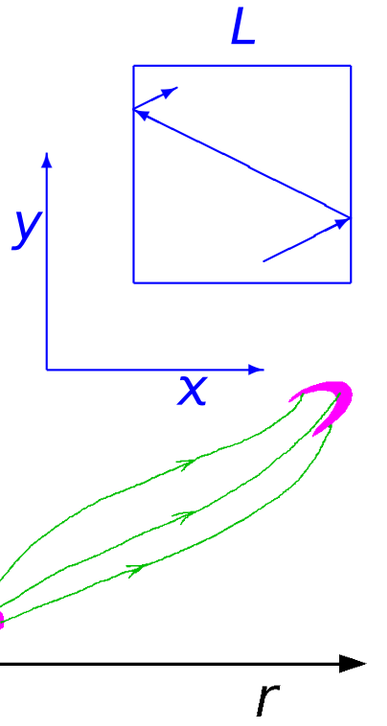
Statistical thermodynamics instant

- Monoatomic classical ideal gas in a box:
  - ideal gas equation of state
  - temperature given by kinetic energy, $\left\langle \frac{1}{2} m \dot{r}_{i,x}^2 \right\rangle = \frac{1}{2} k_\mathrm{B} T$

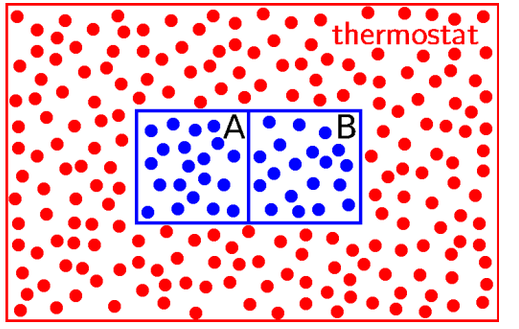
    (equipartition theorem, can be extended to any classical mechanical system)



- Ergodic hypothesis in the microcanonical ensemble:
  - quantum: all eigenstates have the same probability
  - classical: density of states is constant on the constant-energy manifold in phase space ($\{r^N, p^N\}$, because of the Liouville's theorem)
- $\boldsymbol{\pi} \propto \exp(-E/k_\mathrm{B}T)$ in the canonical ensemble is derived by:
  - set of heat-exchanging sub-ensembles = big microcanonical ensemble
  - multiplication of prob. of two noninteracting systems, $\boldsymbol{\pi}(E_1 + E_2) = \boldsymbol{\pi}(E_1)\boldsymbol{\pi}(E_2)$
- Boltzmann equation for entropy:

$$U = \langle \mathcal{E} \rangle \quad \Rightarrow \quad \mathrm{d}U = \sum_\psi \boldsymbol{\pi}(\psi) \cdot \mathrm{d}\mathcal{E}(\psi) + \sum_\psi \mathrm{d}\boldsymbol{\pi}(\psi) \cdot \mathcal{E}(\psi) = -p\,\mathrm{d}V + T\,\mathrm{d}S$$

$$\Rightarrow \quad S = -k_\mathrm{B} \sum_\psi \boldsymbol{\pi}(\psi) \ln \boldsymbol{\pi}(\psi), \text{ microcanonical ensemble: } S = k_\mathrm{B} \ln W$$



- Boltzmann H-theorem (second law) vs. Loschmidt's paradox

Canonical ensemble: Helmholtz energy

$$\boldsymbol{\pi}(\psi) = \frac{\mathrm{e}^{-\beta\mathcal{E}(\psi)}}{Z}, \qquad Z = \sum_{\psi} \mathrm{e}^{-\beta\mathcal{E}(\psi)}$$

$$\beta = \frac{1}{k_\mathrm{B} T}$$

$$S = -k_\mathrm{B} \sum_{\psi} \boldsymbol{\pi}(\psi) \ln \boldsymbol{\pi}(\psi) = -k_\mathrm{B} \sum_{\psi} \boldsymbol{\pi}(\psi) [-\beta\mathcal{E}(\psi) - \ln Z] = \frac{U}{T} + k_\mathrm{B} \ln Z$$

⇒ Helmholtz energy:

$$F = -k_\mathrm{B} T \ln Z$$

Z = **canonical partition function** = **statistical sum** (also denoted Q)

Interpretation: number of “accessible” states (low-energy states are easily accessible, high-energy states are not)

From the Helmholtz energy F we can obtain all equilibrium quantities ($\mathrm{d}F = -p\mathrm{d}V - S\mathrm{d}T$):

$$p = -\frac{\partial F}{\partial V} \qquad U = F + TS$$

$$S = -\frac{\partial F}{\partial T} \qquad H = U + pV$$

$$G = F + pV$$

Classical partition function

Positions of atoms = $\vec{r}_i$, momenta = $\vec{p}_i$ (Hamilton formalism)

$$\mathcal{E} = \mathcal{H}(\vec{r}_1, \ldots, \vec{p}_N) = E_{\text{pot}} + E_{\text{kin}}, \quad E_{\text{pot}} = U(\vec{r}_1, \ldots, \vec{r}_N), \quad E_{\text{kin}} = \sum_i \frac{\vec{p}_i^{\,2}}{2m}$$

