4261 HW 1

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1a

The partition function given corresponds to

$$Z(\beta) = \frac{1}{(2\pi h)^3} \int \exp\left(-\beta \frac{\vec{p}^2}{2m}\right) d\vec{p} \int \exp\left(-\beta k \frac{\vec{x}^2}{2}\right) d\vec{x}$$

The integral in one dimension

$$I = \int_{-\infty}^{\infty} e^{-ax^2} dx$$

may be calculated by first squaring the integral:

$$I^2 = \int_{-\infty}^{\infty} e^{-ax^2} dx \int_{-\infty}^{\infty} e^{-ay^2} dy = \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} e^{-a(x^2+y^2)} dxdy$$

Transforming to polar coordinates, the Jacobian determinant of which you'll recall is $rdrd\theta$, the above becomes

$$I^2 = \int_0^{2\pi} \int_0^{\infty} re^{-ar^2} drd\theta$$

This can be solved trivially by a u-substitution $u = r^2$, $du = 2rdr$:

$$I^2 = 2\pi \left(\frac{1}{2} \int_0^{\infty} e^{-au} du\right) = \pi \left(-\frac{e^{-au}}{a}\bigg|_0^{\infty}\right) = \frac{\pi}{a}$$

Therefore, the integral is equal to $\sqrt{\frac{\pi}{a}}$.

The integral terms of the partition function are then a product of three such integrals with $a = \frac{\beta}{2m}$ for the three scalar variables of momentum and a product of three such integrals with $a = \frac{\beta k}{2}$ for the three scalar variables of position, i.e.

$$Z(\beta) = \frac{1}{(2\pi h)^3} \left(\sqrt{\frac{\pi}{\beta/2m}}\right)^3 \left(\sqrt{\frac{\pi}{\beta k/2}}\right)^3 = \frac{m^{3/2}}{h^3 \beta^3 k^{3/2}}$$

1b

The expectation of the energy based on the partition function is

$$\langle E\rangle = -\frac{1}{Z}\frac{\partial Z}{\partial \beta} = \frac{h^3\beta^3k^{3/2}}{m^{3/2}}\frac{3m^{3/2}}{h^3\beta^4k^{3/2}} = \frac{3}{\beta} = 3k_BT$$

Differentiating to find the heat capacity,

$$C = \frac{\partial\langle E\rangle}{\partial T} = 3k_B$$

as desired.

2a

The energies of the eigenstates of a one-dimensional harmonic oscillator are $E_{n1D} = \hbar\omega(n+\frac{1}{2})$, so the energies of the eigenstates in the three-dimensional case are

$$E_n = E_x + E_y + E_z = \hbar\omega\left(n_x + n_y + n_z + \frac{3}{2}\right)$$

implying the partition function is

$$Z(\beta) = \sum_{n_x,n_y,n_z\geq 0} e^{-\beta\hbar\omega(n_x+n_y+n_z+3/2)} = e^{-3\beta\hbar\omega/2}\sum_{n_x} e^{-\beta\hbar\omega n_x}\sum_{n_y} e^{-\beta\hbar\omega n_y}\sum_{n_z} e^{-\beta\hbar\omega n_z}$$

$$= e^{-3\beta\hbar\omega/2}\left(\frac{1}{1-e^{-\beta\hbar\omega}}\right)^3$$

The Bose occupation factor is the negative of the term in the cube;

$$n_B(x) = \frac{1}{e^x - 1}$$

Functions with this behavior appear in descriptions of the collective behavior of any particles for which multiple may occupy the same quantum state (so-called bosons).

2b

The general expression for the expectation value of the energy is

$$\langle E\rangle = -\frac{1}{Z}\frac{\partial Z}{\partial \beta} = -e^{3\beta\hbar\omega/2}\left(1-e^{-\beta\hbar\omega}\right)^3\left(e^{-3\beta\hbar\omega/2}\left[-3\hbar\omega e^{-\beta\hbar\omega}\left(\frac{1}{1-e^{-\beta\hbar\omega}}\right)^4\right] - \frac{3}{2}\hbar\omega e^{-3\beta\hbar\omega/2}\left(\frac{1}{1-e^{-\beta\hbar\omega}}\right)^3\right)$$

$$= \frac{-3\hbar\omega e^{-\beta\hbar\omega}}{e^{-\beta\hbar\omega}-1} + \frac{3}{2}\hbar\omega = 3\hbar\omega\left(\frac{1}{e^{\beta\hbar\omega}-1} + \frac{1}{2}\right)$$

