Thermal Physics

The Einstein Model of Heat Capacity of Solids

Problem 1.- The result of the classical model of heat capacity of solids (Dulong and Petit) does not agree with observations. The heat capacity of the lattice varies with temperature and goes to zero at T = 0.

Einstein assumed that the atoms are statistically independent and execute harmonic motion about their mean positions. He found the heat capacity using the quantum mechanical result that $E=n\hbar\omega$, where n=0, 1, 2… Assuming, for simplicity, that the frequencies are identical and equal to ω.

Reproduce Einstein result and obtain the limiting behavior of C_V for

$k_B T \ll \hbar\omega$

and for

$k_B T \gg \hbar\omega$.

Solution: The partition function for one harmonic oscillator is:

$$Z_1 = \sum_{s=0}^{\infty} e^{-s\omega\hbar/\tau} = \frac{1}{1-e^{-\omega\hbar/\tau}}$$

Given 3 independent oscillators per atom, there will be 3N oscillators for the whole solid, so the partition becomes:

$$Z_1 = (Z_1)^{3N} = \left(\frac{1}{1-e^{-\omega\hbar/\tau}}\right)^{3N}$$

The energy of such a system can be calculated as follows:

$$U = \tau^2 \frac{\partial \log(Z)}{\partial\tau} = \tau^2 \frac{\partial \log\left(\frac{1}{1-e^{-\omega\hbar/\tau}}\right)^{3N}}{\partial\tau} = -3N\tau^2 \frac{\partial \log(1-e^{-\omega\hbar/\tau})}{\partial\tau} = -3N\tau^2 \frac{-e^{-\omega\hbar/\tau}\left(\frac{\omega\hbar}{\tau^2}\right)}{1-e^{-\omega\hbar/\tau}}$$

$$U = 3N\frac{\omega\hbar}{e^{\omega\hbar/\tau}-1}$$

To get C_V, we take the derivative with respect to temperature:

$$C_V = \frac{\partial U}{\partial\tau} = 3N\frac{\omega\hbar e^{\omega\hbar/\tau}(\omega\hbar/\tau^2)}{(e^{\omega\hbar/\tau}-1)^2} = 3N(\omega\hbar/\tau)^2\frac{e^{\omega\hbar/\tau}}{(e^{\omega\hbar/\tau}-1)^2}$$

The limit for high temperature is:

$$\lim_{\tau\to\infty} C_V = 3N(\omega\hbar/\tau)^2 \frac{1}{(\omega\hbar/\tau)^2} = 3N$$

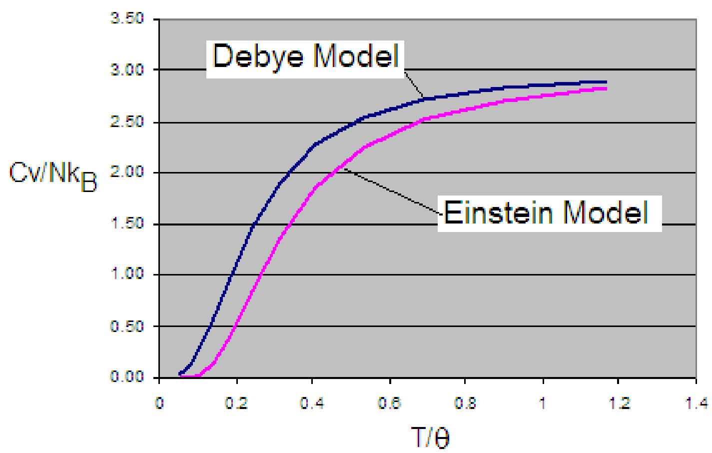
This is the appropriate limit because it coincides with the Dulong and Petit result.

The limit for low temperature is: $\lim_{\tau\to 0} C_V \approx 3N(\omega\hbar/\tau)^2 e^{-\omega\hbar/\tau}$

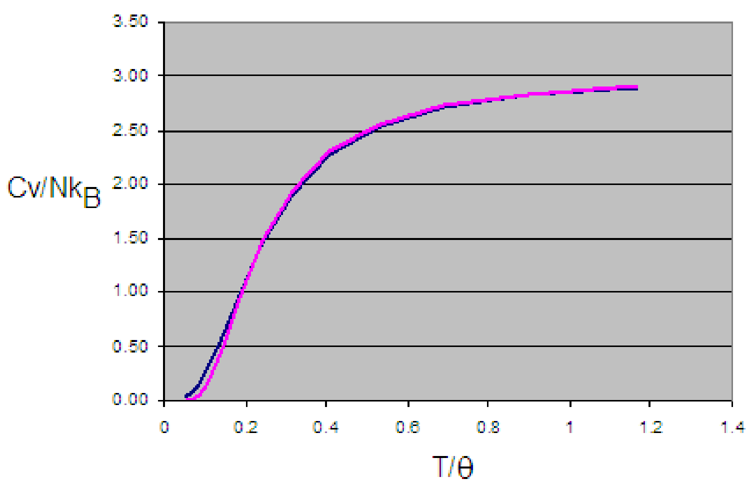
Although this limit reproduces the observation that the heat capacity of the lattice goes to zero at T = 0, this model poorly fits the data because it decays exponentially fast (faster than in the Debye model, which correctly predicts a T^3 dependence of the heat capacity).

Comparison with the Debye model:

If we assume that the parameter ω in the Einstein model is equal to $\frac{k_B\theta}{\hbar}$ the two heat capacities will compare as follows:



A closer approximation between the models will happen if $\omega_{einstein} = 0.73\frac{k_B\theta}{\hbar}$ in which case we obtain:



In the Debye model, the parameter θ can be determined with the speed of sound, while in the Einstein model ω is determined by fitting the data with the function.