Sum over states replaced by integrals (clasical mechanics needed):

$$Z = \sum_\psi \mathrm{e}^{-\beta\mathcal{E}(\psi)} = \frac{1}{N! h^{3N}} \int \exp[-\beta\mathcal{H}(\vec{r}_1, \vec{r}_2, \ldots, \vec{r}_N, \vec{p}_1, \ldots, \vec{p}_N)]\, \mathrm{d}\vec{r}_1 \cdots \mathrm{d}\vec{p}_N,$$

where $h = 2\pi\hbar$ = Planck constant.

$U = U(S, V)$ = internal energy
$U(\vec{r}_1, \ldots)$ = potential (PES)

Why the factorial?

- Particles are indistinguishable . . . but at high enough T they are in different quantum states

Why Planck constant?

- Has the correct dimension (Z must be dimensionless)
- We get the same result for noninteracting quantum particles in a box

but fails if quantum effects are important (vide infra)

Classical partition function

Integrals over positions and momenta are separated

Gauss: $\int \mathrm{e}^{-x^2}\,\mathrm{d}x = \sqrt{\pi}$

Integrals over momenta can be evaluated: $\int_{-\infty}^{\infty} \exp\left(-\frac{p_{1,x}^2/2m}{k_\mathrm{B}T}\right)\mathrm{d}p_{1,x} = \sqrt{2\pi k_\mathrm{B}T m}$

After $3N$ integrations we get:

$$Z = \frac{Q}{N!\Lambda^{3N}}, \qquad \text{Thermal de Broglie wavelength: } \Lambda = \frac{h}{\sqrt{2\pi m k_\mathrm{B}T}}$$

Λ = de Broglie wavelength at typical particle velocity at given T

requirement: $\Lambda \ll$ typical atom–atom separation $\approx (V/N)^{1/3}$

Configurational integral: $Q = \int \exp[-\beta U(\vec{r}_1, \ldots, \vec{r}_N)]\,\mathrm{d}\vec{r}_1 \ldots \mathrm{d}\vec{r}_N$

Mean value of a **static** quantity (observable):

$$\langle X \rangle = \frac{1}{Q}\int X(\vec{r}_1, \ldots, \vec{r}_N) \exp[-\beta U(\vec{r}_1, \ldots, \vec{r}_N)]\,\mathrm{d}\vec{r}_1 \ldots \mathrm{d}\vec{r}_N$$

Thermal de Broglie wavelength

Example

a) Calculate Λ for helium at $T = 2$ K.

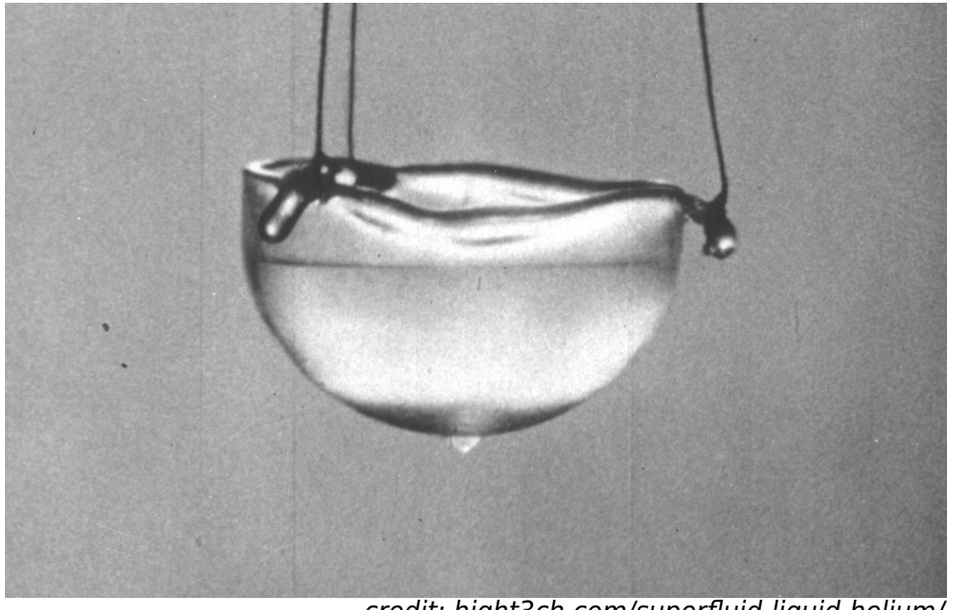
b) Compare to the typical distance of atoms in liquid helium (density $0.125\,\mathrm{g/cm^3}$).

