Lecture 3.1

Kittel Chapter 5

Aschroft & Mermin Chapter 23

Specific heat capacity is a macroscopic, experimentally accessible property, the behaviour of which allows us to test models of the lattice

Recall, the specific heat at constant volume

$$c_V = \left(\frac{\partial u}{\partial T}\right)_V .$$

u is the entire internal energy of the crystal, per unit volume.

Phonons contribute an amount c_{lat} to this total.

Einstein model for c_{lat}

Inspired by success of Planck model in describing black-body radiation (using Bose–Einstein statistics)

Assume quantised oscillations (phonons) can have **only one frequency** $\omega = \omega_E$ ("E" for Einstein) and hence can only contain energies

$$E = \left(n + \frac{1}{2}\right)\hbar\omega_E$$

where n is an integer. The additional half comes from a proper quantum mechanical treatment and is the ground-state energy of the quantum harmonic oscillator and does not affect the heat capacity.

(We know a range of frequencies are allowed (see disperion relation earlier), but let's try this simple model and see where it leads.)

Assume that phonons obey the same quantum statistics as photons i.e. assume phonons are bosons.

This gives the **Planck** distribution. This allows us to find the **expectation value** for the energy stored (i.e. the average value of E) when the system is in thermal equilibrium at some temperature T:

$$\langle E \rangle = \frac{\hbar\omega_E}{e^{\hbar\omega_E/k_B T} - 1}.$$

For the following, see also `Einstein-heat-capacity.nb`

A solid with n atoms per unit volume has $3n$ modes of vibration per unit volume. Hence, the total energy per unit volume is

$$u_{\text{lat}}^{\text{Ein}} = \frac{3n\hbar\omega_E}{e^{\hbar\omega_E/k_B T} - 1}.$$

To find the specific heat capacity, we differentiate this specific energy by temperature T:

$$c_{\text{lat}}^{\text{Ein}} = \frac{\partial u_{\text{lat}}^{\text{Ein}}}{\partial T} = 3nk_B \left(\frac{\hbar\omega_E}{k_B T}\right)^2 \frac{e^{\hbar\omega_E/k_B T}}{\left(e^{\hbar\omega_E/k_B T} - 1\right)^2}.$$

It is usual to write

$$\theta_E = \hbar\omega_E / k_B$$

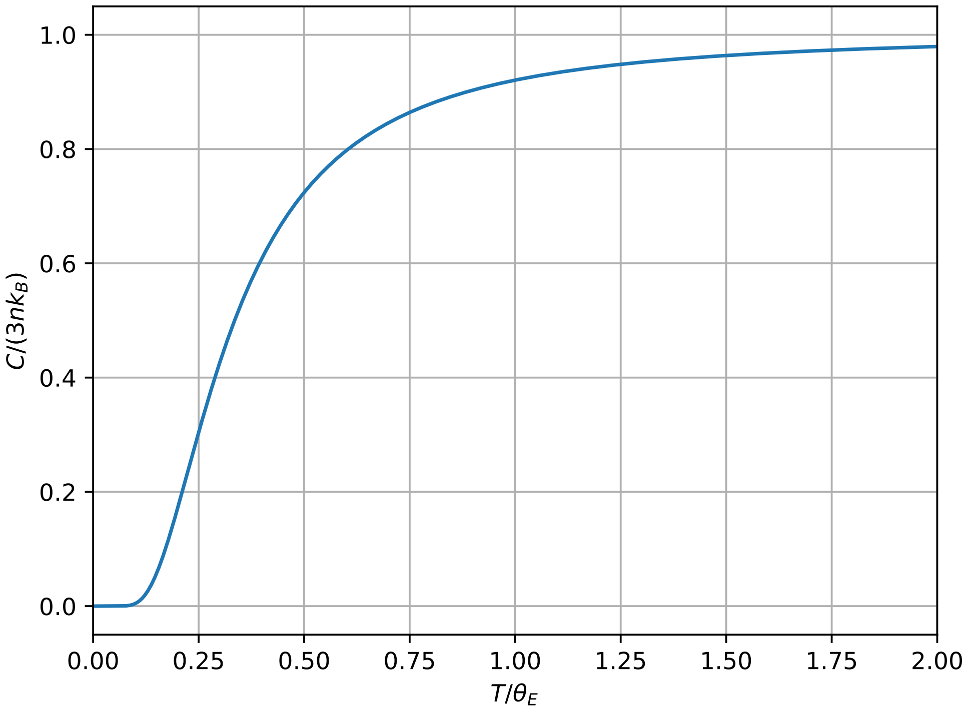
as the characteristic **Einstein temperature**.

