Lecture 16  Statistical Physics

* Statistics & probability theory are very useful & powerful in physics.
  In particular, Stat. Mechanics provides a solid foundation for Thermodynamics
devolved in 19th Century for Heat engine & Industrial Revolution.
Thermodynamic systems: 
  # of microscopic particles ~ Avogadro's # (\(N_A = 6.02 \times 10^{23}\))

1. **Ideal gas.** (A good approximation for most gases at ambient)
   Ideal gas: non-interacting gas molecules (except collisions), randomly moving in space
   → Thus, internal energy \(U\) is solely determined by kinetic energy of molecule

   **Ideal gas law:** \(PV = nRT\)
   \(P\): pressure (N/m\(^2\)) \(V\): volume (m\(^3\)) \(n\): # of moles of the gas
   \(R\): universal gas constant (J/K·mol)
   \(T\): Temperature (K)
   \(R = 8.31\) (J/K·mol).
   \(R = N_A \cdot k_B \) \(k_B\): Boltzmann constant. \(k_B = 1.381 \times 10^{-23}\) J/K.

   Total # of molecules: \(N = n \cdot N_A\)

   **Ideal gas law:** \(PV = N k_B T\) more convenient for physicists.
   Ideal gas law can be derived from Stat. Mech. (microcanonical ensemble)

1. **Kinetic Theory of ideal gas.** (for convenience, called gas)
   Consider a molecule inside a container (box).
   Moving w/ speed \(u_x\) along \(x\) axis.
   only elastic collision on walls.
   Pressure on 1 side \(P = \frac{F}{A}\)
   \(F \cdot \Delta t = \Delta P = 2m u_x \Rightarrow \langle F \rangle = \frac{\Delta P}{\Delta t} = \frac{2m u_x}{\Delta t}\)
   \(\Rightarrow P = \frac{m \langle u_x^2 \rangle}{A \cdot L} = \frac{m \langle u_x^2 \rangle}{V}\)
   \(\langle K.E. \rangle_x = \frac{\langle 1/2 m u_x^2 \rangle}{2} = \frac{1}{2} k_B T\)
   Equipartition theorem
   (will be discussed later).
   \(\Rightarrow PV = 2 \langle K.E. \rangle = m \langle u_x^2 \rangle\)
   \(\Rightarrow PV = k_B T\)

   For gas \(u / N\) molecules (independent), the pressure adds up, i.e. \(PV = N k_B T\)!
Internal energy (random kinetic energy of gas molecules) link to

\[ U = N \left( \frac{1}{2} m v^2 \right) = N \cdot \frac{1}{2} m \left( \langle u_x^2 \rangle + \langle u_y^2 \rangle + \langle u_z^2 \rangle \right) \]

\[ = \frac{1}{2} m \left( \langle u_x^2 \rangle + \langle u_y^2 \rangle + \langle u_z^2 \rangle \right) \]

Equation of motion

\[ \frac{1}{2} m \langle u_x^2 \rangle = \frac{1}{2} k_B T \]

\[ \frac{1}{2} m \langle u_y^2 \rangle = \frac{1}{2} k_B T \]

\[ \frac{1}{2} m \langle u_z^2 \rangle = \frac{1}{2} k_B T \]

Internal # of degree of freedom (DOF)

\[ \frac{3}{2} N k_B T \]

(a good thermometer!)

Constant V Heat capacity:

\[ C_v = \frac{\partial Q}{\partial T} \bigg|_V = \frac{\partial U}{\partial T} \bigg|_V = \frac{3}{2} N k_B = \frac{3}{2} nR. \]

For diatomic molecules there are rotational & vibrational DOF.

\[ 2 \text{ (rotational)} \quad \frac{7}{2} \text{ (vibrational)} \]

Rotation:

\[ E = \frac{1}{2} I \omega^2 \]

Vibration:

\[ E_v = (n+1) \hbar \omega \]

\[ \omega = \sqrt{\frac{k_B T}{4\pi \hbar}} \]

\[ \Delta E \text{ is larger than thermal energy} \]

2. Thermodynamic Laws.

0th = 2 systems are in thermal equilibrium have the same T.

1st = (Energy conservation)

\[ \Delta U = \Delta Q - W \]

\[ \Delta Q \text{ Heat flow into the system} \]

\[ \Delta W \text{ work done by the system} \]

2nd = Entropy (S) of an isolated system always tend to increase

\[ S \geq 0 \]

Arrows of time!

3rd: Absolute zero temperature (0K) is unattainable

\[ T \rightarrow 0 \quad S \rightarrow 0 \]

* These laws can be understood naturally w/ statistical mechanics.

\[ S = k_B \ln \Omega \]

Boltzmann formula:

\[ \Omega = \Omega (M, V, N) \]

multiplicity: # of micro-states for given (U, V, N)
$S(\Omega)$ is a measure of the "randomness" of the system.
Since prob. of a given macro-state $\propto \Omega$, the system will always evolve toward Max. ($S$), i.e. Max ($S$) $\rightarrow$ 2nd law!

