Home work week 3

1. Back to the quantum harmonic oscillator of homework 3. Use the partition function you've obtained then (or if you haven't obtain it now!), to plot as function of temperature

   - the entropy
   - the heat capacity ($C = \frac{\partial U}{\partial T}$)
   - the Helmholtz free energy

2. We're going to use the results obtained from the quantum harmonic oscillator once more. A molecule of H_2 and a molecule of D_2 collide and undergo the reaction:

$$\mathrm{H_2 + D_2 \rightarrow 2HD} \tag{1}$$

   Forget about the rotation and translation for now and consider only quantized harmonic vibrations with angular frequency

$$\omega = \sqrt{\frac{k}{\mu}} \tag{2}$$

   with μ the reduced mass of the oscillator

$$\mu = \frac{m_1 m_2}{m_1 + m_2} \tag{3}$$

   and m_1 and m_2 the masses of the two atoms. The mass of the proton is $m_{\mathrm{H}} = 1.6726\ 10^{-27}$ kg while the mass of the deuteron is $m_{\mathrm{D}} = 3.3435\ 10^{-27}$ kg. The vibrational frequency of H_2 is $\nu = \frac{\omega}{2\pi} = 131$ ThZ, while the frequency of D_2 is 93 THz. Assume furthermore that the force constant k does *not* depend on the mass of the nuclei (This is a reasonable assumption, as the interacton with the electrons, which keep the two nuclei together, does not depend on the nuclear masses). Finally, $\hbar = 1.0546\ 10^{-34}$ Js.

Calculate the change in Helmholtz free energy (ΔA) of the reaction at

- 1 K
- 10 K
- 100 K
- 1,000 K

3. Derive an expression for the partition function of a single *classical* harmonic oscillator:

$$E(p, x) = \frac{p^2}{2m} + \frac{1}{2}m\omega^2 x^2 \tag{4}$$

where $m\omega^2 = k$ as in the quantum harmonic oscillator above, m is the mass, p the momentum and x the position. Because in classical mechanics the energy levels form a continuum rather than a discrete set, we replace the sum by an integral

$$\sum_i \exp[-\beta E_i] \rightarrow \int_0^\infty \exp[-\beta E]dE = \int_{-\infty}^\infty \exp[-\beta E(p, x)]dpdx \tag{5}$$

Hints (equation A.31 in the book):

$$\int_{-\infty}^\infty \exp[-ax^2] = \sqrt{\frac{\pi}{a}} \tag{6}$$

$$\int_{-\infty}^\infty x^2 \exp[-ax^2] = \frac{1}{2a}\sqrt{\frac{\pi}{a}} \tag{7}$$

Next, take N *distinguishable* classical harmonic oscilators and write down an expression for the

- entropy S
- average energy $U = \langle E \rangle$

- Helmholtz free energy A