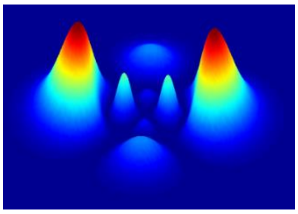

DOING PHYSICS WITH PYTHON

QUANTUM STATISTICS

SPECIFIC HEAT OF CRYSTALLINE SOLIDS

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PYTHON CODES

qmSm08.py Calculation and visualization of the specific heat of crystalline solids: classical, Einstein and Debye models.

INTRODUCTION

The specific heat of a solid at constant volume c_V is the amount of energy required to rise the temperature of a solid by a given amount

$$c_V = \frac{dU}{dT}$$

where U is the internal energy.

Experiments performed at room temperature by Dulong and Petit found that the energy required to raise the temperature a fixed amount was similar for all materials. This observation can be explained using the principles of classical physics. There are N_A atoms in a mole and each atom is regarded as executing simple harmonic motion about a lattice site in three dimensions. This gives $3N_A$ degrees of freedom and each degree of freedom is assigned an average total energy (potential energy + kinetic energy) $k_B T$. According to the classical law of equipartition of energy, the total energy is

$$U = 3N_A k_B T = 3RT$$

and thus, the specific heat (heat capacity) at constant volume is

$$c_V = 3N_A k_B = 3R = 24.94 \text{ J.mol}^{-1}\text{.K}^{-1}$$

This is known as **Dulong and Petit's law** and the specific heat is a constant, thus independent of the temperature.

The specific heat of many solids is indeed constant with temperature especially at higher temperatures with values in agreement with the prediction of the Dulong and Petit law. However, the specific heat of all solids trend to zero as the temperature decreases, and near absolute zero the specific heat is found to vary as T^3.

Albert Einstein in 1907 explained why the classical model did not work at low temperatures. He replaced the factor $k_B T$ by a factor that takes into account the energy quantization of a simple harmonic oscillator. His approach was to represent one mole of the solid as a collection of $3N_A$ simple harmonic oscillators all oscillating with the same frequency ω

$$k_B T \rightarrow \frac{\hbar\omega}{\exp\left(\hbar\omega / k_B T\right) - 1}$$

where $\dfrac{\hbar\omega}{\exp\left(\hbar\omega / k_B T\right) - 1}$ is the average energy of an oscillator.

Thus, the total energy (internal energy) and the specific heat are

$$U = 3N_A \frac{\hbar\omega}{\exp\left(\hbar\omega / k_B T\right) - 1}$$

$$c_V = \frac{dU}{dT} = 3R\left(\frac{\hbar\omega}{k_B T}\right)^2 \frac{\exp\left(\hbar\omega / k_B T\right)}{\left(\exp\left(\hbar\omega / k_B T\right) - 1\right)^2}$$

Einstein’s prediction for the specific heat agreed reasonably well with measurements. However, the Einstein equation at very low temperatures does not give the T^3 temperature dependence required by experiment. The frequency ω is chosen for each material to match experimental results.

Peter Debye improved upon the work of Einstein to give an equation that yields results which are in excellent agreement with experimental results. The Einstein model was based upon the simple harmonic motion of individual atoms whereas the Debye model considers that rather than N atoms vibrating in three dimensions independently at the same frequency, there are $3N$ coupled oscillations. The Debye equation for the specific heat of a solid is

$$c_V = 9R\left[4\left(\frac{T}{T_D}\right)^3\int_0^{T_D/T}\left(\frac{x^3}{e^x-1}\right)dx - \left(\frac{T_D}{T}\right)\left(\frac{1}{e^{T_D/T}-1}\right)\right]$$

where T_{D} the Debye temperature. The Debye temperature is connected to the elastic properties of a solid and can be determined independently of specific heat measurements. Debye’s theory agrees with the observed T^3 law at very low temperatures.

Figure 1 shows the specific heat as a function of temperature for the classical, Einstein and Debye models. Figure 2 shows the excellent agreement between the Debye model and the T^3 dependence shown by experiment at very low temperatures. Figure 3 shows the results of the Debye model for aluminum, gold and lead.