The heat capacity is

$$C = \frac{\partial\langle E\rangle}{\partial T} = 3\hbar\omega\left(-\frac{\hbar\omega}{k_BT^2}e^{\beta\hbar\omega}\frac{1}{(e^{\beta\hbar\omega}-1)^2}\right) = 3k_B\left(\beta\hbar\omega\right)^2\frac{e^{\beta\hbar\omega}}{(e^{\beta\hbar\omega}-1)^2}$$

2c

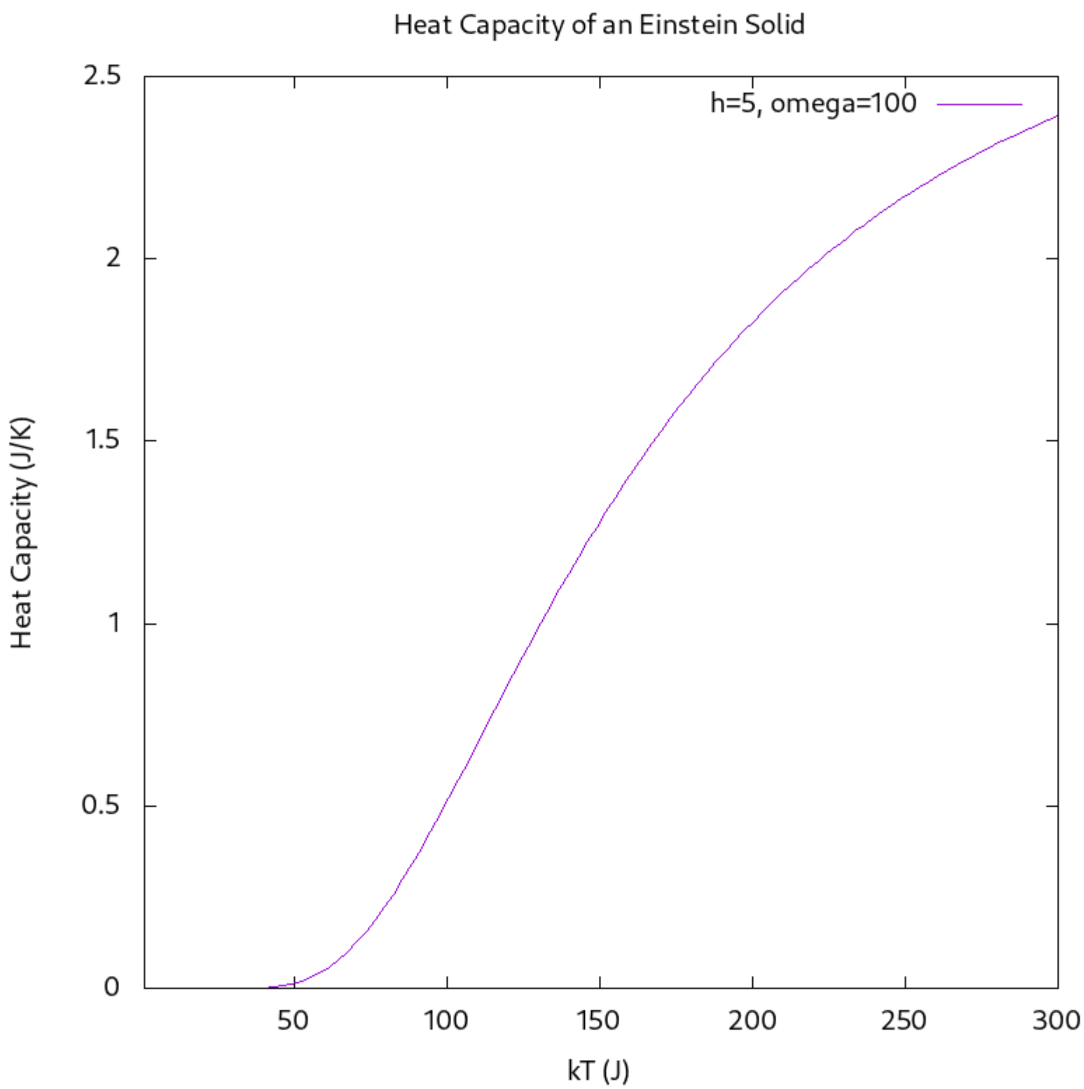
As $\beta \to 0$, and therefore $e^{\beta\hbar\omega} \to 1 + \beta\hbar\omega$, the heat capacity becomes

