sphere with total volume N, then:

$$n_{max} = \left(\frac{6N}{\pi}\right)^{1/3}$$

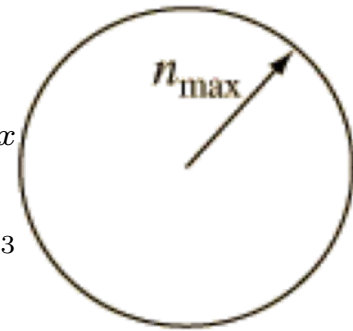The 1/8th sphere approximation is valid in high and low temperature limits.

$$U = 3 \int_0^{n_{max}} dn \int_0^{\pi/2} d\theta \int_0^{\pi/2} d\phi \, n^2 \sin\theta \frac{\epsilon}{e^{\epsilon/kT} - 1}$$

$$n_{max} = N^{1/3}$$

$$N = \frac{1}{8}\frac{4}{3}\pi n_{max}^3$$

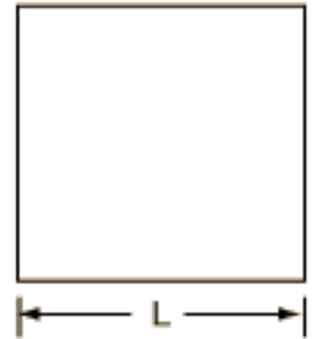$$n_{max} = \left(\frac{6N}{\pi}\right)^{1/3}$$

n_{max}

The total thermal energy
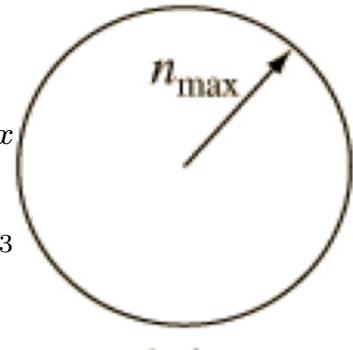
After integrating over all angles, we get

$$U = \frac{3\pi}{2} \int_0^{n_{max}} \frac{hc_s}{2L} \frac{n^3}{e^{hc_s n/2LkT} - 1} dn$$

$$n_{max} = N^{1/3}$$

$$N = \frac{1}{8} \frac{4}{3} \pi n_{max}^3$$

$$n_{max} = \left(\frac{6N}{\pi}\right)^{1/3}$$

n_{max}

Let us now change variables
$$x = \frac{hc_s n}{2LkT}$$

Then the upper limit:

$$x_{max} = \frac{hc_s n_{max}}{2LkT}$$

$$x_{max} = \frac{hc_s}{2kT} \left(\frac{6N}{V\pi} \right)^{1/3}$$

$$x_{max} = \frac{hc_s}{T}$$

Where T_D is the Debye temperature

$$T_D = \frac{hc_s}{2k} \sqrt[3]{\frac{6}{\pi} \frac{N}{V}}$$

Finally... we have a «nicer» espression for U

After substitution:

$$U = \frac{9NkT^4}{T_D^3} \int_0^{T_D/T} \frac{x^3}{e^x - 1} dx$$

In the limit of large *T*:

$$U = 3NkT$$

In the limit of small *T*:
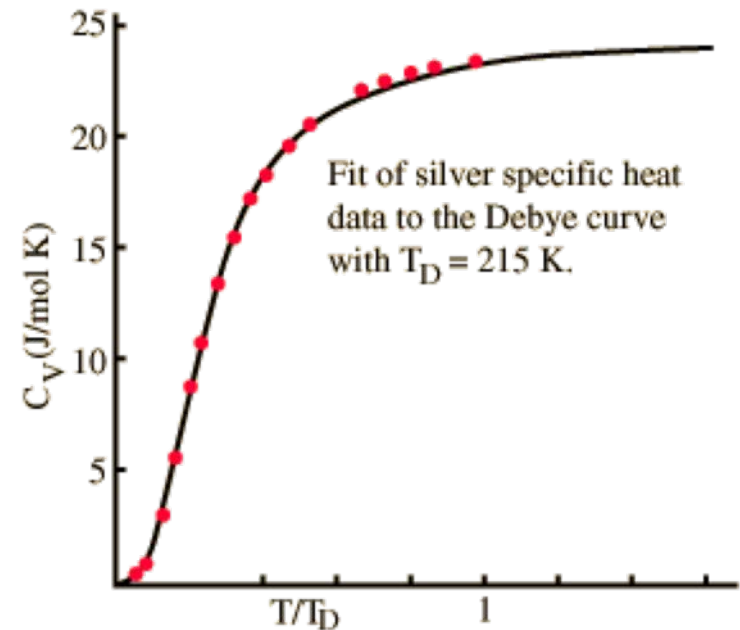
$$U = \frac{3\pi^4}{5} \frac{NkT^4}{T_D^3}$$

Let us look again at C_V

Differentiate with repect to T:

