Week 2 Key Concepts

- **Ideal gases**: large number of molecules; they are small; positions and velocities evenly distributed; Newton's laws; eleastic collisions with each other and walls.
- $P = \frac{1}{3}mn\bar{v^2}$
- $PV = \frac{1}{3}mN\bar{v^2} = \frac{2}{3}U$ (where U is the internal (kinetic) energy)
- Temperature is a measure of internal energy: equipartition theorem says $U/dof = \frac{1}{2}kT$
- Molar heat capacity: $C = \frac{dU}{dT} = \frac{R}{2} \times dof$
- Boltzmann probability: $P(E) \propto e^{-E/kt}$

Tutorial problems

1. We have seen the Boltzman factor P(E) $\propto e^{-E/kT}$ in lectures. Discuss with your tutor the general form of an expression for the mean speed of N molecules in a gas.

   Also give an expression for the fraction of molecules with a speed between v_1 and v_2.

2. The mean speed of a H_2 molecule at room temperature is about $2,000\,\mathrm{m/s}$, while it is $500\,\mathrm{m/s}$ for O_2. Explain how these numbers relate to the near absence of H_2 in the earth atmosphere.

3. We have derived the equation
   $$P = \frac{1}{3}mn\left\langle v^2\right\rangle$$
   expressing the pressure exerted by an ideal gas in terms of the number density of molecules, the mass of one molecule, and the mean-squared speed of molecules. The derivation made the assumption that molecules bounce elastically off solid surfaces. In reality, a molecule may well stick to the surface for a while, until it is "joggled" off – or knocked off by another molecule. Does this invalidate our result?

Problem Class Questions

1. Consider a 1m^3 of nitrogen molecules at standard temperature and pressure. If you treat it as an Ideal gas:

   - how many molecules are there?
   - What is the average speed of a molecule?
   - What is the average kinetic energy of a molecule?
   - Why in reality do the molecules carry a larger amount of energy than this?

2. Consider water vapour at 100C and constant volume. The three vibrational modes of a water molecule have inverse wavelengths (a measure of frequency) 3656.7, 1594.8 and 3755.8cm^{-1}, while the rotational ones are 27.9, 14.5 and 9.3cm^{-1}.

   - Write down the translational mode contribution to the molar heat capacity (at constant volume).
   - Are the vibrational modes active?
   - Are the rotational modes active?
   - Estimate the molar heat capacity (at constant volume).
   - How does this value compare to the experimental one of $C_V = 26.1\text{JK}^{-1}\text{mole}^{-1}$? Suggest a reason for any discrepancy.

3. Cryopumping is the use of very low temperatures to produce a vacuum in an enclosed space. The inner chamber of a helium cryostat (a container that maintains the low temperature) is surrounded by a space to be evacuated. Under these conditions, the number of gas atoms, in the space to be evacuated, hitting the walls per second is given by $\frac{1}{4}n < v > A$, where n is the number of molecules per unit volume, $< v >$ the mean speed of the molecules and A the area of the walls. The chamber is pre-cooled with liquid nitrogen (T = 77 K) before some liquid helium (T = 4.2 K) is transferred to the inner chamber. Once the inner chamber becomes sufficiently cold, every time a gas molecule in the vacuum space hits the chamber wall, it sticks permanently – until the cryostat warms up.

   - Show that if the vacuum space is sealed off, cryopumping will cause its pressure to decrease exponentially with time.
   - Estimate the time constant for the cryopumping process, assuming that the mean speed of a gas molecule in the vacuum space is around 130 ms^{-1}. Assume that the volume of the vacuum space is 10^{-2} m^3 and that the area of the chamber wall is 0.1 m^2.