$$C \to 3k_B(\beta\hbar\omega)^2 \frac{1 + \beta\hbar\omega}{(\beta\hbar\omega)^2} = 3k_B + 3k_B\beta\omega\hbar \to 3k_B$$

which confirms the law of Dulong-Petit.

2d

The heat capacity function with nonsense values of h and ω is gnuplotted below.



3a

The Debeye model presumes that heat-capacity-related oscillations behave like sound waves, and are transverse with three polarizations. It then quantizes these waves following Planck, and imposes a maximum frequency cutoff so that the classical $3N$ vibrational degrees of freedom is retained.

3b

We presume the oscillation modes of the material have frequencies $\omega(k) = v|k|$, and write down the expectation of the energy of an Einstein solid with this firequency:

$$\langle E \rangle = 3 \sum_k \hbar\omega(k) \left(n_B(\beta\hbar\omega(k)) + \frac{1}{2} \right)$$

Applying periodic boundary conditions,

$$\langle E \rangle = 3 \frac{L^3}{(2\pi)^3} \int \hbar\omega(k) \left(n_B(\beta\hbar\omega(k)) + \frac{1}{2} \right) dk$$

Transforming to spherical coordinates and plugging in $k = \omega/v$,

$$\langle E \rangle = 3 \frac{4\pi L^3}{(2\pi)^3} \int_0^\infty \left(\frac{\omega^2}{v^2} \right) \frac{1}{v} \hbar\omega \left(n_B(\beta\hbar\omega) + \frac{1}{2} \right) d\omega = \frac{3L^3}{2\pi^2} \frac{\hbar}{v^3} \int_0^\infty \frac{\omega^3}{e^{\beta\hbar\omega} - 1} + \frac{\omega^3}{2} d\omega$$

$$\langle E \rangle = \frac{3\hbar L^3}{2\pi^2 v^3} \frac{1}{(\beta\hbar)^4} \int_0^\infty \frac{x^3}{e^x - 1} dx + T\text{-independent constant}$$

Differentiating with respect to T,

$$C = \frac{6L^3 k_B^4 T^3}{\pi^2 v^3 \hbar^3} \int_0^\infty \frac{x^3}{e^x - 1} dx$$

3c

This is clearly the T^3 behavior desired for small T. However, for high T, the cutoff frequency becomes important: no longer do we integrate the expected energy over all ω but stop at some ω_c. The original expression for the energy expectation becomes, using $e^x \sim 1 + x$ as $x \to 0$,

$$\langle E \rangle = \frac{3\hbar L^3}{2\pi^2 v^3} \int_0^{\omega_c} \omega^3 \frac{k_B T}{\hbar\omega} d\omega + T\text{-independent constant}$$

The integral is now a finite constant, and so $\langle E \rangle \sim T$ as $T \to \infty$ or $C =$ constant, recovering the $C = 3Nk_B$ behavior of Dulong-Petit.

