Translational Energy Mode

- Begin by examining relations between TD properties and pure translational motion, i.e., translational energy
- Represents
  - complete energy of structureless particle, e.g., electron or proton in absence of electric field
  - TD properties associated with translational mode of particle with internal energy modes assuming ε_{tr} and ε_{int} are separable (most gases)
- Use particle in a “box” model (confined)

Translational Partition Function

- Translational energy modes $\varepsilon_{tr}(n_x, n_y, n_z) = \frac{h^2}{8m}\left(\frac{n_x^2}{L_x^2} + \frac{n_y^2}{L_y^2} + \frac{n_z^2}{L_z^2}\right)$
- Translational partition function

$$Q = \sum_i g_i e^{-\varepsilon_i/kT} \quad \eta_i \equiv \frac{h}{2L_i}\left(\frac{1}{2mkT}\right)^{1/2} \quad Q_{tr} = \sum_{n_x=1}^{\infty} e^{-\eta_x^2 n_x^2} \sum_{n_y=1}^{\infty} e^{-\eta_y^2 n_y^2} \sum_{n_z=1}^{\infty} e^{-\eta_z^2 n_z^2}$$

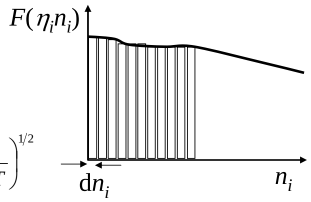
- Can simplify analytically if we replace Σ with ∫
  - spacing of expon. arguments?

$$\Delta_i = \eta_i^2\left[(n_i + 1)^2 - n_i^2\right] = \eta_i^2\left[2n_i + 1\right]$$

  - for N_2 at SATP, η_i~10^{-9}
  - previously (Boltzmann limit), we found $n_{i,KE_{avg}} \approx 4\times10^8$ $\Rightarrow\Delta_i$=O(10^{-9})……small!!!

Translational Partition Function

$$Q_{tr,i} = \sum_{n_i=1}^{\infty} e^{-\eta_i^2 n_i^2} = \sum_{n_i=1}^{\infty} e^{-\eta_i^2 n_i^2} \frac{\eta_i n_i}{\eta_i n_i}$$



- Since Δ_i small

$$Q_{tr,i} \cong \int_0^{\infty} e^{-\eta_i^2 n_i^2} \frac{d(\eta_i n_i)}{\eta_i}$$

$$\cong \frac{1}{\eta_i} \frac{\sqrt{\pi}}{2} \qquad \eta_i \equiv \frac{h}{2L_i}\left(\frac{1}{2mkT}\right)^{1/2}$$

$$Q_{tr} = Q_{tr,x} Q_{tr,y} Q_{tr,z} \cong \frac{\pi^{3/2}}{8}\left[\frac{h}{2}\left(\frac{1}{2mkT}\right)^{1/2} \frac{1}{L_x L_y L_z}\right]^{-1} \qquad L_x L_y L_z = V$$

=volume

$$\boxed{Q_{tr} \cong \left(\frac{2\pi mkT}{h^2}\right)^{3/2} V}$$

Thermal DeBroglie Wavelength (for system)

Boltzmann (dilute) limit valid for

$$Q_{tr} = V/\Lambda^3 \qquad \Lambda \equiv \left(\frac{h^2}{2\pi mkT}\right)^{1/2} \qquad N << V/\Lambda^3$$

Translational TD Properties

- What are TD properties of translating particle
  - use Partition Function relations found previously
- **Pressure**

$$p = NkT \left.\frac{\partial \ln Q}{\partial V}\right|_{E,N} \qquad Q_{tr} = V/\Lambda^3$$

$$p_{tr} = NkT \frac{1}{Q_{tr}} \left.\frac{\partial Q_{tr}}{\partial V}\right|_{E,N} = NkT \frac{\Lambda^3}{V} \frac{1}{\Lambda^3}$$

$$\boxed{p_{tr} V = NkT}$$

Thermally Perfect (Ideal) Gas Eqn. of State

$$k = \overline{R}/N_{Av}$$
$$n(moles) = N/N_{Av}$$

- So purely translating particle produces TD pressure $p = p_{tr}$

pressure associated strictly with translation energy/motion

Translational TD Properties

- **Energy** $$E = NkT^2 \frac{\partial \ln Q}{\partial T}$$

$$\frac{E_{tr}}{N} = kT^2 \frac{\partial \ln Q_{tr}}{\partial T} = kT^2 \frac{1}{Q_{tr}} \frac{\partial Q_{tr}}{\partial T}$$

$$= kT^2 \frac{1}{bVT^{3/2}} \left(\frac{3}{2} bVT^{1/2} \right)$$

$$Q_{tr} = \left(\frac{2\pi mkT}{h^2} \right)^{3/2} V$$

$$= bT^{3/2} V$$

$$\boxed{\frac{E_{tr}}{N} = \frac{3}{2} kT}$$

average KE per molecule

can also get from Kinetic Theory

$$\hat{e}_{tr} = \frac{3}{2} \bar{R} T \qquad e_{tr} = \frac{3}{2} RT$$

$$c_v = \frac{de}{dT} \qquad \boxed{c_{v,tr} = \frac{3}{2} R}$$

Purely transl. particles both thermally and calor. perfect (if Σ→∫)