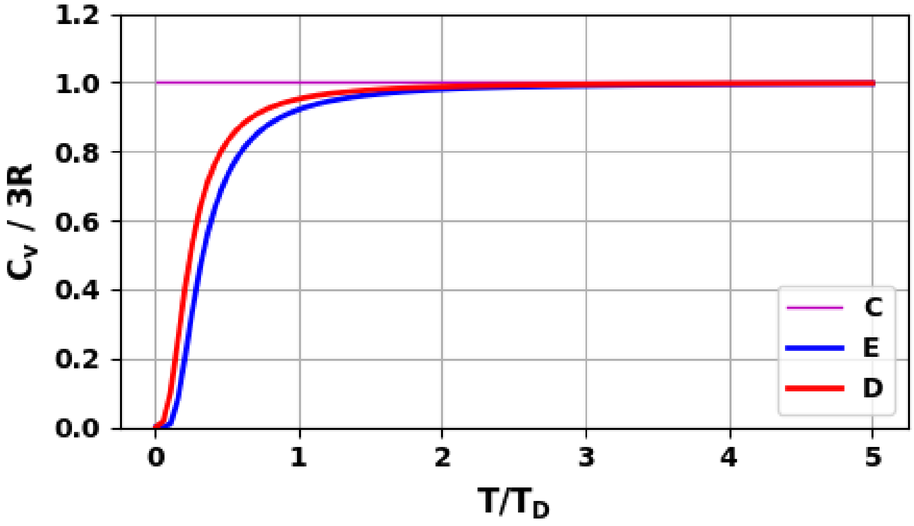

Fig. 1. Specific heat for the three models: Classical, Einstein and Debye.

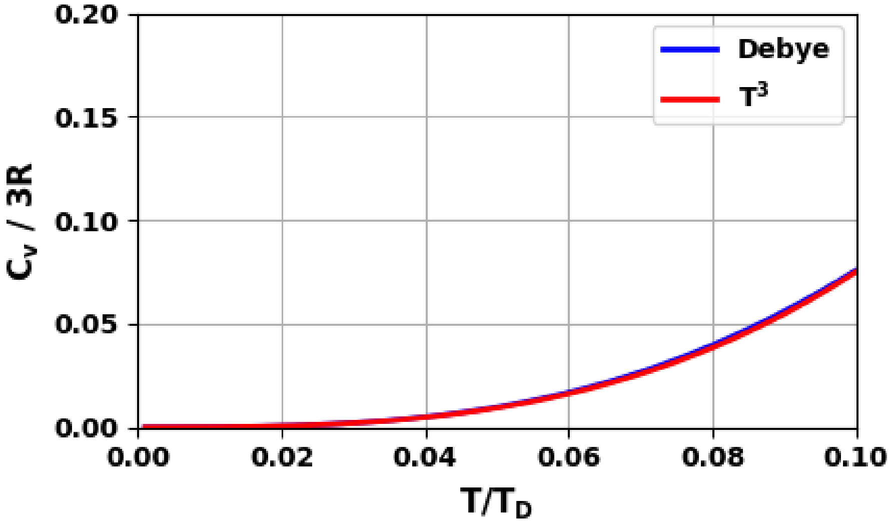

Fig. 2. The excellent agreement between the Debye model and the T^3 dependence shown by experiment at very low temperatures.

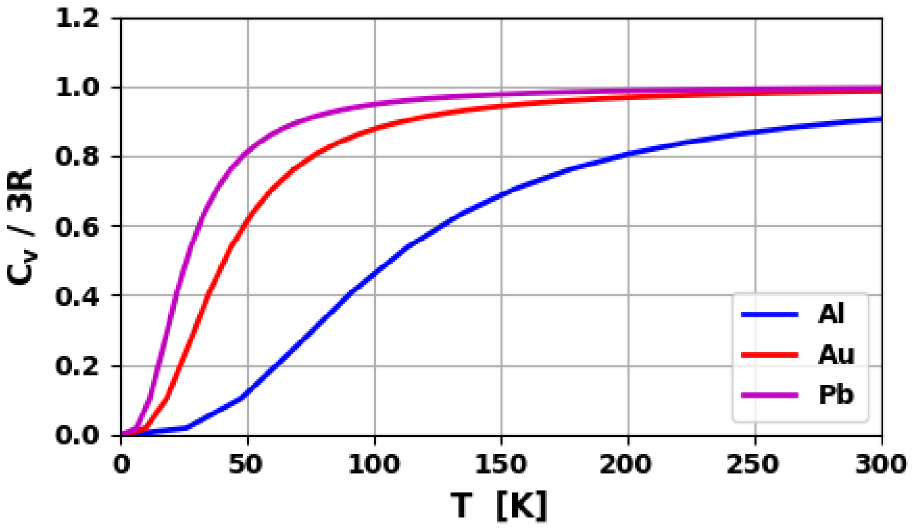

Fig. 3. The Debye model for aluminum (T_D = 428), gold (T_D = 165) and lead (T_D = 105).

It is a remarkable fact that so simple a model as Debye's yields such excellent results.

The integral in the equation for the Debye model must be done numerically. In Python this integral can be evaluated at each temperature step using the Simpson's rule function.

```
# Debye model
c1 = 36*R; c2 = 9*R; CV = zeros(N)
for c in range(N):
    uMax = z[c]
    u = linspace(xMin,uMax,999)
    fn =  u**3/(exp(u)-1)
    I = simps(fn,u)
   CV[c] = c1*x[c]**3 * I - c2*z[c]/(exp(z[c])-1)
```