

## MOLAR HEAT OF SOLIDS

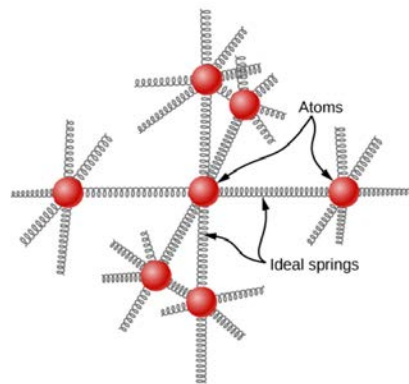
The Dulong–Petit law, a thermodynamic law proposed in 1819 by French physicists Dulong and Petit, states the classical expression for the molar specific heat of certain crystals. The two scientists conducted experiments on three dimensional solid crystals to determine the heat capacities of a variety of these solids. They discovered that all investigated solids had a heat capacity of approximately  $25 \text{ J mol}^{-1} \text{ K}^{-1}$  room temperature. The result from their experiment was explained as follows.

According to the Equipartition Theorem, each degree of freedom has an average energy of

$$E = \frac{1}{2}k_B T$$

where  $k_B$  is the Boltzmann constant and  $T$  is the absolute temperature.

We can model the atoms of a solid as attached to neighboring atoms by springs. These springs extend into three-dimensional space. Each direction has 2 degrees of freedom: one kinetic and one potential. Thus every atom inside the solid was considered as a 3 dimensional oscillator with six degrees of freedom ( $D = 6$ ) The more energy that is added to the solid the more these springs vibrate.



*Figure 1: Model of interaction of atoms of a solid*

Now the energy of each atom is  $E = \frac{6}{2}k_B T = 3k_B T$ . The energy of  $N$  atoms is

$$E = 3Nk_B T = 3nRT$$

where  $n$  is the number of moles. To change the temperature by  $\Delta T$  via heating, one must transfer  $Q=3nR\Delta T$  to the crystal, thus the molar heat is

$$C = 3R \approx 3 \cdot 8.31 \frac{J}{molK} \approx 24.93 \frac{J}{molK}$$

Similarly, the molar heat capacity of an atomic or molecular ideal gas is proportional to its number of degrees of freedom,  $D$ :

$$C_v = \frac{D}{2} R$$

This explanation for Petit and Dulong's experiment was not sufficient when it was discovered that heat capacity decreased and going to zero as a function of  $T^3$  (or, for metals,  $T$ ) as temperature approached absolute zero. As the temperature goes up, the specific heat goes up until it approaches the Dulong and Petit prediction at high temperature.

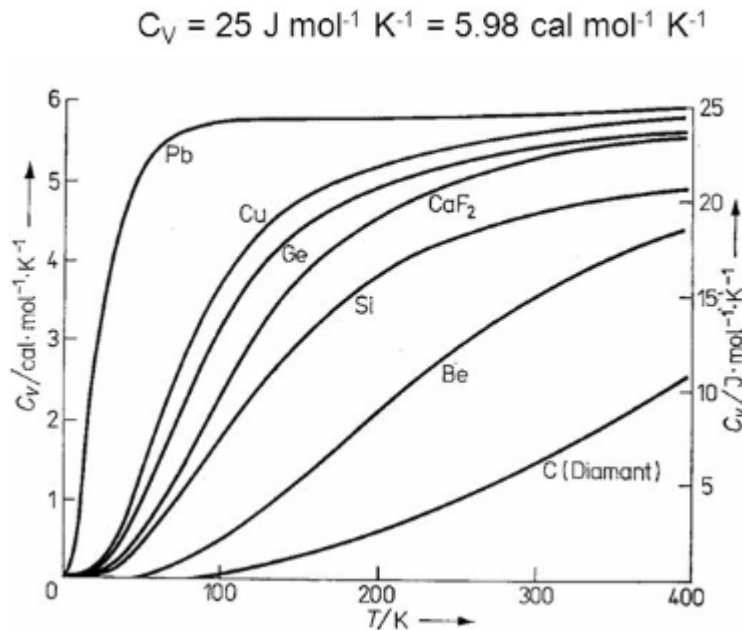


Figure 2: Heat capacity of some solids

Two main theories were developed to explain this deviance in the heat capacity experiments. The first was constructed by Einstein and the second was authored by Debye.

## Einstein Solid

The modern theory of the heat capacity of solids states that it is due to lattice vibrations in the solid and was first derived in crude form from this assumption by Albert Einstein in 1907. The Einstein solid model thus gave for the first time a reason why the Dulong–Petit law should be stated in terms of the classical heat capacities for gases.

The Einstein solid is a model of a solid based on two crude assumptions:

- (1) Each atom in the lattice is an independent 3D **quantum** harmonic oscillator with discrete energy levels  $E_n = nhf$ , where  $n$  is a nonnegative integer,  $h$  is the Planck-constant and  $f$  is the frequency. At low temperatures the small  $k_B T$  average thermal energy is not enough to excite the oscillators, that is the main reason of the decrease of the molar heat.
- (2) All atoms oscillate with the same frequency. To give a simple estimation to this frequency, we recall that that a classical harmonic oscillator has a frequency

$$\omega = 2\pi f = \sqrt{\frac{k}{m}}$$

where  $k$  is the spring-constant,  $m$  is the mass. It means that e.g. the lead has much larger frequencies than diamond, which explains why quantum effect in case of the lead are smaller and become important only at lower temperatures, while they cannot be neglected at room temperatures in case of diamond.

Einstein was aware that getting the frequency of the actual oscillations would be difficult, but he nevertheless proposed this oversimplified theory because it was a particularly clear demonstration that quantum mechanics could solve the specific heat problem in classical mechanics.

By employing Planck's quantization assumption, Einstein's theory accounted for the observed experimental trend for the first time. Together with the photoelectric effect, this became one of the most important pieces of evidence for the need of quantization. Although the Einstein model of the solid gives the heat capacity (the Dulong–Petit law) accurately at high temperatures, at low temperatures it predict an exponential decay, which only qualitatively good, but quantitatively incorrect.

## The Debye Model

The slightly more sophisticated Debye model was developed by Peter Debye in 1912 for estimating the phonon contribution to the heat capacity in a solid. It treats the vibrations of the atomic lattice (heat) as phonons in a box, in contrast to the Einstein model, which treats the solid as many individual, non-interacting quantum harmonic oscillators. The Debye model correctly predicts the low temperature dependence of the heat capacity, i.e. if  $T \ll T_D$ , then

$$C \sim \approx \left( \frac{T}{T_D} \right)^3$$

– the Debye  $T^3$  law, where  $T_D$  is Debye temperature. Just like the Einstein model, it also recovers the Dulong–Petit law at high temperatures. But due to simplifying assumptions, its accuracy suffers at intermediate temperatures.

The approximation that the frequency is inversely proportional to the wavelength (giving a constant speed of sound) is good for low-energy phonons but not for high-energy phonons. This disagreement is one of the limitations of the Debye model, and corresponds to incorrectness of the results at intermediate temperatures, whereas both at low temperatures and high temperatures they are quite accurate. However, it still does not take into account the anharmonicity, which causes the heat capacity to rise further. The total heat capacity of the solid, if it is a conductor or semiconductor, may also contain a non-negligible contribution from the electrons.

To summarize, the heat capacity of solids as predicted by the empirical Dulong–Petit law was coherent with classical mechanics; the specific heat of solids should be independent of temperature. Classical physics was not able to explain the deviance from this law, but quantum physics was.