Hence,

$$c_{\text{lat}}^{\text{Ein}} = 3nk_B \left(\frac{\theta_E}{T}\right)^2 \frac{e^{\theta_E/T}}{\left(e^{\theta_E/T} - 1\right)^2}.$$

How does this depend on temperature?

```
import numpy as np
import matplotlib.pyplot as plt
CLatEin = lambda x: (1/x)**2 * np.exp(1/x)/(np.exp(1/x)-1)**2
x = np.linspace(0,20,10001)
plt.plot(x,CLatEin(x))
plt.xlim([0,2])
plt.xlabel(r'$T/\theta_E$')
plt.ylabel(r'$C/(3nk_B)$')
plt.grid()
plt.savefig('figs/Einstein-heat-capacity.pdf')
plt.close('all')
```



The quantum nature of the statistics of phonons makes the heat capacity go to zero at low temperature. The classical limit is recovered at high temperatures, where the bosonic nature of the quanta is not important.

High temperature (Classical limit)

First-order series expansion: $e^{\theta_E/T} \approx 1 + \theta_E/T$.

Hence,

$$C_{\mathrm{lat}}^{\mathrm{Ein}} \approx 3nk_BT(1 + \theta_E/T) \approx 3nk_BT$$

i.e. the classical limit.

This is just $6n$ oscillators per unit volume, each of which has 2 quadratic degrees of freedom, and hence can store $2 \times (1/2)k_BT$.

Low temperature

At low temperature, $e^{\theta_E/T}$ becomes very large, so we can neglect the -1 in the denominator

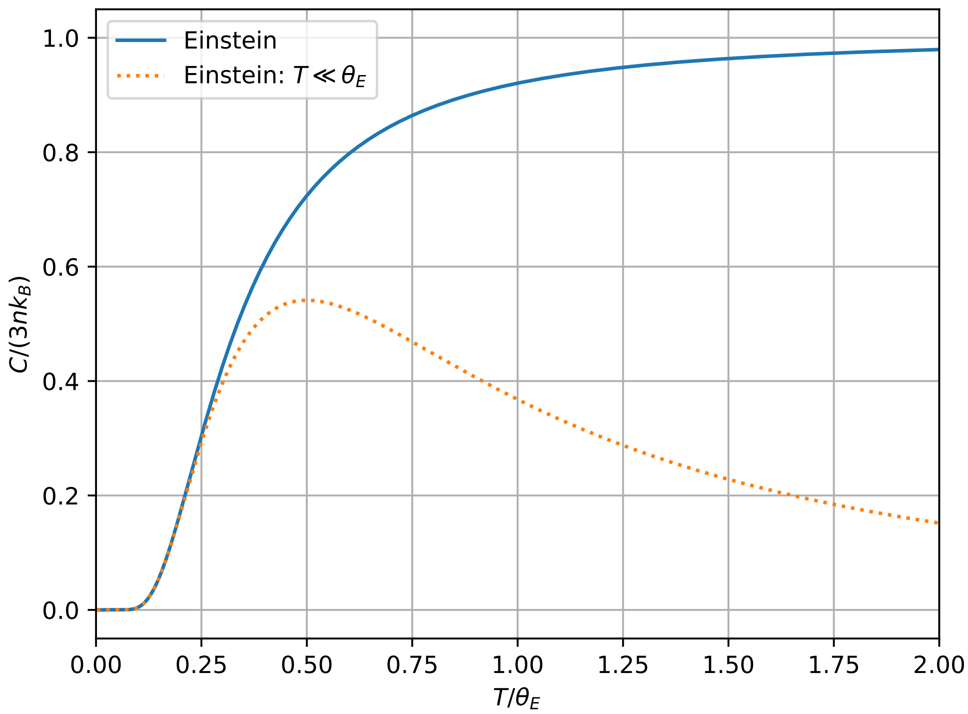
$$C_{\mathrm{lat}}^{\mathrm{Ein}} \approx 3nk_B \left(\frac{\theta_E}{T}\right)^2 e^{-\theta_E/T}$$

The exponential will dominate at very low temperature

Let's illustrate this low-temperature solution:

```
CLatEinLowT = lambda x: (1/x)**2 * np.exp(-1/x)

plt.plot(x,CLatEin(x), label='Einstein')
plt.plot(x,CLatEinLowT(x),':',label=r'Einstein: $T\ll\theta_E$')
plt.xlim([0,2])
plt.xlabel(r'$T/\theta_E$')
plt.ylabel(r'$C/(3nk_B)$')
plt.grid()
plt.legend(loc=2)
plt.savefig('figs/Einstein-heat-capacity-low-T.pdf')
plt.close('all')
```



Clearly, this is **only valid** for $T \lesssim 0.25\theta_E$.

