

Agenda: Quantum Statistical Aspects

- Principal concepts in quantum mechanics
Wave functions for free and bound particles,
Uncertainty Relation, spectroscopy with photons,
- Quantum molecular models for translation, rotations & vibrations, particle-in-a-box model
Maxwell-Boltzmann energy distribution
Application to gas phase rxns, dissociation
Rot-Vib qu. partition function, diatomic molecules,
- Quantum partition function for indistinguishable particles,
Fermions and quantum Fermi Gas,
Bosons and quantum Bose-Einstein gas.

Reading
Assignments

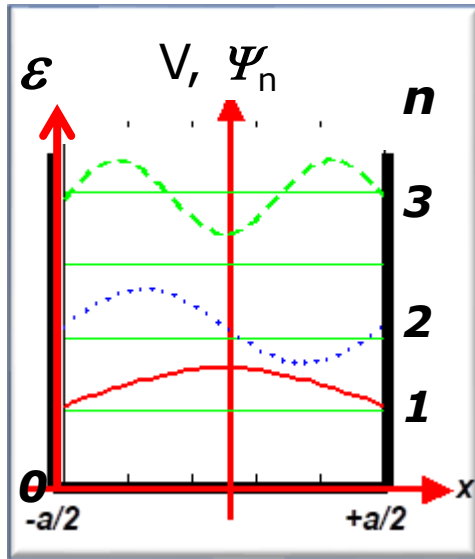
LN IV.4, 6

McQ Ch. 1,4

Kond Ch. 20

Canonical Quantum Translational PF

Quantum Mechanics → energy single particle confined to *box volume* $V = a^3$



3 main spatial quantum numbers $n_x, n_y,$ and n_z :
 $m = \text{mass}, h = \text{Planck constant}$

$$q_a = \sum_{n_x, n_y, n_z} e^{-\beta \cdot (\varepsilon_{n_x} + \varepsilon_{n_y} + \varepsilon_{n_z})} = \left(\sum_i e^{-\beta \cdot \varepsilon_i} \right)^3$$

individual
bound levels

$$\varepsilon_{n_x, n_y, n_z} = \frac{h^2}{8ma^2} (n_x^2 + n_y^2 + n_z^2) \propto V^{-2/3}$$

Large boxes $a \rightarrow \infty$ continuous energies (ε_n)
 → moving particles described by

$$q_{a \rightarrow \infty}^{trans} = \lim_{a \rightarrow \infty} \int_0^\infty dne^{-\left(\beta \cdot \frac{h^2}{8ma^2}\right) \cdot n^2} = \left[\sqrt{\frac{2\pi}{h^2} mk_B T} \cdot a \right]^3$$

$$q^{trans} = \frac{V}{\lambda_{therm}^3} \propto T^{3/2}$$

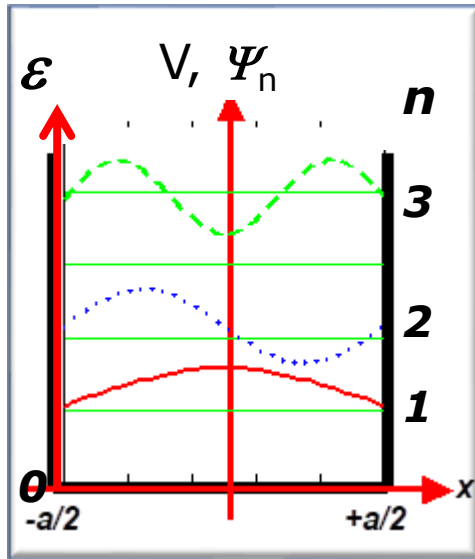
$$\lambda_{therm} = \sqrt{\frac{h^2}{2\pi mk_B T}}$$