a)

$$\Lambda = \frac{h}{\sqrt{2\pi m k_B T}}$$

$$= \frac{6.6\cdot 10^{-34}}{\sqrt{2 \times \pi \times \frac{0.004}{6\times 10^{23}} \times 1.38\cdot 10^{-23} \times 2}}$$

$$= 6.2\cdot 10^{-10}\,\mathrm{m} = \underline{6.2\,\text{Å}}$$



credit: hight3ch.com/superfluid-liquid-helium/

b)

$$l = \sqrt[3]{V_1} = \sqrt[3]{\frac{M}{N_A \rho}} = \sqrt[3]{\frac{0.004}{6\cdot 10^{23} \times 125}} = 3.8\cdot 10^{-10}\,\mathrm{m} = \underline{3.8\,\text{Å}}$$

$\underline{l < \Lambda \Rightarrow \text{cannot use classical mechanics}}$

Ideal gas

Ideal gas is composed of particles, which mutually (almost) do not interact.

= the limit of a real gas at sufficiently low densities (particles are far away).

Ideal gas in chemistry

Formerly also *perfect gas* with unsettled meaning (constant heat capacity/monoatomic/...)

- The ideal gas is (generally) composed of molecules.
- The set of particles (is so diluted that it) behaves classically (no quantum statistics is needed). For the internal degrees of freedom, the quantum description may be essential.

Ideal gas in physics +

- The ideal gas is (often) monomolecular, the particle do not interact with each other (except for consequences of quantum statistics).
- Particles may be:

– bosons (Bose–Einstein statistics),
– fermions (Fermi–Dirac statistics),
– approximated classically (Maxwell–Boltzmann statistics, „chemical“ ideal gas).

The ideal fermionic gas has a higher pressure than the ideal bosonic gas.

Monoatomic ideal gas from the classical canonical partition function

$$Q = \int \exp[0]\,\mathrm{d}\vec{r}_1 \ldots \mathrm{d}\vec{r}_N = \int_V \mathrm{d}\vec{r}_1 \cdots \int_V \mathrm{d}\vec{r}_N = V^N$$

$$Z = \frac{Q}{N!\Lambda^{3N}} = \frac{V^N}{N!\Lambda^{3N}} \approx \frac{V^N}{N^N \mathrm{e}^{-N}\Lambda^{3N}}, \quad F = -k_\mathrm{B}T \ln Z = -k_\mathrm{B}TN \ln \frac{V\mathrm{e}}{N\Lambda^3}$$

$$p = -\left(\frac{\partial F}{\partial V}\right)_T = \frac{k_\mathrm{B}TN}{V} = \frac{nRT}{V}$$

e = Euler number
e = elementary charge

$$U = F + TS = F - T\left(\frac{\partial F}{\partial T}\right)_V = \frac{3Nk_\mathrm{B}T}{2}$$

Chemical potential with respect to the standard state of a free molecule at zero temperature:

$$\mu = \left(\frac{\partial F}{\partial N}\right)_{T,V} = k_\mathrm{B}T \ln\left(\frac{\Lambda^3}{V}\right) \overset{V=k_\mathrm{B}T/p}{=} k_\mathrm{B}T \ln\left(\frac{p\Lambda^3}{k_\mathrm{B}T}\right) = -k_\mathrm{B}T \ln q_\mathrm{tr}$$

And verification: $G = F + pV = k_\mathrm{B}TN \ln \frac{N\Lambda^3}{V\mathrm{e}} + Nk_\mathrm{B}T = N\mu$

$$q_\mathrm{tr} = \frac{V}{\Lambda^3} = \frac{1}{\rho\Lambda^3} = \frac{k_\mathrm{B}T}{p\Lambda^3}, \; \rho = \frac{N}{V} = \frac{1}{V}$$

. . . from the quantum canonical partition function

In other words, q_{tr} from quantum theory.

Eigenvalues of energy of a point mass (atom of monoatomic ideal gas) in a $a \times b \times c$ box:

$$\mathcal{E} = \frac{h^2}{8m}\left(\frac{n_x^2}{a^2} + \frac{n_y^2}{b^2} + \frac{n_z^2}{c^2}\right)$$

Maxwell–Boltzmann statistics: high enough temperature so that a few particles compete for the same quantum state – it does not matter whether we have fermions or bosons; equivalently, $\Lambda \ll$ distance between particles.