TPG ⇒ $\hat{c}_p - \hat{c}_v = \bar{R}$ $\quad \hat{c}_{p,tr} = 5/2\,\bar{R}$ $\quad \gamma = c_p / c_v = 5/3$

Equipartition of Energy

- In classical Statistical Mechanics (before QM)
  - can be shown that every energy mode that is a quadratic function of a degree of freedom of the system (e.g., position or momentum) contributes a value of ½ to c_v/R
  - **Principle of Equipartion of Energy**
- Thus
  $$c_v / R = \text{number of quadratic "modes"} \times \frac{1}{2}$$
- For translational energy mode $\quad \varepsilon_x = \frac{1}{2} m v_x^2 \quad \varepsilon_y = \frac{1}{2} m v_y^2 \quad \varepsilon_z = \frac{1}{2} m v_z^2$

$$\Rightarrow \quad c_{v,tr} / R = 3 \times \frac{1}{2}$$

Same result we got with QM Stat Mech(for Σ→∫)

Translational TD Properties

- **Entropy** $S = Nk\left(1+\ln\frac{Q}{N}\right)+\frac{E}{T}$ $Q_{tr} = \left(\frac{2\pi mkT}{h^2}\right)^{3/2} V = bT^{3/2}V$

$$S_{tr} = Nk\left(1+\ln b+\ln\frac{T^{3/2}V}{N}\right)+\frac{3}{2}Nk$$

$E_{tr} = 3/2\,NkT$

$$= Nk\left(1+\ln b+\frac{3}{2}\ln T+\ln\frac{kT}{p}+\frac{3}{2}\right)$$

$$= Nk\left(\frac{5}{2}\ln T-\ln p+\frac{5}{2}+\ln bk\right)$$

Sachur-Tetrode Equation

absolute entropy

$$\boxed{\frac{\hat{s}_{tr}}{\bar{R}} = \underset{\uparrow\ \hat{c}_p/\bar{R}}{\frac{5}{2}}\ln T-\ln p+\underbrace{\left(\frac{5}{2}+\ln\frac{(2\pi m)^{3/2}k^{5/2}}{h^3}\right)}_{\text{const. for given particle } m}}$$

gives familiar cpg result

$$\frac{\Delta\hat{s}_{12}}{\bar{R}} = \frac{\hat{c}_p}{\bar{R}}\ln\frac{T_2}{T_1}-\ln\frac{p_2}{p_1}$$

Translational TD Properties

- **Chemical Potential** $\tilde{\mu} = -kT\ln\frac{Q}{N}$

$Q_{tr} = \left(\frac{2\pi mkT}{h^2}\right)^{3/2} V = bT^{3/2}V$

$$\tilde{\mu}_{tr} = -kT\left(1+\ln b+\ln\frac{T^{3/2}V}{N}\right)$$

$$= -kT\left(\frac{5}{2}\ln T-\ln p+\ln bk\right)$$

$$\boxed{\mu_{tr} = \underbrace{\bar{R}T\left(\ln\frac{h^3}{(2\pi m)^{3/2}k^{5/2}}-\frac{5}{2}\ln T\right)}_{\mu_{tr}^{o}(T)}+\bar{R}T\ln p}$$

compare to tpg result

$$\mu = \mu^{o}(T)+\bar{R}T\ln p$$

sign ($<$ *or* $>$ 0?)

Summary – Translational Energy Mode

- In the limit Δ_i small $\quad Q_{tr} \cong \left(\frac{2\pi mkT}{h^2}\right)^{3/2} V$

$$E_{tr}/N = \frac{3}{2}kT \qquad c_{v,tr}/R = 3/2$$

$$p_{tr} = p = NkT/V$$

$$\frac{\hat{s}_{tr}}{\overline{R}} = \frac{5}{2}\ln T - \ln p + \left(\frac{5}{2} + \ln\frac{(2\pi m)^{3/2}k^{5/2}}{h^3}\right)$$

$$\mu_{tr} = \left(\ln\frac{h^3}{(2\pi m)^{3/2}k^{5/2}} - \frac{5}{2}\ln T\right)\overline{R}T + \overline{R}T\ln p$$