Thermal
Wavelength

Value of h	Units
$6.626\,070\,15 \times 10^{-34}$	J·s
$4.135\,667\,696 \times 10^{-15}$	eV·s
Values of \hbar (h-bar)	Units
$1.054\,571\,817 \times 10^{-34}$	J·s
$6.582\,119\,569 \times 10^{-16}$	eV·s
Values of hc	Units
$1.986\,445\,86 \times 10^{-25}$	J·m
1.239 841 93	eV·μm
Values of $\hbar c$ (h-bar)	Units
$3.161\,526\,49 \times 10^{-26}$	J·m
0.197 326 9804	eV·μm

Mean Translational Energy (Canonical Ensemble)

Quantum Mechanics → energy single particle confined to *box volume* $V = a^3$



$$q_{a \rightarrow \infty}^{trans} \approx \left[\sqrt{\frac{2\pi}{h^2} m k_B T} \cdot a \right]^3 = \left[\sqrt{\frac{2\pi}{h^2} m} \right]^3 \cdot (k_B T)^{3/2} \cdot a^3$$

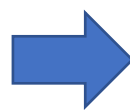
$$= \text{const} \cdot (k_B T)^{3/2} \cdot V$$

Derive thermodynamic observables from PF

$$\langle \varepsilon^{trans} \rangle = k_B T^2 \cdot \frac{\partial}{\partial T} \ln q^{trans} = k_B T^2 \cdot \frac{\partial}{\partial T} \ln T^{3/2}$$

$$= k_B T^2 \cdot \frac{1}{T^{3/2}} \frac{\partial}{\partial T} T^{3/2} = k_B T^2 \cdot \frac{3/2}{T^{3/2}} T^{1/2} = \frac{3}{2} k_B T^2$$

Value of h	Units
$6.626\,070\,15 \times 10^{-34}$	J·s
$4.135\,667\,696 \times 10^{-15}$	eV·s
Values of \hbar (h-bar)	Units
$1.054\,571\,817 \times 10^{-34}$	J·s
$6.582\,119\,569 \times 10^{-16}$	eV·s
Values of hc	Units
$1.986\,445\,86 \times 10^{-25}$	J·m
1.239 841 93	eV·μm
Values of $\hbar c$ (h-bar)	Units
$3.161\,526\,49 \times 10^{-26}$	J·m
0.197 326 9804	eV·μm



$$\langle \varepsilon^{trans} \rangle = \frac{3}{2} k_B \cdot T$$

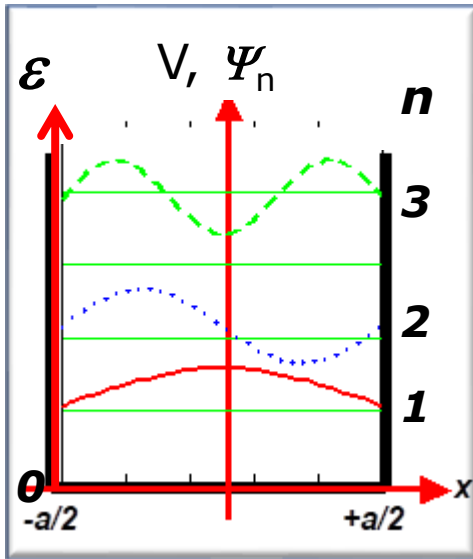
As expected!
Equipartition

$$C_V^{trans} = \frac{C_V^{trans}}{N} = \frac{3}{2} k_B$$

Independent
of mass !

Example: Mean Translational Energy

Quantum Mechanics → energy single particle confined to *box volume* $V = a^3$



$$\langle \varepsilon^{trans} \rangle = \frac{3}{2} kT$$

Room temperature ($\sim 298\text{K}$) characteristic thermal energy: $k_B \cdot T \approx (1/40)\text{eV} = 25\text{meV}$

Proton mass $m_p c^2 \sim 1\text{ GeV}$

$$\frac{m_p c^2}{2} \left(\frac{v}{c} \right)^2 = 25\text{meV} \rightarrow$$

$$\rightarrow \frac{v}{c} = \sqrt{\frac{50 \cdot 10^{-3}\text{eV}}{1 \cdot 10^9\text{eV}}} \sim 7 \cdot 10^{-6} \rightarrow v \sim 2\text{ km/s}$$