Partition function:

$$Z_1 = \sum_{n_x=1}^{\infty}\sum_{n_y=1}^{\infty}\sum_{n_z=1}^{\infty} \exp(-\beta\mathcal{E}) \overset{\sum\to\int}{\approx} \int_0^{\infty}\int_0^{\infty}\int_0^{\infty} \exp(-\beta\mathcal{E})\,\mathrm{d}n_x\mathrm{d}n_y\mathrm{d}n_z = \frac{V}{\Lambda^3}$$

$$E = \sum_{i=1}^{N} E_i \quad \Rightarrow \quad Z = \frac{1}{N!}Z_1^N$$

Yes, it is the same! The choice of factor $1/h^{3N}$ in the classical Z is correct.

Ideal gas with internal degrees of freedom

The internal degrees of freedom (electronic, vibrational, rotational*) are separated from the translational ones. The internal partition function is the sum over the internal degrees of freedom:

$$q_{\mathrm{in}} = \sum_{\psi} \mathrm{e}^{-\beta\mathcal{E}(\psi)}$$

The entire canonical partition function: $Z = \dfrac{(q_{\mathrm{in}}V)^N}{N!\Lambda^{3N}}, \quad F = -k_{\mathrm{B}}T\ln Z = -k_{\mathrm{B}}TN\ln\dfrac{V\mathrm{e}q_{\mathrm{in}}}{N\Lambda^3}$

Chemical potential:

$$\mu = \left(\frac{\partial F}{\partial N}\right)_{T,V} = k_{\mathrm{B}}T\ln\left(\frac{N\Lambda^3}{q_{\mathrm{in}}V}\right) = k_{\mathrm{B}}T\ln\left(\frac{p\Lambda^3}{q_{\mathrm{in}}k_{\mathrm{B}}T}\right) = -k_{\mathrm{B}}T\ln(q_{\mathrm{tr}}q_{\mathrm{in}})$$

Standard reaction Gibbs energy (for standard state ideal gas at temperature T and pressure p^{st}):

$$\Delta_{\mathrm{r}}G^{\circ}_{\mathrm{m}} = \sum_i \nu_i\mu_i^{\circ} + E, \quad \text{where } \mu_i^{\circ} = k_{\mathrm{B}}T\ln\left(\frac{p^{\mathrm{st}}\Lambda^3}{q_{\mathrm{in}}k_{\mathrm{B}}T}\right), \tag{1}$$

the sum is over components, ν_i = stoichiometry coefficients, and E = reaction energy at $T = 0$.

*The rotional partition function (except for light molecules as H_2) can be calculated “semiclassically” from the moment of inertia and symmetry number by replacing the sum over quantum states by integration.

Internal partition function of molecular ideal gas

Approximation: for small molecules, the energy is a sum of contributions and the internal partition function can be factorized:

$$q_{\text{in}} = q_{\text{rot}} q_{\text{vib}} q_{\text{el}}$$

Rotational partition function of a nonsymmetric linear molecule:

$$q_{\text{rot}} = \sum_{J=0}^{\infty} (2J+1) \exp\left[-\frac{E_{\text{rot}}}{k_{\text{B}}T}\right] \overset{\text{classical limit}}{\approx} \int_{J=0}^{\infty} (2J+1) \exp\left[-\frac{\hbar^2 J(J+1)}{2k_{\text{B}}TI}\right] \mathrm{d}J$$

$$= \frac{2Ik_{\text{B}}T}{\hbar^2} = \frac{k_{\text{B}}T}{hc\tilde{B}} = \frac{T}{\Theta_{\text{rot}}} \qquad (I = \text{moment of inertia}, \tilde{B} = \frac{\hbar^2}{2Ihc} = \text{rotational constant})$$

Symmetric linear molecule (half states, **symmetry number** $\sigma = 2$): $q_{\text{rot}} = \frac{Ik_{\text{B}}T}{\hbar^2} = \frac{k_{\text{B}}T}{\sigma hc\tilde{B}}$

General molecule: $q_{\text{rot}} = \frac{\sqrt{\pi}}{\sigma} \prod_{a=\{x,y,z\}} \left(\frac{2I_a k_{\text{B}}T}{\hbar^2}\right)^{1/2} = \frac{\sqrt{\pi}}{\sigma}\left(\frac{k_{\text{B}}T}{hc}\right)^{3/2} \frac{1}{\sqrt{\tilde{A}\tilde{B}\tilde{C}}}$,

where $\text{diag}(I_x, I_y, I_z)$ is the diagonalized moment of inertia (x, y, z are the main axes).

Vibrational partition function

Each fundamental harmonic vibration:

$$q_{\text{vib}} = \sum_{\upsilon=0}^{\infty} \exp\left[-\frac{h\nu}{k_{\text{B}}T}\upsilon\right] = \frac{1}{1-\mathrm{e}^{-x}}, \quad \text{where } x = \frac{h\tilde{\nu}c}{k_{\text{B}}T}$$

Since the partition function is *defined* so that the lowest energy is zero, $E_0 = 0$, the zero-point energy is not included.