At equilibrium, $S$ is a state function of $(U, V, N)$, i.e. independent of the path. Often called $S = \text{thermodynamic potential}$

$S$ is also a thermodynamic potential,

$$ds = \frac{1}{T} du + \frac{P}{T} dv (-\frac{1}{T} dN). \quad T^{-1} \equiv \frac{\partial S}{\partial u} \text{at} \; N, \; V.$$

or

$$dU = Tds - Pdv (\text{at} \; u, \; N) \rightarrow 1\text{st law}!$$

Heat: $Q = \Delta W$ (4th Law)

[Note: $S$ of ideal gas can be obtained using particle in a box (QM).]

$\times \quad \text{Boltzmann factor} \cdot P(e) \propto e^{-\beta E}$ \hspace{1cm} $\beta = \frac{1}{k_b T}$

$E$: energy of a microstate of a system in thermal equilibrium w/ a bath $T$.

Canonical Ensembles: $(U, V, N)$, closed system

Probability of the system @ $E$: $\mathcal{P}$:

$$\mathcal{P}(e) \propto e^{-\beta E} \cdot \frac{S_{\text{Bath}}}{S_{\text{Bath}}(U-e)} = \frac{S_{\text{Bath}}(U-e)}{S_{\text{Bath}}(U)}$$

$S = k_b \ln \Omega = \mathcal{P} = \frac{S_{\text{Bath}}(U-e)}{S_{\text{Bath}}(U)}$ \hspace{1cm} $\rightarrow$ $\mathcal{P}(e) \propto e^{\frac{S_{\text{Bath}}(U-e)}{k_b T}}$

$S_{\text{Bath}}(U-e) \approx S_{\text{Bath}}(U) + 8 \frac{\partial S}{\partial U} \cdot (-e) = S_{\text{Bath}}(U) - \frac{e}{T}$

Taylor expansion \hspace{1cm} $= T^{-1}$ \hspace{1cm} a constant

$\rightarrow \mathcal{P}(e) \propto e^{\frac{S_{\text{Bath}}(U)}{k_b T}} \cdot e^{-\frac{e}{k_b T}} \propto e^{-\beta E}$ !

$\times \quad$ Application of Boltzmann factor ($e^{-\beta E}$) on ideal gas $\rightarrow$ Maxwell velocity distribution

often called: Maxwell-Boltzmann distribution
Maxwell's velocity distribution.

\[ P(v_x) \propto e^{-\beta v_x^2} \quad E_x = \frac{1}{2} m v_x^2 \quad \text{for a molecule in ideal gas.} \]

\[ P(u_x) = c e^{-\beta (\frac{1}{2} m u_x^2)}, \quad u_x \in (-\infty, +\infty) \quad c: \text{constant.} \]

\[ \Rightarrow \int_{-\infty}^{\infty} P(u_x) du_x = 1 \Rightarrow \Phi = c \int_{-\infty}^{\infty} e^{-\beta (\frac{1}{2} m u_x^2)} du_x = 1 \]

\[ \Rightarrow c = \frac{1}{\int_{-\infty}^{\infty} e^{-\beta (\frac{1}{2} m u_x^2)} du_x}. \]

\[ \text{Let} \quad u = \sqrt{\frac{m}{2 k_b T}} v_x \quad v_x = \sqrt{\frac{2 k_b T}{m}} u \quad \Rightarrow du_x = \frac{2 k_b T}{m} du. \]

\[ \int_{-\infty}^{\infty} e^{-u^2} du \quad \text{Gaussian integral} \quad \int_{-\infty}^{\infty} e^{-y^2} dy = \pi \Rightarrow I = \sqrt{\pi}. \]

\[ P(v_x) = \sqrt{\frac{m}{2\pi k_b T}} e^{-\frac{m v_x^2}{2 k_b T}} \quad [\text{HW. show } \langle v_x^2 \rangle = \frac{k_b T}{m}] \]

Similarly

\[ P(v_y) = \sqrt{\frac{m}{2\pi k_b T}} e^{-\frac{m v_y^2}{2 k_b T}} \quad P(v_z) = \sqrt{\frac{m}{2\pi k_b T}} e^{-\frac{m v_z^2}{2 k_b T}} \]

\[ \Rightarrow P(v_x, v_y, v_z) = P(v_x) \cdot P(v_y) \cdot P(v_z) = \left( \sqrt{\frac{m}{2\pi k_b T}} \right)^3 e^{-\frac{m (v_x^2 + v_y^2 + v_z^2)}{2 k_b T}} \]

MB \( \overline{v^2} \): Speed distribution. \( \overline{v^2} = v_x^2 + v_y^2 + v_z^2 \)

\[ P(v) \, dv = (P(v_x) P(v_y) P(v_z)) \, dv_x \, dv_y \, dv_z = \left( \frac{m}{2\pi k_b T} \right)^{\frac{3}{2}} v^2 e^{-\frac{m v^2}{2 k_b T}} \]

\[ \Rightarrow \overline{v^2} = 4\pi \cdot \left( \frac{m}{2\pi k_b T} \right)^{\frac{3}{2}} \quad \overline{v^2} = \overline{v_x^2} + \overline{v_y^2} + \overline{v_z^2} \]

\[ \overline{v} = \left( \frac{3}{4} \right)^{\frac{1}{2}} \overline{v^2} \cdot \overline{v} \quad \overline{v} = \frac{1}{\sqrt{3}} \overline{v^2} \]

\[ \overline{v_{rms}} = \sqrt{\overline{v^2}} \]