Stat Mech II

Tuesday, February 10, 2026 2:30 PM

Properties from Q

- thermodynamic properties from Q

specify (N,V,T)

$Q = \sum_i e^{-E_i/k_BT}$ $\quad p_i = \frac{e^{-E_i/k_BT}}{Q}$

$= \sum_i e^{-\beta E_i}$; $\beta = 1/k_BT$

- internal energy

$$U = \sum_i p_i E_i = -\left(\frac{\partial \ln Q}{\partial \beta}\right)_{N,V} = k_BT^2\left(\frac{\partial \ln Q}{\partial T}\right)_{N,V}$$

proof:

$$U = -\frac{\partial \ln Q}{\partial Q}\left(\frac{\partial Q}{\partial \beta}\right)_{N,V}$$

$$= \frac{-1}{Q}\sum_i -E_i e^{-\beta E_i}$$

$$= \sum_i \frac{e^{-\beta E_i}}{Q} E_i$$

$$= \sum_i p_i E_i$$

- entropy

$$S = -k_B \sum_i p_i \ln p_i = \frac{U}{T} + k_B \ln Q$$

proof on pset 2

- other properties

↳ $P, C_V, \ldots$

Energy

- how does a molecule carry energy?

energy of a molecule $\quad \varepsilon = \underbrace{\varepsilon_{trans} + \varepsilon_{rot} + \varepsilon_{vib}}_{\text{nuclear motion}} + \underbrace{\varepsilon_{el}}_{e^-}$

molecular partition fxn $\quad q = q_{trans} \cdot q_{rot} \cdot q_{vib} \cdot q_{el}$ } q is the # of thermally accessible states!

proof:

$$q = \left(e^{-\beta\varepsilon_{trans,1}} + e^{-\beta\varepsilon_{trans,2}} + \ldots\right)$$

$$\cdot\left(e^{-\beta\varepsilon_{rot,1}} + \ldots\right)\left(e^{-\beta\varepsilon_{vib,1}} + \ldots\right)\left(e^{-\beta\varepsilon_{el,1}} + \ldots\right)$$

$$= e^{-\beta\underbrace{(\varepsilon_{trans,1} + \varepsilon_{rot,1} + \varepsilon_{vib,1} + \varepsilon_{el,1})}_{\text{energy is additive}}} + \ldots$$

partition functions multiplicative!

- nuclear motion (molecular degrees of freedom)

let n = # of atoms in a molecule

total DoF: 3n → 3 direction for each atom

motion	DOF	quantum-mech. approx. → energy levels are quantized!
translation	3	"particle in a box"
rotation	2 linear 3 nonlinear	"rigid rotor"
vibration	3n-5 3n-6	"harmonic oscillator"

example:

→ He, monatomic (n=1): 3 trans, 0 rot, 0 vib

→ HCl, diatomic (n=2): 3 trans, 2 rot, 1 vib

- spacing between energy levels

$\boxed{\text{trans} \ll \text{rot} < \text{vib} \ll \text{el}}$

- q_{trans} enormous even at low T
- $q_{el} \approx g_{el,0}$ unless T extremely high

Ideal Gas

- assumptions:
  - no intermolecular forces ⇒ $U = \sum_j N_j \varepsilon_j$
  - molecules have neglible size
- real gases approach ideal-gas behaviors under certain limiting conditions:
  - low P, high T, high V
- For ideal gas of N identical molecules

$$\boxed{Q = \frac{q^N}{N!}}$$

Monatomic Ideal Gas

$q = q_{trans} \cdot \cancel{q_{el}}$ (neglect) $= q_x q_y q_z$

- QM Problem: $\quad (\varepsilon_{trans} = \varepsilon_x + \varepsilon_y + \varepsilon_z)$

"particle in a 1-D box"

$\varepsilon_{x,n} = \frac{n^2h^2}{8mL_x^2}$, $n = 1, 2, \ldots$ (all levels nondegenerate)

$$q_x = \sum_{n=1}^{\infty} e^{-\varepsilon_{x,n}/k_BT} \approx \int_0^\infty e^{-\varepsilon_{x,n}/k_BT}\,dn \overset{\text{Gaussian integral}}{=} \left(\frac{2\pi m k_BT}{h^2}\right)^{1/2} L_x$$

$$\boxed{\begin{aligned} q_{trans}(T,V) &= q_x q_y q_z = \left(\frac{2\pi m k_BT}{h^2}\right)^{3/2} V \\ Q(N,V,T) &= \frac{q_{trans}^N}{N!} = \frac{1}{N!}\left(\frac{2\pi m k_BT}{h^2}\right)^{\frac{3N}{2}} V^N \end{aligned}}$$

- internal energy

$$\ln Q = \ln[\beta^{-3N/2}\ldots] = -\frac{3N}{2}\ln(\beta) + \ldots$$

$$U = -\left(\frac{\partial \ln Q}{\partial \beta}\right)_{N,V} = \frac{3N}{2\beta} = \frac{3}{2}Nk_BT = \boxed{\frac{3}{2}nRT}$$

$u = U/n = \frac{3}{2}RT$

- heat capacity

$C_v = \left(\partial u/\partial T\right)_V = \frac{3}{2}R$

- for an ideal gas in general:
  - $U = U(T)$ Special feature, only need 1 property!
  - each degree of freedom contributes $\frac{1}{2}RT$ to u