If E (reaction energy at $T = 0$) does not include the zero point energy (quantum calculation without Hessian and fundamental frequency analysis), the zero-point energy be should be included:

$$q_{\text{vib}}^{\text{with zero-point}} = \frac{\mathrm{e}^{-x/2}}{1-\mathrm{e}^{-x}}$$

Classical limit (equipartition theorem: usually not accurate enough):

$$q_{\text{vib}} \approx \int_0^{\infty} \exp\left[-\frac{h\nu}{k_{\text{B}}T}\upsilon\right] \mathrm{d}\upsilon = \frac{k_{\text{B}}T}{h\tilde{\nu}c} = \frac{T}{\Theta_{\text{vib}}}$$

or using the $T \to \infty$ limit ($x \to 0$)

$$\frac{1}{1-\mathrm{e}^{-x}} \overset{x\to 0}{\to} \frac{1}{x} = \frac{k_{\text{B}}T}{h\tilde{\nu}c}$$

Electronic partition function of an atom

Calculated directly: $q_{\mathrm{el}} = \sum_i g_i \exp\left(\frac{-\mathcal{E}_i}{k_{\mathrm{B}}T}\right)$

Term ${}^{2S+1}L_J$ (Russell–Saunders) describes the atom state:

- S = total spin number ($2S+1$ = multiplicity – seen as multiplet in the spectrum due to the spin–orbit coupling (for $L > 0$)
- L = orbital number (the electron angular momentum is $\hbar\sqrt{L(L+1)}$), key: $S = 0$, $P = 1$, $D = 2$, $F = 3$ ...
- J = total angular quantum number ($J \in \{|L-S|, \ldots, L+S\}$)

$\Rightarrow$ Multiplicity (number of states in this level): $g = 2J+1$

Example. A boron atom has a dublet ${}^2\mathrm{P}_{1/2}$ (multiplicity 2) as the ground state, the first excited state is ${}^2\mathrm{P}_{3/2}$ (multiplicity 4), only $E = 15.254\,\mathrm{cm}^{-1}$ above).

a) Calculate the electronic partition function at 1000 K.
b) The next higher excited state lies $28870\,\mathrm{cm}^{-1}$ above the ground state. Can it be neglected?

a) $q_{\mathrm{el}} = 5.913$; b) yes ($\exp(-E/kT) = 1\cdot10^{-18}$)

Conformers

If the molecule exists in several distinct enough conformers, we sum them up. Example (butane):

$$q_{\text{in}} = q_{\text{in}}(anti) + 2q_{\text{in}}(gauche)$$

More precise:

- Do not separate rotations/vibrations (centrifugal correction).
- Integrate over dihedral angle (torsional potential minima are not deep enough and not harmonic).
- Anharmonic corrections.

Equilibrium constant in the gas phase – summary

Reaction written formally: $0 = \sum_{i=1}^{k} \nu_i \mathrm{R}_i$

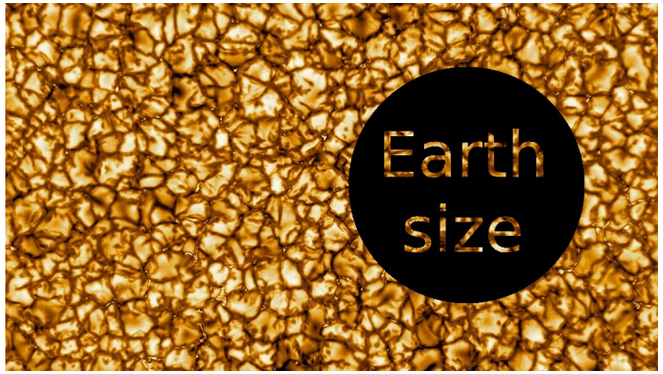
Equilibrium constant for standard state ideal gas at pressure p^{st} and temperature T:

$$K = \exp\left(-\frac{E}{k_{\mathrm{B}}T}\right) \prod_i q_i^{\nu_i}$$

- E = reaction energy at $T = 0$ (with|without zero point energy)
- Molecular partition function: $q_i = q_{\mathrm{tr}} q_{\mathrm{in}}$, $q_{\mathrm{tr}} = \frac{k_{\mathrm{B}}T}{p^{\mathrm{st}}\Lambda_i^3}$
- Internal partition function: $q_{\mathrm{in},i} \approx q_{\mathrm{rot},i} q_{\mathrm{vib},i} q_{\mathrm{el},i}$
- Linear molecule: $q_{\mathrm{rot},i} = \frac{2Ik_{\mathrm{B}}T}{\sigma\hbar^2}$ ($\sigma = 2$: symmetric, $\sigma = 1$: nonsymmetric)
- Harmonic vibrations: $q_{\mathrm{vib},i} = \prod_\nu \frac{1\exp(-h\nu/2k_{\mathrm{B}}T)}{1-\exp(-h\nu/k_{\mathrm{B}}T)}$ (product over fundamental frequences ν)

