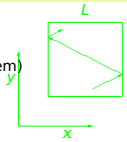
Statistical thermodynamics instant

[jkv pic/BoltzmannTomb.jpg] 1/14 s01/3



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

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

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

- Boltzmann H-theorem (second law)

Canonical ensemble: Helmholtz energy

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$$\boldsymbol{\pi}(\psi) = \frac{\mathrm{e}^{-\beta\mathcal{E}(\psi)}}{Z}, \quad Z = \sum_\psi \mathrm{e}^{-\beta\mathcal{E}(\psi)} \qquad \beta = \frac{1}{k_\mathrm{B}T}$$

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

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

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

Semiclassical partition function

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

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

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

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Integrals over positions and momenta are separated

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

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Example

a) Calculate Λ for helium at $T = 2$ K.
b) Compare to the typical distance of atoms in liquid helium (density 0.125 g/cm^3).

a) 6.2 Å; b) 3.8 Å

a)

$$\Lambda = \frac{h}{\sqrt{2\pi m k_\mathrm{B} T}} = \frac{6.6\times10^{-34}}{\sqrt{2 \times \pi \times \frac{0.004}{6\times10^{23}} \times 1.38\times10^{-23} \times 2}} = 6.2\times10^{-10}\,\mathrm{m}$$

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

b)

$$l = \sqrt[3]{V_1} = \sqrt[3]{\frac{M}{N_\mathrm{A}\rho}} = \sqrt[3]{\frac{0.004}{6\times10^{23} \times 125}} = 3.8\times10^{-10}\,\mathrm{m}$$

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

Semiclassical monoatomic ideal gas

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

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

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

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

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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

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The internal degrees of freedom are separated from the translational ones.
The internal partition function is the sum over the internal degrees of freedom:

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

Canonical partition function:

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

Chemical potential:

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

NPT ensemble: T, p = const

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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

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

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

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

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

NPT ensemble (contd.)

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

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

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

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

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

We easily get::

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

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

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: $\mu = \text{const}$

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

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

Tricks used:

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

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

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

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

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

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

where

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

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

$$\mathrm{d}F = -S\mathrm{d}T - p\mathrm{d}V + \mu\mathrm{d}N \;\Rightarrow\; \mathrm{d}\Omega = -S\mathrm{d}T - p\mathrm{d}V - N\mathrm{d}\mu$$

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

The expectation value of X in the grandcanonical ensemble is

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

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

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

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

The quotient in series (1) can be expressed as $\mathrm{e}^{\beta\mu_{\text{id}}} = \rho\Lambda^3/q$

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

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).