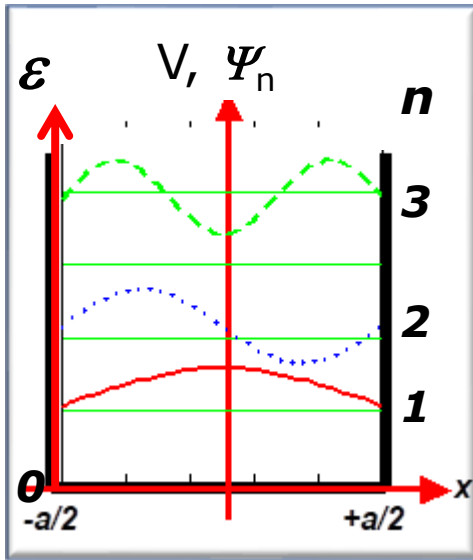
Value of h	Units
$6.626\,070\,15 \times 10^{-34}$	J·s
$4.135\,667\,696 \times 10^{-15}$	eV·s
Values of \hbar (h-bar)	Units
$1.054\,571\,817 \times 10^{-34}$	J·s
$6.582\,119\,569 \times 10^{-16}$	eV·s
Values of hc	Units
$1.986\,445\,86 \times 10^{-25}$	J·m
1.239 841 93	eV· μm
Values of hc (h-bar)	Units
$3.161\,526\,49 \times 10^{-26}$	J·m
0.197 326 9804	eV· μm

In many circumstances, it is (almost) sufficient to approximate independent particles in gas or liquid phases as "ideal particles." This implies that internal particle structure does not play a significant role. Then, the translational PF *essentially* determines system behavior.

→ But internal structure must not be neglected entirely!

Boltzmann High-T Limit (Canonical Ensemble)

Quantum Mechanics → energy single particle confined to *box volume* $V = a^3$



Always present internal DoF: Combined canonical *translational electronic-nuclear PF* for N identical mono-atomic gases @ high T :

Energetic *d.o.f.* (electronic, nuclear) **only the g.s. degeneracy counts, e.g. spin** $\Omega_0 = 2 \cdot \text{spin} + 1$

$$q^{elect} = \sum_{\epsilon_i} \Omega_i e^{-\beta \epsilon_i} = \Omega_0 + \Omega_1 \cdot e^{-\beta \epsilon_1} + \dots \approx \Omega^{elect}$$

$$q^{nucl} = \sum_{\epsilon_i} \Omega_i e^{-\beta \epsilon_i} = \Omega_0 + \Omega_1 \cdot e^{-\beta \epsilon_1} + \dots \approx \Omega^{nucl}$$

Value of h	Units
$6.626\,070\,15 \times 10^{-34}$	J·s
$4.135\,667\,696 \times 10^{-15}$	eV·s
Values of \hbar (h-bar)	Units
$1.054\,571\,817 \times 10^{-34}$	J·s
$6.582\,119\,569 \times 10^{-16}$	eV·s
Values of hc	Units
$1.986\,445\,86 \times 10^{-25}$	J·m
1.239 841 93	eV·μm
Values of hc (h-bar)	Units
$3.161\,526\,49 \times 10^{-26}$	J·m
0.197 326 9804	eV·μm

$$Q_N(V, T) = \frac{1}{N!} (2 \cdot I_{nucl} + 1)^N \cdot (\Omega_0^{elect})^N \cdot \left[\frac{V}{\lambda_{therm}^3} \right]^N = \frac{1}{N!} \cdot q^N$$

Stirling's Formula $N! \approx (N/e)^N \rightarrow$ *1 outer-shell electron*

$$Q_N(V, T) = \left[(2I_{nucl} + 1) \cdot (\Omega_0^{elect}) \cdot \left(\frac{2\pi mkT}{h^2} \right)^{\frac{3}{2}} \left(\frac{eV}{N} \right) \right]^N$$

Agenda: Quantum Statistical Aspects

- Principal concepts in quantum mechanics
Wave functions for free and bound particles,
Uncertainty Relation, spectroscopy with photons,
- Quantum molecular models for translation, rotations & vibrations, particle-in-a-box model
Maxwell-Boltzmann energy distribution
Application to gas phase rxns, dissociation
Rot-Vib qu. partition function, diatomic molecules,
- Quantum partition function for indistinguishable particles,
Fermions and quantum Fermi Gas,
Bosons and quantum Bose-Einstein gas.