Example: Ionization in stellar atmosphere

The density of solar photosphere is about $0.3\,\mathrm{g\,m^{-3}}$, of which 75 mol.% is hydrogen and the rest helium, the temperature is 5800 K. Calculate the degree of dissociation of hydrogen; ignore ion $\mathrm{H^-}$ and the exited states of H atom. The H ionization energy is 13.6 eV.



$$\mathrm{H} \rightarrow \mathrm{H^+} + \mathrm{e^-}$$

Solution. From (1) we get

$$K = \exp\left(-\frac{\Delta_\mathrm{r}G^\circ_\mathrm{m}}{RT}\right) = \exp\left(-\frac{E_\mathrm{dis}}{RT}\right) \frac{\dfrac{g(\mathrm{H^+})k_\mathrm{B}T}{p^\mathrm{st}\Lambda^3(\mathrm{H^+})} \cdot \dfrac{g(\mathrm{e^-})k_\mathrm{B}T}{p^\mathrm{st}\Lambda^3(\mathrm{e^-})}}{\dfrac{g(\mathrm{H})k_\mathrm{B}T}{p^\mathrm{st}\Lambda^3(\mathrm{H})}} \approx \exp\left(-\frac{E_\mathrm{dis}}{RT}\right) \frac{k_\mathrm{B}T}{p^\mathrm{st}\Lambda^3(\mathrm{e^-})}$$

where $q_\mathrm{in}(\mathrm{H^+}) = g(\mathrm{H^+}) = 1$, $g(\mathrm{H}) = g(\mathrm{e}) = 2$ (cancels out). Also $M(\mathrm{H}) \approx M(\mathrm{H^+}) \Rightarrow \Lambda(\mathrm{H^+})/\Lambda(\mathrm{H}) \approx 1$.

In the equilibrium and after inserting $p = cRT$ we get the Saha equation:

$$K = \frac{p(\mathrm{H^+})p(\mathrm{e})}{p^\mathrm{st}p(\mathrm{H})} = \frac{c(\mathrm{H^+})c(\mathrm{e})RT}{p^\mathrm{st}c(\mathrm{H})} = \frac{\alpha c(\mathrm{H})RT}{p^\mathrm{st}} = \frac{\alpha c(\mathrm{H})RT}{p^\mathrm{st}(1-\alpha)} \approx \frac{\alpha^2 c_0(\mathrm{H})RT}{p^\mathrm{st}}$$

where in the last step we have assumed that α is tiny.

Example: Ionization in stellar atmosphere

The concentration of H je 75 % of the total concentration:

$$c_{\mathrm{tot}} = \frac{\rho}{0.75M(\mathrm{H}) + 0.25M(\mathrm{He})}, \quad c_0(\mathrm{H}) = 0.75c_{\mathrm{tot}}$$

Finally

$$\alpha = \sqrt{\frac{\exp(-E_{\mathrm{dis}}/RT)}{\Lambda^3(\mathrm{e}^+)c_0(\mathrm{H})}} = \underline{0.0145\,\%}$$

T=5800[K]	
rho=0.3[g.m-3]	$0.0003\,\mathrm{kg\,m^{-3}}$
C=rho/(M(H)*0.75+M(He)*0.25)	$0.170784\,\mathrm{mol\,m^{-3}}$
C0=C*0.75	$0.128088\,\mathrm{mol\,m^{-3}}$
Ei=13.6[eV]	$2.17896 \cdot 10^{-18}$ J
Lambdae=h/sqrt(2*pi*me*k*T)	$9.78737 \cdot 10^{-10}$ m
alfa=sqrt(exp(-Ei/k/T)/Lambdae**3/C0/NA)	$\underline{0.0001451}$

Isothermal-isobaric ensemble

Also *NPT* or *NpT*, loosely "isobaric": Legendre transform $V \to p$ from *NVT*.
The same argument as for $E \to T$ now applies to $V \to p$:

$$\boldsymbol{\pi}(V_{1+2}) = \boldsymbol{\pi}(V_1 + V_2) = \boldsymbol{\pi}(V_1)\,\boldsymbol{\pi}(V_2)$$

Together: $\boldsymbol{\pi} = \exp(\alpha_i - \beta E - \gamma V)$
γ is a universal property of a barostat – to be determined from ideal gas.

