

The heat capacity of solids

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1. Background

We now turn our attention (briefly) to study heat capacity in solids. In a solid, as opposed to gas, there are a few sources of heat capacity:

- Vibration of the atoms
- Ordering of atoms (defects, etc).
- conduction of electrons

and others. However, in fact we will be interested mainly in the first point (vibrations of the atoms), which are the most significant.

Experimentally, we know two facts:

- Near room temperature, the heat capacity of *most* solids is $\sim 3^\circ \text{K} / \text{atom}$. This experimental result is known as **Dulong and Petit law**.
- At $T \rightarrow 0$, $C_V \rightarrow 0$, in accordance to the third law. Moreover, it is found experimentally that in low temperatures,

$$C_V = \alpha T^3 + \gamma T, \quad (1)$$

where α and γ are constants. The first term, containing α is connected to the lattice vibrations; the second term (with γ) is connected to the conducting electrons, and for some solids is 0. This is shown in Figure 1.

Classical statistical mechanics predicts that all mono-atomic solids should have molar heat capacity = $3R$ at all temperatures - in contradiction to observations.

This inconsistency was solved by Einstein.

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2. Einstein theory of solids

Einstein considered a model in which atoms in a solid vibrate **independently of each other**. Each vibration can be considered as a simple harmonic oscillator. Thus, the equation of motion is

$$\frac{d^2r}{dt^2} = -\omega_E^2 r \quad (2)$$

Since oscillation is independent in the x , y and z directions, for N atoms there are $3N$ independent oscillators. Here, ω_E is the circular frequency. Of course, this model is too simplified, as the atoms are coupled, but apparently it captures the essence of the problem.

In **quantum mechanics** (QM) the energy of an oscillator in a state r is

$$E_r = \hbar\omega_E \left(r + \frac{1}{2} \right) \quad r = 0, 1, 2, \dots \quad (3)$$

Where $r = 0$ represents the ground state, and \hbar is Planck's constant.

Since in QM there is an energy also in the ground state, atoms are never at rest (this is a consequence of **Heisenberg's uncertainty principle**). We can thus treat any atom as if it is in contact with a heat bath at temperature T .

This makes our life very easy, since we already discussed the theory of a system in contact with a heat bath. The partition function for one oscillator is

$$Z_1 = \sum_{r=0}^{\infty} e^{-\beta E_r} = \sum_{r=0}^{\infty} e^{-\beta\hbar\omega_E(r+\frac{1}{2})} \quad (4)$$

Writing $\chi = \beta\hbar\omega_E = \hbar\omega_E/k_B T$, we find

$$Z_1 = e^{-\frac{\chi}{2}} \sum_{r=0}^{\infty} e^{-\chi r} \quad (5)$$

We can now use a mathematical identity:

$$\sum_{r=0}^{\infty} t^r = \frac{1}{1-t}, \quad (6)$$

which is true for $|t| < 1$. In our example, $t = e^{-\chi}$, and thus we can write

$$Z_1 = \frac{e^{-\frac{\chi}{2}}}{1 - e^{-\chi}} \quad (7)$$

We can use the partition function to find the mean energy of an oscillator:

$$\langle E_1 \rangle = -\frac{\partial \ln Z_1}{\partial \beta} = -\frac{\partial}{\partial \beta} \left[-\frac{\chi}{2} - \ln(1 - e^{-\chi}) \right] = \frac{1}{2}\hbar\omega_E + \frac{\hbar\omega_E}{e^{\beta\hbar\omega_E} - 1}. \quad (8)$$

Equation 8 gives the energy of a single oscillator - recall that we have $3N$ oscillators, and $E = 3N\langle E_1 \rangle$.

We can now calculate the heat capacity,

$$C_V = \left(\frac{\partial E}{\partial T} \right)_V = 3N \frac{\partial E}{\partial \beta} \frac{\partial \beta}{\partial T} \quad (9)$$

or

$$C_V = 3Nk_B \frac{\chi^2 e^\chi}{(e^\chi - 1)^2}, \quad (10)$$

where

$$\chi \equiv \frac{\hbar\omega_E}{k_B T} \equiv \frac{\theta_E}{T} \quad (11)$$

where $\theta_E \equiv \hbar\omega_E/k_B$ is known as **Einstein temperature**, which depends on the solid at hand.

The heat capacity C_V thus depends on the temperature only through $\chi = \theta_E/T$. Its behavior for different temperatures is shown in Figure 2. For $T \gg \theta_E$, $\chi \ll 1$ and $C_V = 3NK_B$. On the other extreme, $T \ll \theta_E$, $\chi \gg 1$ and $C_V = 3Nk_B(\theta_E/T)^2 e^{-\theta_E/T}$, which goes to 0 as T decreases, in accordance to observations.