Reading
Assignments

LN IV.4, 6

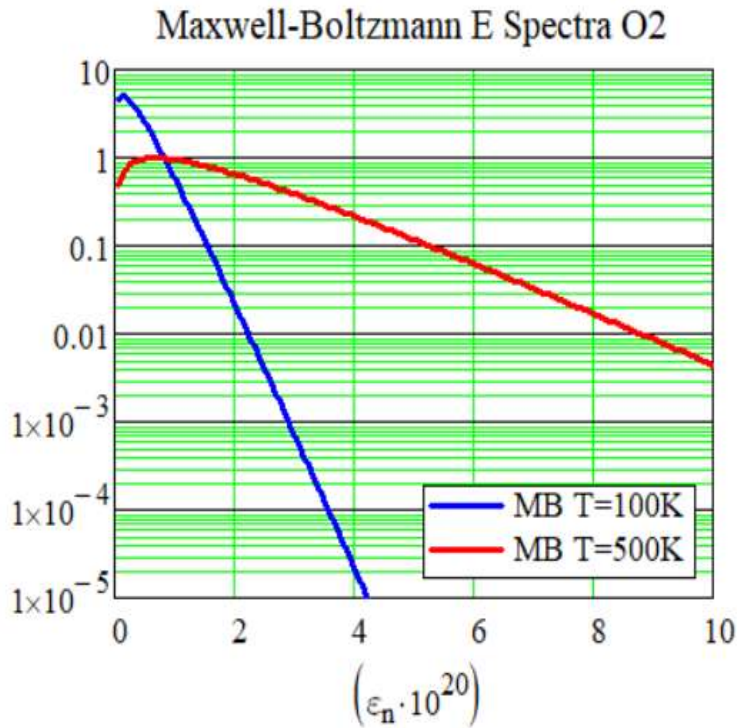
McQ Ch. 1,4

Kond Ch. 20

Maxwell-Boltzmann Energy Spectrum

Continuous canonical *translational electronic-nuclear* PF for single particle of ideal, mono-atomic gas @ high T , 1D

$$q_{a \rightarrow \infty}^{trans} = \lim_{a \rightarrow \infty} \left[\int_0^{\infty} dn e^{-\left(\beta \cdot \frac{h^2}{8ma^2}\right) \cdot n^2} \right]^3 = \left[\sqrt{\frac{2\pi}{h^2} mk_B T} \cdot a \right]^3$$



s.p. 1D : $q(V, T) = (2I_{nucl} + 1) \cdot (\Omega_0^{elect}) \cdot \left(\frac{2\pi mk_B T}{h^2}\right)^{\frac{3}{2}} \cdot V$

Probability for kinetic energy ϵ : $n^2 := n_x^2 + n_y^2 + n_z^2$

$$P(\epsilon) = \frac{\varpi(n) \cdot e^{-\left(\beta \cdot \frac{h^2}{8ma^2}\right) \cdot n^2}}{\left(\frac{2\pi}{h^2} mk_B T\right)^{3/2} V} \rightarrow \frac{\varpi(\epsilon) \cdot e^{-\frac{\epsilon}{k_B T}}}{\left(\frac{2\pi}{h^2} m \cdot k_B T\right)^{3/2} V}$$

$$\frac{dP(\epsilon)}{d\epsilon} = \frac{2\pi}{(\pi k_B T)^{3/2}} \sqrt{\epsilon} \cdot e^{-\frac{\epsilon}{k_B T}} \sim \sqrt{\epsilon} \cdot e^{-\frac{\epsilon}{k_B T}}$$

Exponential fore-factor depends on degeneracy, quantal Fermi/Bose population.