$$\langle V \rangle = \frac{\int V \mathrm{e}^{-\beta E_{\mathrm{kin}}} \mathrm{e}^{-\gamma V} \boldsymbol{\mu}(V) \mathrm{d}V \mathrm{d}\vec{r}_1 \ldots \mathrm{d}\vec{p}_N}{\int \mathrm{e}^{-\beta E_{\mathrm{kin}}} \mathrm{e}^{-\gamma V} \boldsymbol{\mu}(V) \mathrm{d}V \mathrm{d}\vec{r}_1 \ldots \mathrm{d}\vec{p}_N} = \frac{\int V^{N+1} \mathrm{e}^{-\gamma V} \boldsymbol{\mu}(V) \mathrm{d}V}{\int V^{N} \mathrm{e}^{-\gamma V} \boldsymbol{\mu}(V) \mathrm{d}V} \overset{\boldsymbol{\mu}(V) \propto V^k}{=} \frac{N+1+k}{\gamma}$$

Tricks used:

- $\int \mathrm{d}\vec{p}_1 \ldots \mathrm{d}\vec{p}_N$ gives the same factor, Λ^{-3N}
- $\int \mathrm{d}\vec{r}_1 \ldots \mathrm{d}\vec{r}_N = V^N$
  correctly: $\int X \mathrm{d}V \mathrm{d}\vec{r}_1 \ldots \mathrm{d}\vec{r}_N = \int_0^\infty \left[\int_V \ldots \int_V X \mathrm{d}\vec{r}_1 \ldots \mathrm{d}\vec{r}_N\right] \mathrm{d}V$ (the order of integration is important)
  or by substituting $V^{1/3}\xi_i = \vec{r}_i$ one gets $\mathrm{d}\vec{r}_1 \ldots \mathrm{d}\vec{r}_N = V^N \mathrm{d}\xi_1 \ldots \mathrm{d}\xi_N$ (int. order is irrelevant)
- $\int_0^\infty V^N \mathrm{e}^{-\gamma V} \mathrm{d}V = N!/\gamma^{N+1}$ (recursively by parts)

$\boldsymbol{\mu}(V)$ maintains Z_{NpT} dimensionless, $N \to \infty$ leads to the same results.

$\langle V \rangle$ should be equal to $Nk_{\mathrm{B}}T/p$ (at limit $N \to \infty$) $\Rightarrow$ $\gamma = \frac{N+1+k}{N} \frac{p}{k_{\mathrm{B}}T} \approx \frac{p}{k_{\mathrm{B}}T}$

Isothermal-isobaric ensemble (contd.)

Normalization constant α (from the Boltzmann eq. and $\mathrm{e}^{\alpha} = 1/Z_{NpT}$):

$$S = k_\mathrm{B} \sum_\psi \boldsymbol{\pi}(\psi)[\alpha - \beta\mathcal{E}(\psi) - \gamma V] = k_\mathrm{B}\alpha - \frac{U}{T} - \frac{p\langle V\rangle}{T}$$

$$-k_\mathrm{B}T \ln Z_{NpT} = U - TS + p\langle V\rangle = G$$

$$Z_{NpT} = \frac{1}{N!h^{3N}} \int \mathrm{e}^{-\beta(E+pV)} \mathrm{d}\vec{r}_1 \ldots \mathrm{d}\vec{p}_N \, \boldsymbol{\mu}(V) \mathrm{d}V,$$

where $\boldsymbol{\mu}(V) = \{1/V, 1/\Lambda^3, \beta p, N/V, \partial \ln Q_N/\partial V \ldots\}$.

We easily get:

$$\mathrm{d}G = -S\mathrm{d}T + V\mathrm{d}p$$

$$\left(\frac{\partial \ln Z_{NpT}}{\partial p}\right)_T = -\beta\langle V\rangle \frac{N+1}{N} + \frac{1}{p} \quad \Rightarrow \quad \left(\frac{\partial G}{\partial p}\right)_T = \langle V\rangle \frac{N+1}{N} - \frac{k_\mathrm{B}T}{p} \overset{N\to\infty}{\approx} \langle V\rangle$$

The expectation value of X in the isobaric ensemble is

$$\langle X\rangle = \frac{\int X \mathrm{e}^{-\beta(E+pV)} \mathrm{d}V \mathrm{d}\vec{r}_1 \ldots \mathrm{d}\vec{p}_N}{Z_{NpT}}$$

Grandcanonical ensemble

Also μVT (from NVT by Legendre transform $N \to \mu$): the same argument now applies to N:

$$\boldsymbol{\pi}(N_{1+2}) = \boldsymbol{\pi}(N_1 + N_2) = \boldsymbol{\pi}(N_1)\,\boldsymbol{\pi}(N_2)$$