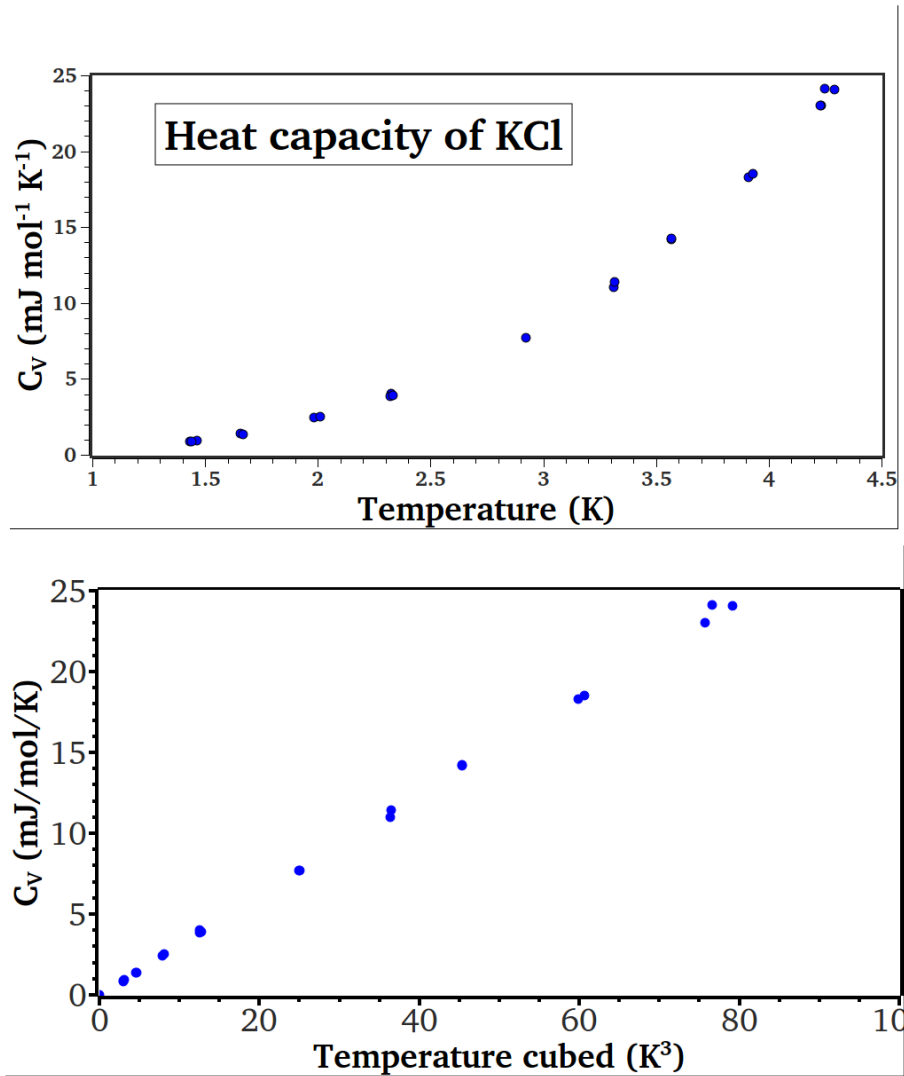


Fig. 1.— Heat capacity of KCl. Upper plot: as a function of T . Lower plot: as a function of T^3 .

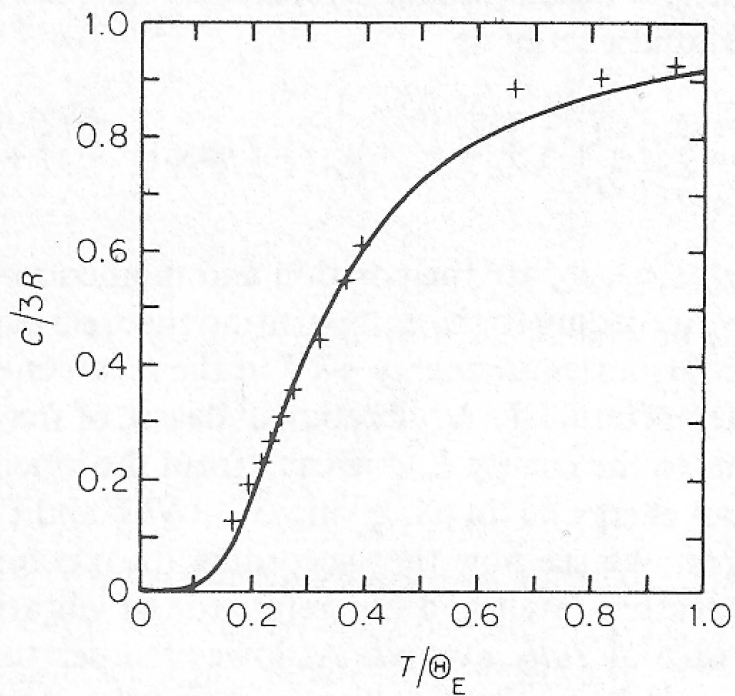


Fig. 6.5. Comparison of the observed molar heat capacity of diamond (+ experimental points with $\Theta_E = 1325$ K) with Einstein's model (full line). (After Einstein's original 1907 paper.)

Fig. 2.— Einstein's model for heat capacity in a diamond- theory vs. experiment.