Lecture 20 (2-3), Mar 3, 2023

Equipartition Theorem Continued

- For an n-atom molecule, there is always $3n$ total degrees of freedom since there are 3 DoF for each atom
  - For linear and nonlinear molecules, CoM translation takes up 3 DoF
  - For nonlinear molecules, rotation takes up 3 DoF; for linear molecules rotation only take up 2 DoF because rotation around the axis of symmetry is not a degree of freedom
  - This leaves $3n-6$ vibrational degrees of freedom for nonlinear molecules and $3n-5$ for linear molecules
- This gives energy per molecule of $3\frac{kT}{2}+2\frac{kT}{2}+2(3n-5)\frac{kT}{2}=\frac{kT}{2}(6n-5)$ for a linear molecule and $\frac{kT}{2}(6n-6)=(3n-3)kT$ for a nonlinear molecule

Heat and Work

- For ideal gases energy is given by the equipartition theorem, equal to the number of particles times the energy of each particle
  - The ideal gas assumes the total energy is just the kinetic energy; this implies that the particles don't interact, because interactions would require potential energy
  - However interactions between particles is required for the gas to reach equilibrium
  - An ideal gas is a gas where there is just enough interaction to enable the gas to go to TD equilibrium, but interactions are rare enough that the ideal gas law holds
- How do we change the energy of a system?
  - We will use a diatomic molecule, $U=\frac{7}{2}kTN$
  - Consider putting a thermostat (a very large thermal body) with temperature T' in contact with a small body of temperature T; heat transfer will occur
  - After a while, the thermostat is removed, and now we have a system with temperature T'
  - The initial energy is $U_i=\frac{7}{2}NkT$, the final energy is $U_f=\frac{7}{2}NkT'$, which give a difference in energy of $\frac{7}{2}Nk(T'-T)$ which is the total heat absorbed
  - This is the first law of thermodynamics, $\Delta U=Q+W$ or energy conservation
- When we do work on the system, the particles that hit the wall will bounce back with greater velocity; this is why doing work on the system heats it up

Heat Capacity

Definition

The heat capacity is the amount of energy needed to change T by 1 degree

- However we have to specify which quantity we would like to keep fixed, whether that's V or p or something else
- We know $U=\frac{7}{2}NkT$ which gives a heat capacity of $\frac{7}{2}Nk$
- Heat capacity should stay constant with increasing T, but it does not – the constant only occurs around temperatures of 10000K
  - Below this temperature the heat capacity increases to discrete levels with increasing T
  - This is because of quantum mechanics
- At low temperatures there are only translational movements, then vibrational and transitional, and finally rotational, vibrational and translational at higher temperatures
  - At lower temperatures the collisions do not have enough energy to excite vibrational/rotational modes

- Because of quantum mechanics, the molecules can either not rotate but rotate with some minimum energy