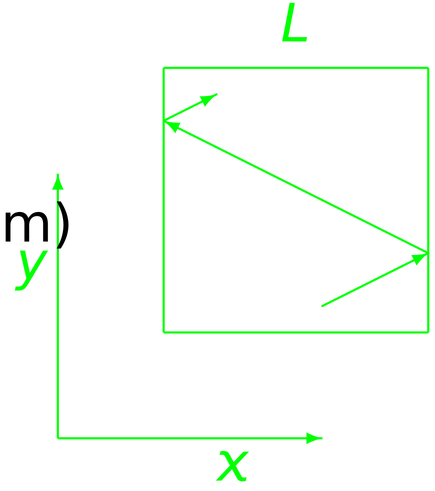
Statistical thermodynamics instant



- monoatomic ideal gas in a box:
  - ideal gas equation of state
  - temperature given by kinetic energy, $\left\langle \frac{1}{2} m \dot{r}_{i,x}^2 \right\rangle = \frac{1}{2} k_B T$ (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 phase-space states is constant on the constant-energy manifold
- $\boldsymbol{\pi} \propto \exp(-E/k_B T)$ 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

$$dU = \sum_\psi \boldsymbol{\pi}(\psi) \cdot d\mathcal{E}(\psi) + \sum_\psi d\boldsymbol{\pi}(\psi) \cdot \mathcal{E}(\psi) = -p\,dV + T dS$$

$$\Rightarrow \quad S = -k_B \sum_\psi \boldsymbol{\pi}(\psi) \ln \boldsymbol{\pi}(\psi) \quad \text{or} \quad S = k_B \ln W \quad \Rightarrow \; F, G, \text{ etc.}$$

- Boltzmann H-theorem (second law)

Canonical ensemble: Helmholtz energy

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

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

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

⇒ 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 quantities ($\mathrm{d}F = -p\mathrm{d}V - S\mathrm{d}T$):

$$p = -\frac{\partial F}{\partial V}$$

$$S = -\frac{\partial F}{\partial T}$$

$$U = F + TS$$

$$H = U + pV$$

$$G = F + pV$$

Semiclassical partition function

Hamilton formalism: positions of atoms = $\vec{r}_i$, momenta = $\vec{p}_i$.

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

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.

Why the factorial?

- Particles are indistinguishable . . . but at high enough T appear 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)

Semiclassical partition function

Integrals over positions and momenta are separated

Integrals over momenta can be evaluated: $\int \exp\left(-\frac{p_{1,x}^2/2m}{k_\mathrm{B}T}\right) \mathrm{d}p_{1,x} = \sqrt{2\pi k_\mathrm{B}Tm}$ After $3N$ integrations we get:

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

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:

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

do not confuse:
U = internal energy
$U(\vec{r}_1, \ldots)$ = potential

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) 6.2 Å; b) 3.8 Å

a)

$$\Lambda = \frac{h}{\sqrt{2\pi m k_\mathrm{B} T}} = \frac{6.6\times10^{-34}}{\sqrt{2\times\pi\times\frac{0.004}{6\times10^{23}}\times1.38\times10^{-23}\times2}} = 6.2\times10^{-10}\,\mathrm{m}$$

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

b)

$$l = \sqrt[3]{V_1} = \sqrt[3]{\frac{M}{N_\mathrm{A}\rho}} = \sqrt[3]{\frac{0.004}{6\times10^{23}\times125}} = 3.8\times10^{-10}\,\mathrm{m}$$

$l < \Lambda \Rightarrow$ cannot use classical mechanics

Semiclassical monoatomic ideal gas

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

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

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

e = Euler number
e = elementary charge

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

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

(with respect to the standard state of a free molecule at zero temperature)

And verification:

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

Monoatomic ideal gas

Or quantum calculation of the translational partition function:

Eigenvalues of energy of a point mass 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 semiclassical Z was correct.