Method to measure temperature via kinetic energy of particles.

Energetics of Gas Phase Reactions

Translational PF does not include: intrinsic molecular structure, energies

$$q = g_{s,n} \cdot \left(\frac{2\pi}{h^2} m \cdot k_B T \right)^{3/2} \cdot V$$

with $g_{s,n} = 2S + 1$ ($= 2$ for spin = 1 / 2) degeneracy $\varpi(E)$

Gas of N free particles : pressure $P = N \cdot k_B T \cdot \frac{\partial}{\partial V} \text{Ln} \left(\frac{q}{N} \right) = N \cdot k_B T / V$

Helmholtz Free Energy $A = -k_B \cdot N \cdot T \cdot \text{Ln} \left(\frac{q}{N} \right) - k_B \cdot N \cdot T$

Gibbs free energy $G = A + P \cdot V$

$$G = -k_B \cdot N \cdot T \cdot \text{Ln} \left(\frac{q}{N} \right); \rightarrow \mu = \frac{G}{N} = -k_B \cdot T \cdot \text{Ln} \left(\frac{q}{N} \right) \text{ rel to } \mu^0$$

Chem Rxn : $\nu_A \cdot A + \nu_B \cdot B + \nu_C \cdot C + \nu_D \cdot D = 0$, ($\nu_A, \nu_B < 0, \nu_C, \nu_D > 0$)

Energetics of Gas Phase Reactions

Not considered: intrinsic molecular structure, energies

Chem Rxn : $\boxed{v_A \cdot \mu_A + v_B \cdot \mu_B + v_C \cdot \mu_C + v_D \cdot \mu_D = 0}$, ($v_A, v_B < 0, v_C, v_D > 0$)

In stationary state (equilibrium), assuming reference $\sum_i^{A,B,C,D} v_i \cdot \mu_i^0 = 0$

$$0 = \sum_i^{A,B,C,D} v_i \cdot \mu_i = -k_B \cdot T \cdot \sum_i v_i \cdot \ln\left(\frac{q_i}{N_i}\right) \rightarrow \sum_i v_i \cdot \ln\left(\frac{q_i}{N_i}\right) = 0$$

$$0 = \sum_i v_i \cdot \ln\left(\frac{q_i}{N_i}\right) = \sum_i \ln\left(\frac{q_i}{N_i}\right)^{v_i} = \ln \prod_i \left(\frac{q_i}{N_i}\right)^{v_i} \quad \boxed{\ln(a) + \ln(b) = \ln(a \cdot b)}$$

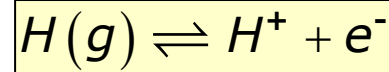
$$\rightarrow 1 = \prod_i \left(\frac{q_i}{N_i}\right)^{v_i} \rightarrow \text{Equilibrium constant } \boxed{K_N = \prod_i N_i^{v_i} = \prod_i q_i^{v_i}}$$

$$\boxed{K_N = \frac{N_C^{v_C} \cdot N_D^{v_D}}{N_A^{v_A} \cdot N_B^{v_B}} = \frac{q_C^{v_C} \cdot q_D^{v_D}}{q_A^{v_A} \cdot q_B^{v_B}}}$$

$\longrightarrow K_p, K_c$

Application: Gas Phase Dissociation

Monoatomic hydrogen gas, electrically neutral \rightarrow dissociates in thermal equilibrium T , ionization energy $E_D = 13.6$ eV
disregard molecular species H_2 .



