# Lecture 19 (2-2), Mar 2, 2023

## Temperature as a Measure of Average Kinetic Energy

- Several assumptions:
  - Molecules are uniformly distributed in space (at TD equilibrium)
  - Velocities are isotropically distributed (i.e. the number of particles with velocity in any given direction is the same)
    * This means $\frac{1}{N}\sum_{i=1}^{N} v_{xi} = 0$ since there are always the same number of particles going in the positive vs. negative directions
  - The major assumption of the molecular model: all molecules have the same average speed in time
    * Let $\frac{1}{N}\sum_{i=1}^{N} v_{xi}^2 = \bar{v}^2$
    * For now we assume all molecules move with the same speed that is the average
- Consider one wall with area $A$; what is the average force exerted on the wall due to the molecules?
  - How many molecules collide with the wall in time $\Delta t$?
    * Consider a volume formed by extending the area $A$ a distance $L$ into the gas, where $L = \bar{v}\Delta t$
    * Assume all molecules in the volume are moving either in the $+x$ or $-x$ directions (by isotropy this means each would have half the molecules)
      - We can integrate over solid angles if we don't make this assumption, but the conclusion is the same
      - Combined with the speed, this means all molecules in the box that are moving in the $+x$ direction would hit the wall, and no molecules outside the box will hit the wall (i.e. half of the molecules hit the wall)
    * Therefore the number of molecules that hit is $\frac{1}{2}\frac{N}{V}V = \frac{1}{2}\frac{N}{V}LA = \frac{1}{2}\frac{N}{V}\bar{v}\Delta tA$
  - What is the force caused by the collisions?
    * Each molecule has momentum $m\bar{v}$, which becomes $-m\bar{v}$ after colliding with the wall; therefore the total momentum transferred is $2m\bar{v}$
    * Total momentum transferred is then $\frac{N}{V}m\bar{v}^2\Delta tA$
    * Since $F = \frac{\mathrm{d}p}{\mathrm{d}t}$ the force is $\frac{N}{V}m\bar{v}^2A$
  - Therefore the pressure produced by this is $m\bar{v}^2\frac{N}{V}$
- Bring in the ideal gas law: $p = kT\frac{N}{V} = m\bar{v}^2\frac{N}{V}$, we get the conclusion that $kT = m\bar{v}^2$
  - Therefore temperature is a measure of the kinetic energy
  - But note $\bar{v}$ is only in the $x$ direction - what if we bring in the other directions?
  - With our isotropic assumption, we know that $\bar{v}$ is the same in any direction
  - Now consider $\overline{\vec{v}^2} = \frac{1}{N}\sum_i \|\vec{v}\|^2 = \frac{1}{N}\sum_i v_{xi}^2 + v_{yi}^2 + v_{zi}^2 = 3\bar{v}^2$
  - Therefore $kT = m\bar{v}^2 = \frac{1}{3}m\overline{\vec{v}^2} \implies \frac{1}{2}m\overline{\vec{v}^2} = \frac{3}{2}kT$
- $\overline{\vec{v}^2} = \frac{3kT}{m}$ let $v_{rms} = \sqrt{\overline{\vec{v}^2}} = \sqrt{\frac{3kT}{m}}$
  - If we plugin numbers for e.g. nitrogen, we get hundreds of meters per second
  - This is also roughly the speed of sound

**Important**

For an ideal gas, $\frac{3}{2}kT$ is the average kinetic energy of the molecules in the gas

## Classical Equipartition Theorem

- $T$ being a measure of average kinetic energy is an example of the classical equipartition theorem, which is proven using SM

**Theorem**

Classical equipartition theorem: In thermodynamic equilibrium of a classical ideal gas, the average energy per degree of freedom of a molecule is:

1. Translational: $\frac{1}{2}kT$
2. Rotational: $\frac{1}{2}kT$
3. Vibrational: $kT$

- Depending on the kind of molecule, we can calculate what degrees of freedom it has and how many, from which we can calculate the average energy from the temperature
- This allows us to predict the heat capacity of gases
  - Actual heat capacities deviated from the prediction of the classical equipartition theorem because of quantum mechanics
- e.g. For a diatomic molecule, each atom has 3 DoF; overall in the molecule there are 3 translational degrees of freedom of the CoM, and 2 rotational degrees of freedom, and 1 vibrational degree of freedom
  - Therefore the average energy is $\frac{3}{2}kT + \frac{2}{2}kT + kT = \frac{7}{2}kT$
  - $U = N\frac{7}{2}kT$
- The idea of the equipartition theorem is that through collisions energy is distributed into all degrees of freedom (translational, rotational and vibrational)
- The reason reality deviates from this is due to the quantized vibrational energies in $\hbar\omega$ (since vibrations are harmonic oscillators), so if a molecule doesn't have enough energy it can't transfer energy into the vibrational degrees of freedom
  - If $kT \gg \hbar\omega$ then this won't have much effect, but at much lower temperatures this becomes important