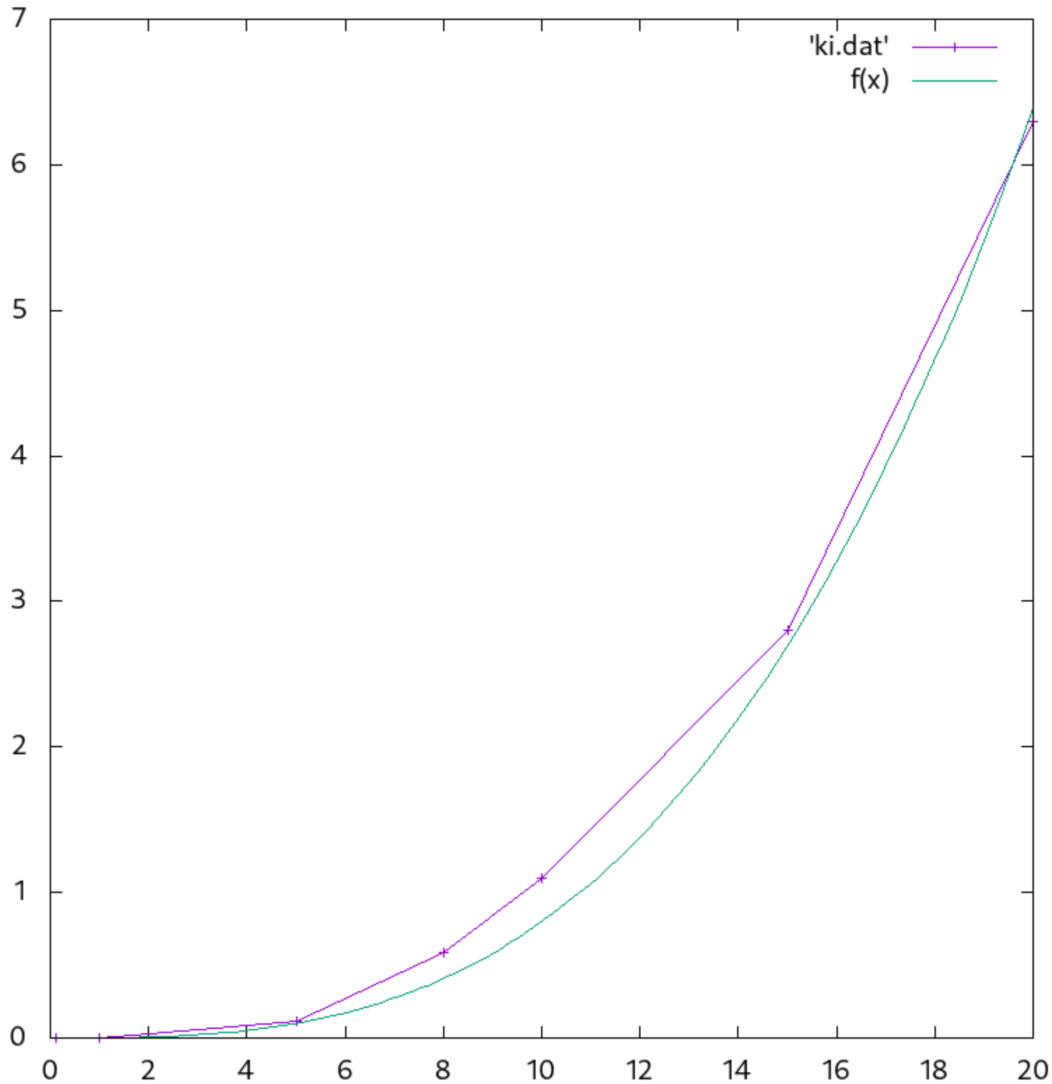
3d

Since the Debeye temperature has the relation

$$C = Nk_B \frac{T^3}{T^3_{Debeye}} \frac{12\pi^4}{5}$$

Computing a fit of c against aT^3 will yield a value for a from which one may compute an estimate of the Debeye temperature. The fit was performed in gnuplot and resulted in

$a = (8.0 \pm 0.2) \times 10^{-4}$ J/mol $\cdot$ K^4; a plot of the data and the fit appear below.



We expect

$$a = \frac{12\pi^4 N_A k_B}{5T^3_{Debeye}} \Leftrightarrow T_{Debeye} = \sqrt[3]{\frac{12\pi^4 N_A k_B}{5a}} = \sqrt[3]{\frac{12\pi^4(6.28 \times 10^{23}\,\mathrm{mol}^{-1})(1.38 \times 10^{-23}\,\mathrm{J/K})}{5(8.0 \times 10^{-4}\,\mathrm{J/mol \cdot K^4})}} = 136{\pm}1\ \mathrm{K}$$

where the error has been computed by $\sigma_{f(a)} = \frac{\partial f}{\partial a}\sigma_a$.