Polyatomic ideal gas

The internal degrees of freedom are separated from the translational ones.

The internal partition function is the sum over the internal degrees of freedom:

$$q = \sum_{\psi_{\rm in}} {\rm e}^{-\beta\mathcal{E}(\psi)}$$

Canonical partition function:

$$Z = \frac{(qV)^N}{N!\Lambda^{3N}}, \quad F = -k_{\rm B}T\ln Z = -k_{\rm B}TN\ln\frac{Veq}{N\Lambda^3}$$

Chemical potential:

$$\mu = \left(\frac{\partial F}{\partial N}\right)_{T,V} = k_{\rm B}T\ln\left(\frac{N\Lambda^3}{qV}\right) = k_{\rm B}T\ln\left(\frac{p\Lambda^3}{qk_{\rm B}T}\right)$$

NPT ensemble: $T, p = \text{const}$

Also isothermal–isobaric, loosely "isobaric": $V \to p$
The same argument now applied to V (as for E before):

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

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

$$\langle V\rangle = \frac{\int V e^{-\beta E_\text{kin}} e^{-\gamma V} dV d\vec{r}_1 \dots d\vec{p}_N}{\int e^{-\beta E_\text{kin}} e^{-\gamma V} dV d\vec{r}_1 \dots d\vec{p}_N} = \frac{\int V^{N+1} e^{-\gamma V} dV}{\int V^N e^{-\gamma V} dV} = \frac{N+1}{\gamma}$$

Tricks used:

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

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

For nitpickers:
(more in simen10):
$\langle V_{NPT}(p_{NVT})\rangle - V \approx \frac{k_\text{B}T}{2N}\left(\frac{\partial\rho}{\partial p}\right)_T \rho^2 \frac{\partial^2 V}{\partial \rho^2} \overset{\text{id. gas}}{=} \frac{V}{N} = \frac{p}{k_\text{B}T}$
so that $+1$ below can be safely ignored...

NPT ensemble (contd.)

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

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

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

$$Z_{NpT} = \frac{1}{N!h^{3N}} \int \chi e^{-\beta(E+pV)} d\vec{r}_1 \dots d\vec{p}_N dV$$

where $\chi = \{1/\Lambda^3, \beta p, N/V, 1/V, \dots\}$ zajišťuje bezrozměrnost ($N \to \infty$ stejné)

We easily get:: $dG = -SdT + Vdp$

$$\left(\frac{\partial \ln Z_{NpT}}{\partial p}\right)_T = -\beta\langle V\rangle \frac{N+1}{N} + \frac{1}{p} \quad \text{čili} \quad \left(\frac{\partial G}{\partial p}\right)_T = \langle V\rangle \frac{N+1}{N} - \frac{k_B T}{p} \stackrel{N\to\infty}{\approx} \langle V\rangle$$

The expectation value of X in the isobaric ensemble is

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

Grandcanonical ensemble: $\mu = \text{const}$

The same argument now applied to N (as for E, V before):

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

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

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

Tricks used:

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

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

Grandcanonical ensemble: $\mu = \text{const}$ (contd.)

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

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

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

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: $\mu = \text{const}$ (contd.)

The expectation value of X in the grandcanonical ensemble is

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

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

$$\langle X \rangle = \frac{\sum_0^\infty \frac{a'^N}{N!} \int X e^{-\beta E} d\vec{r}_1 \dots d\vec{r}_N}{\sum_0^\infty \frac{a'^N}{N!} \int e^{-\beta E} d\vec{r}_1 \dots d\vec{r}_N}, \quad \text{where } a' = \frac{aq}{\Lambda^3} \tag{1}$$

Grandcanonical ensemble: $\mu = \text{const}$ (contd.)

$$e^{\beta\mu_{\rm id}} = \rho\Lambda^3/q$$

The quotient in series (1) can be expressed as

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

where $\mu_{\rm res}$ 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 $p^{\rm st}$ using the ideal gas equation of state).