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

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

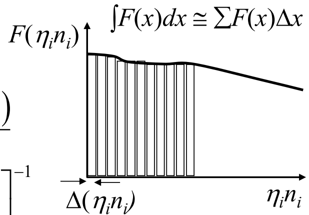
- Can simplify analytically if we replace Σ with $\int$
  - spacing of exponential arguments ($\eta_i n_i$)?

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

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

Translational Partition Function

$$Q_{tr,i} = \sum_{n_i=1}^{\infty} e^{-\eta_i^2 n_i^2} \qquad \eta_i \equiv \frac{h}{2L_i}\left(\frac{1}{2mkT}\right)^{1/2}$$



- Since $\Delta(\eta_i n_i)$ small

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

$\int_0^{\infty} e^{-x^2} dx = \sqrt{\pi}/2$

$$\cong \frac{\sqrt{\pi}}{2}\frac{1}{\eta_i} = \frac{\pi^{1/2}}{2}\left[\left(\frac{h^2}{2mkT}\right)^{1/2}\frac{1}{L_i}\right]^{-1}$$

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

$L_x L_y L_z = V$ =volume

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

this result valid only for temperature "high enough" that integral is good approximation for sum

generally valid for most practical conditions, e.g., $T >$ O(1K)

Thermal DeBroglie Wavelength

- Can define a **Thermal DeBroglie Wavelength** (thermally averaged for system of translating particles)

$$\Lambda \equiv \left(\frac{h^2}{2\pi mkT}\right)^{1/2} \cong 1.746\times10^{-9}\left(\frac{1}{\bar{M}T}\right)^{1/2} \quad \text{with units } mK^{1/2}$$

molecular weight (amu)

  – then $Q_{tr} = V/\Lambda^3$
- Example: for N_2, Λ is
  – 0.033 *nm* @ 100 *K*, 0.006 *nm* @ 3000 *K*
- Turns out **Boltzmann** (dilute) **limit** considering just translational energy is **valid for $V/N >> \Lambda^3$**
  – *so normalized box size >> Λ*
- For N_2 @ SATP, $(V/N)/\Lambda^3 \sim 5\times10^6$…Boltzmann limit okay!

Translational TD Properties: p

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

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

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

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

Thermally Perfect (Ideal) Gas Eqn. of State

$k = \bar{R}/N_{Av}$

$n(moles) = N/N_{Av}$

- So purely translating particles produce TD pressure $p = p_{tr}$

pressure associated strictly with translation energy/motion

Translational TD Properties: E

- **Energy**

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

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

$$= k\cancel{T^2} \frac{1}{\cancel{bV}\cancel{T^{3/2}}} \left(\frac{3}{2} \cancel{bV}\cancel{T^{1/2}} \right)$$

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

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

average KE per molecule

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

can also get from Kinetic Theory

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

*purely translating particles are thermally **and** calor. perfect (if independent, Boltzmann limit applies and if $\Sigma \to \int$)*

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

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

$$c_v/R = \text{number of quadratic “modes”} \times ½$$

- For translational energy mode $\varepsilon_x = ½\, m v_x^2 \quad \varepsilon_y = ½\, m v_y^2 \quad \varepsilon_z = ½\, m v_z^2$

$\Rightarrow c_{v,tr}/R = 3 \times ½$ *same result we got with QM Stat Mech (for $\Sigma \rightarrow \int$)*

Translational TD Properties: S

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

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

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

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

Sachur-Tetrode Equation

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

absolute entropy

watch units!!

$\hat{c}_p/R$ *for transl.*

gives familiar cpg result

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

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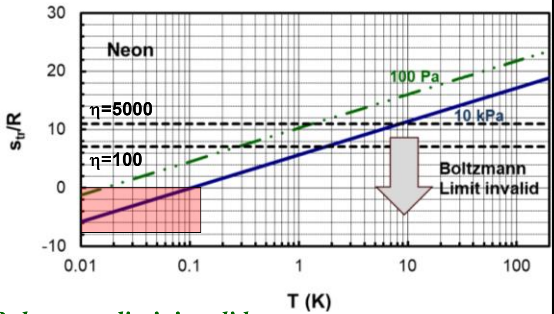
Translational TD Properties: S

- Example: noble gas, low p & T (negligible elec. energy)
- As expected, tpg $s\downarrow$ as $T\downarrow$ and $p\uparrow$
  - why is this consistent with Stat. Mechanics reasoning?
- 3rd Law: $S \to 0$ as $T \to 0$?



  - No! why S<0? ***Boltzmann limit invalid***
  - recall $s/kN = s/R = \ln(Q/N) + 1 + E/NT$
    - if require $Q_{tr}/N >> \eta$ then only valid for $s_{tr}/R = \ln\eta + 5/2$

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Translational TD Properties: μ

- **Chemical Potential**

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

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

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

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

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

sign (< or > 0?)

compare to tpg result

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

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Summary – Translational Energy Mode

- In the limit where Q_{tr} $\Sigma \rightarrow \int$ (+Boltzmann limit valid)

$$Q_{tr} \cong \left(\frac{2\pi mkT}{h^2}\right)^{3/2} V \quad = \textit{function of T and V}$$

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

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

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

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