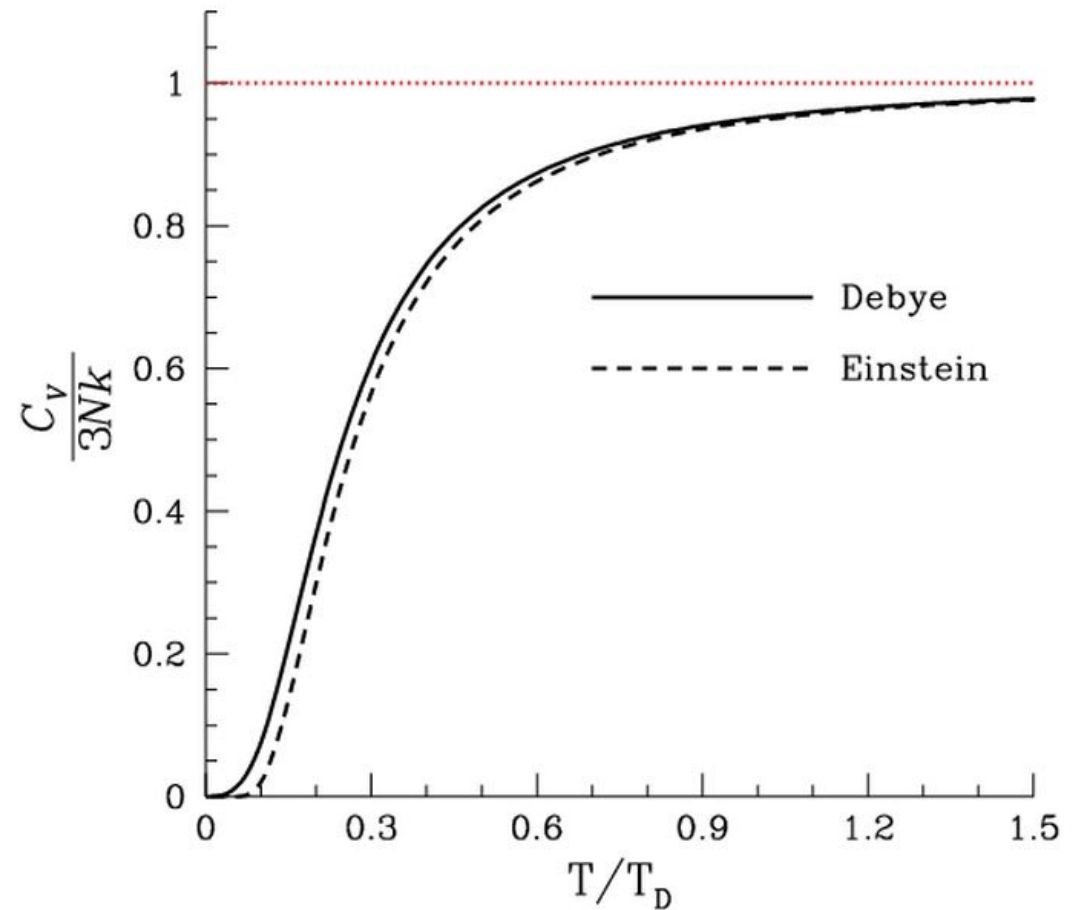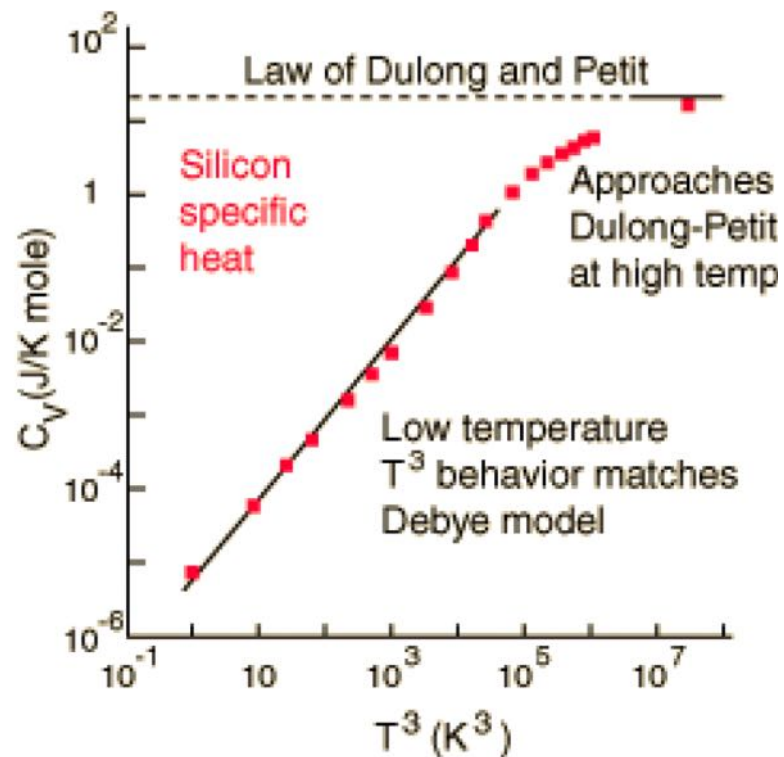$$C_V = \frac{12\pi^4}{5}\left(\frac{T}{T_D}\right)^3 Nk$$

It works great for low temperature experiments with solids!