Volume V , proton mass m_p , spin $\mathbf{I}_p = 1/2$. Electron mass m_e , spin $\mathbf{s}_e = 1/2$

$$q(m) = g_s \cdot \left(\frac{2\pi}{h^2} m \cdot k_B T \right)^{3/2} \cdot V \quad \text{with } g_s = 2 \text{ for each spin} = 1/2 \text{ degeneracy}$$

$$q(H^+) = 2 \cdot \left(\frac{2\pi}{h^2} m_p \cdot k_B T \right)^{3/2} \cdot V \quad q(e^-) = 2 \cdot \left(\frac{2\pi}{h^2} m_e \cdot k_B T \right)^{3/2} \cdot V$$

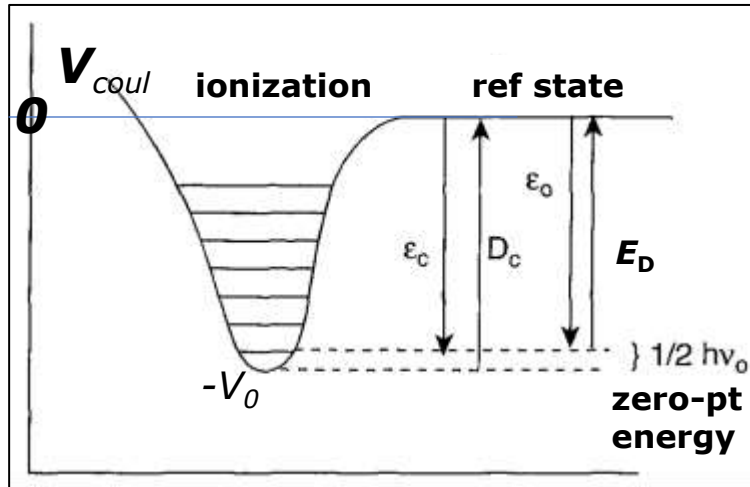
$$q(H(g)) = 2 \cdot 2 \cdot \left(\frac{2\pi}{h^2} m_H \cdot k_B T \right)^{3/2} \cdot V \cdot e^{-\beta \cdot E_D} \quad \text{nuclear} \times \text{electronic spin factors}$$

$$K_N = \frac{N_{H^+} \cdot N_{e^-}}{N_{Hg}} = \frac{q_{H^+} \cdot q_{e^-}}{q_{Hg}} = V \cdot \left(\frac{2\pi}{h^2} k_B \cdot T \cdot m_e \right)^{3/2} \cdot e^{-\beta E_D} \quad m_H \approx m_p$$

$$x := \frac{N_{H^+}}{N} = \frac{N_{e^-}}{N} \quad \text{and} \quad N_{H^+} + N_{e^-} = N \rightarrow K_N = \frac{x^2}{(1-x)}$$

$$\rightarrow x = \frac{K_N}{2} \left[\sqrt{1 + \frac{4}{K_N}} - 1 \right]$$

Energy Reference in Dissociation Rxns



Energies (E , A , G) are counted relative to $E=0$, either *ground state* or dissociated state of composite systems.

QM: bound systems have negative energies.

QM g.s. has zero-point energy

Excitation energy of electron = E_D

Have to define G , μ and μ^0 consistently.

Energy balance for reactive chemical systems: $\sum_i \nu_i (\mu_i - \mu_i^0) = 0$

Account for degeneracy factors for PF. Example diss of $H(g)$, include e-state

$$q(H(g)) = 2 \cdot 2 \cdot \left(\frac{2\pi}{h^2} m_H \cdot k_B T \right)^{3/2} \cdot V \cdot \left(\frac{e^{-\beta \cdot E_D}}{1 + e^{-\beta \cdot E_D}} \right); \text{diss energy } E_D = -\epsilon_0$$

Diss equ. constant $K_N \propto e^{+\beta E_D} = e^{-\epsilon_0/k_B T}$ increases with incr. T

Agenda: Quantum Statistical Aspects

- Principal concepts in quantum mechanics
Wave functions for free and bound particles,
Uncertainty Relation, spectroscopy with photons,
- Quantum molecular models for translation, rotations & vibrations, particle-in-a-box model
Maxwell-Boltzmann energy distribution
Application to gas phase rxns, dissociation
Rot-Vib qu. partition function, diatomic molecules,
- Quantum partition function for indistinguishable particles,
Fermions and quantum Fermi Gas,
Bosons and quantum Bose-Einstein gas.

Reading
Assignments

LN IV.4, 6

McQ Ch. 1,4

Kond Ch. 20