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Year 2, Energy and Entropy
Problem Set 3

Boltzmann factor and equipartition theorem

1. The average kinetic energy ($3k_BT/2$) of hydrogen atoms in a stellar gas is 1eV. What is the ratio of the number of atoms in the second excited state ($n = 3$) to the number in the ground state ($n = 1$)? The energy levels of the hydrogen atom are $\epsilon_n = -\alpha/n^2$ where $\alpha = 13.6$eV, and the degeneracy of the nth level is $2n^2$.

2. A box contains a large number N of non-interacting 2-state systems, each of which can have energy 0 or ϵ. The box is in thermodynamic equilibrium with a heat reservoir at temperature T. Draw labelled diagrams showing

(a) the energy

(b) the heat capacity of the box

as a function of T, and explain the behaviour.

3. A system has non-degenerate energy levels with energy $\epsilon = (n + \frac{1}{2})\hbar\omega$ where $\hbar\omega = 1.4 \times 10^{-23}$J and n a positive integer or zero. What is the probability that the system is in the $n = 1$ state if it is in contact with a heat bath of temperature 1K?

4. Consider the partition function of a *classical* simple harmonic oscillator (SHO),

$$Z = c\int_{-\infty}^{\infty} \mathrm{d}p \int_{-\infty}^{\infty} \mathrm{d}x \exp\left[-(p^2/2m + fx^2/2)/kT\right],$$

where x is the position of the particle, measured from the bottom of the potential well, $fx^2/2$ is the potential energy (f is the spring constant), p is the momentum of the particle in the well and $p^2/2m$ its kinetic energy. Calculate this partition function and compare it with the partition function of a quantum-mechanical SHO.

Find the high temperature limit of the quantum SHO and show that it has the same form as the partition function of a classical SHO, i.e., same dependence on temperature.

You may need:

$$\int_{-\infty}^{\infty} \exp(-Az^2)dz = \left(\frac{\pi}{A}\right)^{1/2},$$

when A is any positive constant.

5. If a system is known to obey the equipartition theorem, and has a heat capacity of $5k_B$,where k_B is Boltzmann's constant, how many degrees of freedom does it have?

6. Using the equipartition theorem estimate the typical thermal kinetic energy of a molecule of oxygen. Using this energy estimate the typical thermal velocity of a molecule of oxygen (molecular mass $= 5 \times 10^{-26}$kg) at room temperature, 300 K. If the temperature is doubled, by what factor does the typical thermal velocity increase by?

7. Calculate the average rotational energy per molecule and the rotational heat capacity per molecule for heteronuclear diatomic molecules in the region $k_B T \gg \epsilon$.

8. A non-linear triatomic molecule has nine modes: three for translation, three for rotation, and three for vibration. What is the expected heat capacity per molecule at high temperatures?

Sketch the heat capacity as the temperature is lowered.

Maxwell-Boltzmann distribution

9. Molecules adsorbed onto the surface of a solid can behave like a two-dimensional gas, so long as they are not too crowded. Assuming that they behave like an ideal gas, show that the mean kinetic energy per molecule is $k_B T$ and find the distribution of molecular speeds (analogous to the Maxwellian distribution for a 3-D gas).

Hint: Use polar coordinates to reexpress the velocity distribution

10. A monatomic gas is contained in a vessel from which it leaks through a fine hole. The number of atoms striking unit area in unit time is $dN = \frac{1}{4} n v P(v) dv$ where

$$P(v) = 4\pi \left(\frac{m}{2\pi k_B T} \right)^{\frac{3}{2}} v^2 \mathrm{exp} \left(-\frac{mv^2}{2k_B T} \right)$$

is the Maxwell-Boltzmann distribution. Determine the number of atoms passing per second through a small hole in the gas container by integrating dN over all velocities. Obtain their total kinetic energy by integrating $\frac{1}{2} m v^2 dN$ over all velocities, and hence show then mean kinetic energy of the atoms leaving the container is $2k_B T$. Comment on why this is greater than $3/2 k_B T$.

Hint: First find $N = \int_0^\infty \frac{1}{4} n v P(v) dv$, then calculate $KE = \int_0^\infty \frac{1}{2} m v^2 \frac{1}{4} n v P(v) dv$. KE/N gives the average kinetic energy. Note that $\int_0^\infty x^n e^{-x} dx = n!$