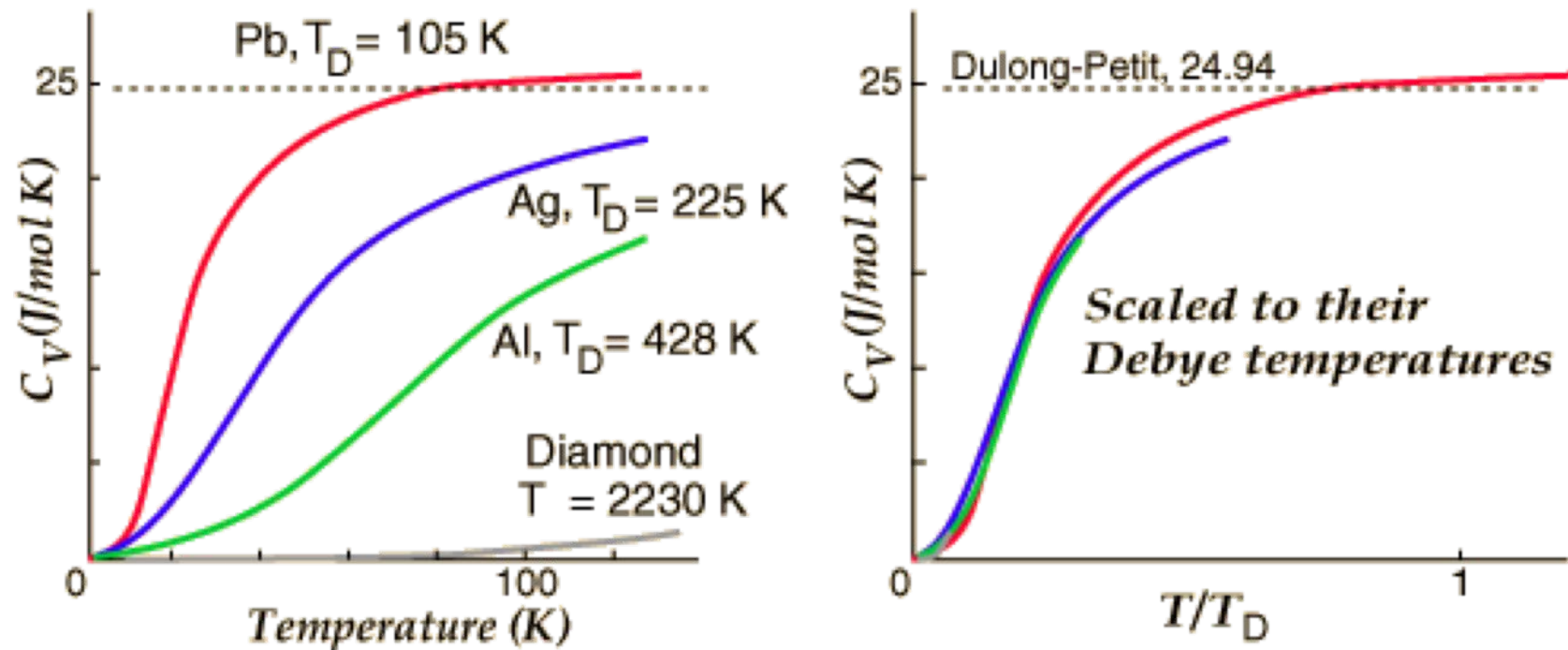Note that there is a small add-on for metals to the heat capacity due to conduction electrons (γT)

Fit of silver specific heat data to the Debye curve with $T_D = 215$ K.

Debye vs. Einstein

Debye works well for low temperatures

Debye theory

Debye works well for low temperatures

Debye temperature

- Heat capacity reaches 95% of its maximum value at T_D
- Can be found from sound speed – which is the metal specific parameter.
- The higher the sound speed and the density of ions, the higher the Debye temperature
- Easiest to treat T_D as an experimental fitting parameter.

Aluminum	426K		Platinum	240K
Cadmium	186K		Silicon	640K
Chromium	610K		Silver	225K
Copper	344.5K		Tin (white)	195K
Gold	165K		Titanium	420K
α-Iron	464K		Tungsten	405K
Lead	96K		Zinc	300K
α-Manganese	476K		Diamond	2200K
Nickel	440K		Ice	192K

Debye temperature

- Heat capacity reaches 95% of its maximum value at T_D

- Can be found from sound speed – which is the metal specific parameter.

- The higher the sound speed and the density of ions, the higher the Debye temperature

- Easiest to treat T_D as an experimental fitting parameter.