Together: $\boldsymbol{\pi} = \exp(\alpha_i - \beta E + \delta N)$
δ is a universal property of a source of particles – to be determined from ideal gas

$$\langle N \rangle = \frac{\sum_{N=0}^{\infty} \int \frac{N}{h^{3N} N!} \mathrm{e}^{-\beta E_{\mathrm{kin}}} \mathrm{e}^{\delta N} \mathrm{d}\vec{r}_1 \ldots \mathrm{d}\vec{p}_N}{\sum_{N=0}^{\infty} \int \frac{1}{h^{3N} N!} \mathrm{e}^{-\beta E_{\mathrm{kin}}} \mathrm{e}^{\delta N} \mathrm{d}\vec{r}_1 \ldots \mathrm{d}\vec{p}_N} \overset{\text{id.}}{=} \frac{\sum_{N=0}^{\infty} \frac{N}{N!} \frac{V^N}{\Lambda^{3N}} \mathrm{e}^{\delta N}}{\sum_{N=0}^{\infty} \frac{1}{N!} \frac{V^N}{\Lambda^{3N}} \mathrm{e}^{\delta N}} = \frac{V}{\Lambda^3} \mathrm{e}^{\delta}$$

Tricks used in the calculation:

- $\int \mathrm{d}\vec{p}_1 \ldots \mathrm{d}\vec{p}_N = \Lambda^{-3N}$
- $\int \mathrm{d}\vec{r}_1 \ldots \mathrm{d}\vec{r}_N = V^N$
- $\sum \frac{1}{N!} x^N = \mathrm{e}^x$, where $x = \frac{V^N}{\Lambda^{3N}} \mathrm{e}^{\delta N}$
- derivative by x: $\sum \frac{1}{N!} N x^{N-1} = \mathrm{e}^x \Rightarrow \sum_0^{\infty} \frac{N}{N!} x^N = x \mathrm{e}^x$

On comparing with $\exp(-\beta \mu_{\text{id, point particle}}) = V/\Lambda^3 N$, one gets $\delta = \beta\mu$.

Grandcanonical ensemble (contd.)

Normalization constant α (from the Boltzmann eq. and $e^{\alpha} = 1/Z_{\mu VT}$):

$$S = k_B \sum_{\psi} \pi(\psi)[\alpha - \beta\mathcal{E}(\psi) + \delta N] = k_B\alpha - \frac{U}{T} + \frac{\mu\langle N\rangle}{T}$$

$$-k_B T \ln Z_{\mu VT} = U - TS - \mu\langle N\rangle = \Omega$$

where

$$Z_{\mu VT} = \sum_{N=0}^{\infty} \frac{e^{\beta\mu N}}{N! h^{3N}} \int e^{-\beta E} d\vec{r}_1 \ldots\ldots d\vec{p}_N$$

Grandcanonical potential $\Omega = F - \mu N = F - G = -pV$

$$dF = -SdT - pdV + \mu dN \;\Rightarrow\; d\Omega = -SdT - pdV - Nd\mu$$

Grandcanonical ensemble (contd.)

The expectation value of X in the grandcanonical ensemble is

$$\langle X \rangle = \frac{\sum_0^\infty \frac{\alpha^N}{N!} \int X \mathrm{e}^{-\beta E} \mathrm{d}\vec{r}_1 \ldots \mathrm{d}\vec{p}_N}{\sum_0^\infty \frac{\alpha^N}{N!} \int \mathrm{e}^{-\beta E} \mathrm{d}\vec{r}_1 \ldots \mathrm{d}\vec{p}_N}, \quad \text{where } \alpha = \mathrm{e}^{\beta\mu}.$$

The last eq. is usually integrated over momenta (incl. internal degrees of freedom provided that they can be separated); for $X = X(N, \vec{r}^N)$ it holds:

$$\langle X \rangle = \frac{\sum_0^\infty \frac{\alpha'^N}{N!} \int X \mathrm{e}^{-\beta E} \mathrm{d}\vec{r}_1 \ldots \mathrm{d}\vec{r}_N}{\sum_0^\infty \frac{\alpha'^N}{N!} \int \mathrm{e}^{-\beta E} \mathrm{d}\vec{r}_1 \ldots \mathrm{d}\vec{r}_N}, \quad \text{where } \alpha' = \frac{\alpha q_{\mathrm{in}}}{\Lambda^3} \tag{2}$$

Grandcanonical ensemble (contd.)

The quotient in series (2) can be expressed as

$$\mu_{\mathrm{id}} = -k_{\mathrm{B}} T \ln(q_{\mathrm{tr}} q_{\mathrm{in}})$$

$$\alpha' = \frac{\alpha q}{\Lambda^3} = \mathrm{e}^{\beta\mu_{\mathrm{res}}}\rho, \quad \rho = \frac{\langle N \rangle}{V}, \quad \mu_{\mathrm{res}} = \mu - \mu^{\mathrm{id}}(\rho)$$

where μ_{res} is the **residual chemical potential** = chemical potential with respect to the standard state of ideal gas at given temperature and volume (= density), which can be compared with tables (after pressure is recalculated from p^{st} using the ideal gas equation of state).

Also called the Ben-Naim standard state (esp. for ions).