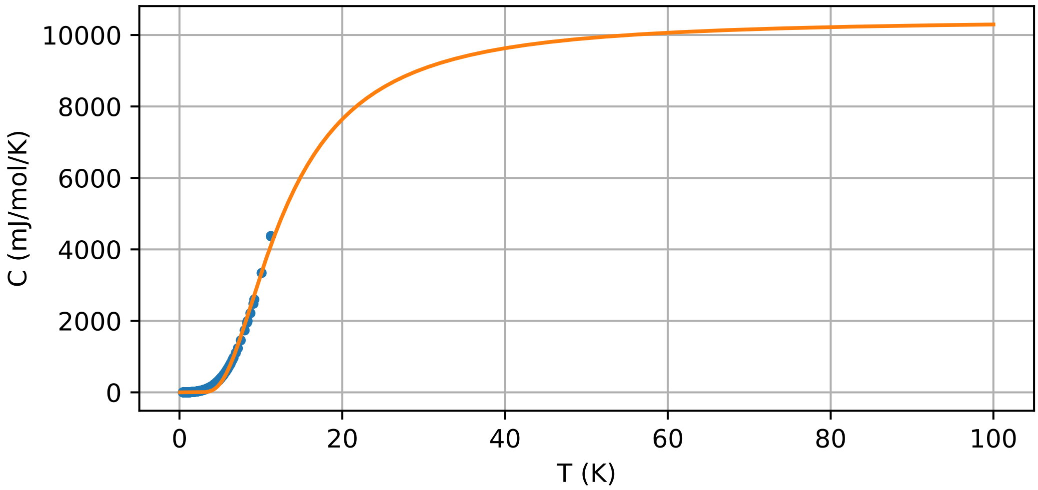
Comparison with experiment

Let's compare with experimental data. The frozen nobel gases again provide a simple physical system which should be described by this model. See Phys Rev 117 1383 (1968), Table I.

The best fit of our model (adjusting Einstein temperature θ_E and number density n), gives something which looks sensible:

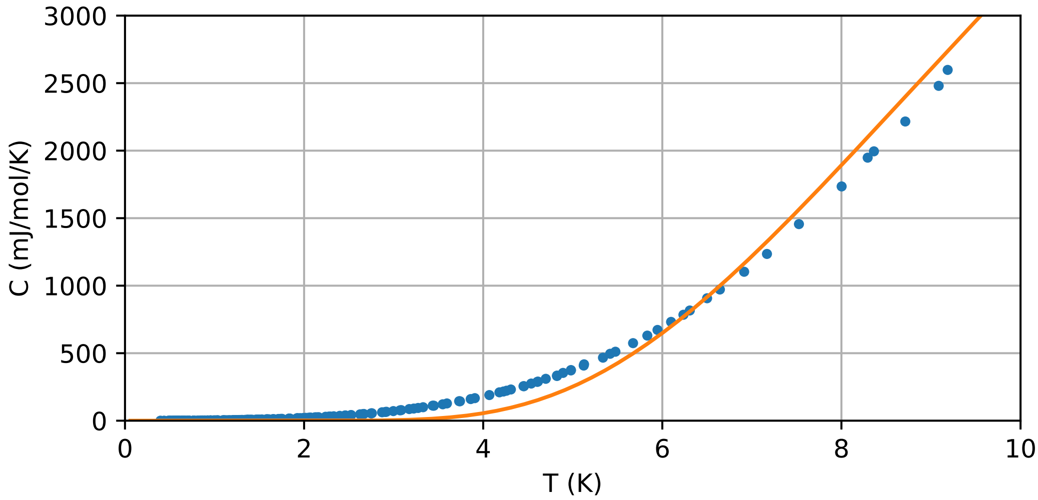
```
from scipy.optimize import curve_fit
data = np.loadtxt('other/finegold1968lowtemperature.csv')
CLatEinScaled = lambda T, TE, U0: U0*CLatEin(T/TE)
pGuessEin = (40., 1e4)
p0Ein, covarianceEin = curve_fit(CLatEinScaled, data[:,0], data[:,1], pGuessEin)

T = np.linspace(0,100,10001)
plt.figure(figsize=(6,3))
plt.plot(data[:,0],data[:,1],'.')
plt.plot(T,CLatEinScaled(T,*p0Ein))
plt.ylabel('C (mJ/mol/K)'); plt.xlabel('T (K)'); plt.grid(); plt.tight_layout()
plt.savefig('figs/Einstein-model-fit.pdf')
```



but if we zoom in on the low-temperature range, we see that it doesn't fit:

```
plt.xlim([0,10]); plt.ylim([0,3000])
plt.savefig('figs/Einstein-model-zoom.pdf'); plt.close('all')
```



Clearly we are missing some important physics. This descrepancy motivates us to try a more sophisticated model: The Debye model.