

Pressure of ideal gas from the kinetic theory I

Molecule = point mass

N molecules of masses m_i , $i = 1, \dots, N$, in a cube of edge L

Velocity of molecule i is $\vec{v}_i = (v_{i,x}, v_{i,y}, v_{i,z})$

After elastic reflection: $v_{i,x} \rightarrow -v_{i,x}$

A molecule hits the same wall again after time $t = 2L/v_{i,x}$

Force = change of momentum in a time unit

Momentum $\vec{P} = m\vec{v}$

Change of momentum = $\Delta P_x = 2m_i v_{i,x}$

Averaged force caused by impacts of one molecule:

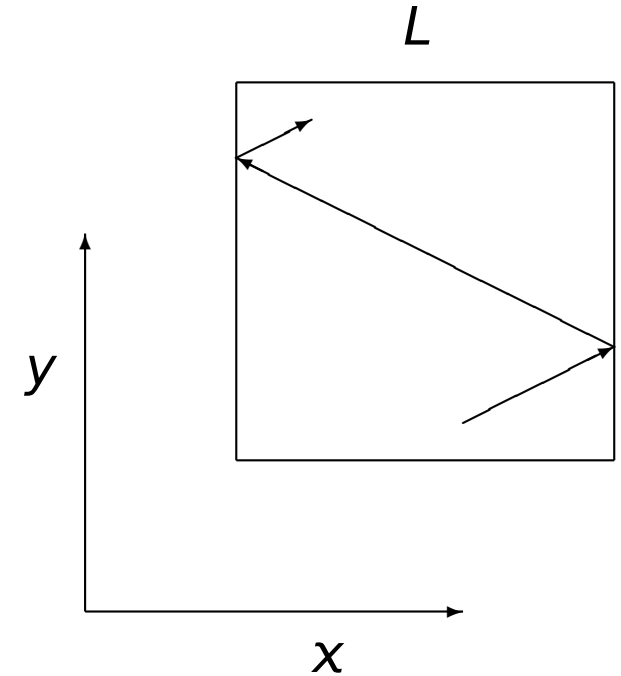
$$F_{i,x} = \frac{\Delta P_x}{t} = \frac{2m_i v_{i,x}}{2L/v_{i,x}} = \frac{m_i v_{i,x}^2}{L}$$

Pressure = force of all N molecules, divided by the area

$$p = \frac{\sum_{i=1}^N F_{i,x}}{L^2} = \frac{\sum_{i=1}^N m_i v_{i,x}^2}{L^3}$$

Kinetic energy of one molecule

$$\frac{1}{2} m_i |\vec{v}_i|^2 \equiv \frac{1}{2} m_i v_i^2 = \frac{1}{2} m_i (v_{i,x}^2 + v_{i,y}^2 + v_{i,z}^2)$$



Kinetic energy of gas = internal energy (monoatomic gas)

$$E_{\text{kin}} = \frac{1}{2} \sum_{i=1}^N m_i v_i^2 = \frac{3}{2} \sum_{i=1}^N m_i v_{i,x}^2$$

⇒

$$p = \frac{\sum_{i=1}^N m_i v_{i,x}^2}{L^3} = \frac{2}{3} \frac{E_{\text{kin}}}{V}$$

In other words

$$pV = \frac{2}{3} E_{\text{kin}} \stackrel{!}{=} nRT$$

Temperature is a measure of kinetic energy

Assumptions:

- Pressure is a result of **averaged** impacts of molecules
- We used the **classical mechanics**

Per one molecule:

$$n = \frac{N}{N_A}$$

$$k_B = \frac{R}{N_A} = 1.38065 \times 10^{-23} \text{ J K}^{-1}$$

Equation of state:

$$pV = nRT = Nk_B T$$

Internal energy:

$$U \equiv E_{\text{kin}} = \frac{3n}{2}RT = \frac{3N}{2}k_B T$$



Ludwig Eduard Boltzmann (1844–1906)

credit: scienceworld.wolfram.com/biography/Boltzmann.html

Expression E_{kin} is composed of $f = 3N$ terms of the form $\frac{1}{2}m_i v_{i,k}^2$, where $k \in \{x, y, z\}$.

$$pV = Nk_B T = \frac{f}{3}k_B T = \frac{2}{3}E_{\text{kin}}$$

f = **number of mechanical degrees of freedom.**

Average energy contribution per one degree of freedom:

$$\frac{E_{\text{kin}}}{f} = \frac{1}{2}k_B T$$

Generalization: any quadratic function in the Hamiltonian

Heat capacity in molar units ($N = N_A$):

$$C_{V,m} = \left(\frac{\partial U}{\partial T}\right)_V = \left(\frac{\partial E_{\text{kin}}}{\partial T}\right)_V = \frac{\frac{1}{2}f k_B T}{N_A T} = \frac{3}{2}R$$

degrees of freedom per molec.

Extension:

- Linear molecules: + 2 rotations, $C_{V,m} = \frac{5}{2}R$ (but: hydrogen)
- Nonlinear molecules: + 3 rotations, $C_{V,m} = 3R$
- (Vibrations **classically**: + 2 for each (incl. E_{pot}) – **imprecise!**)

Equipartition principle – example

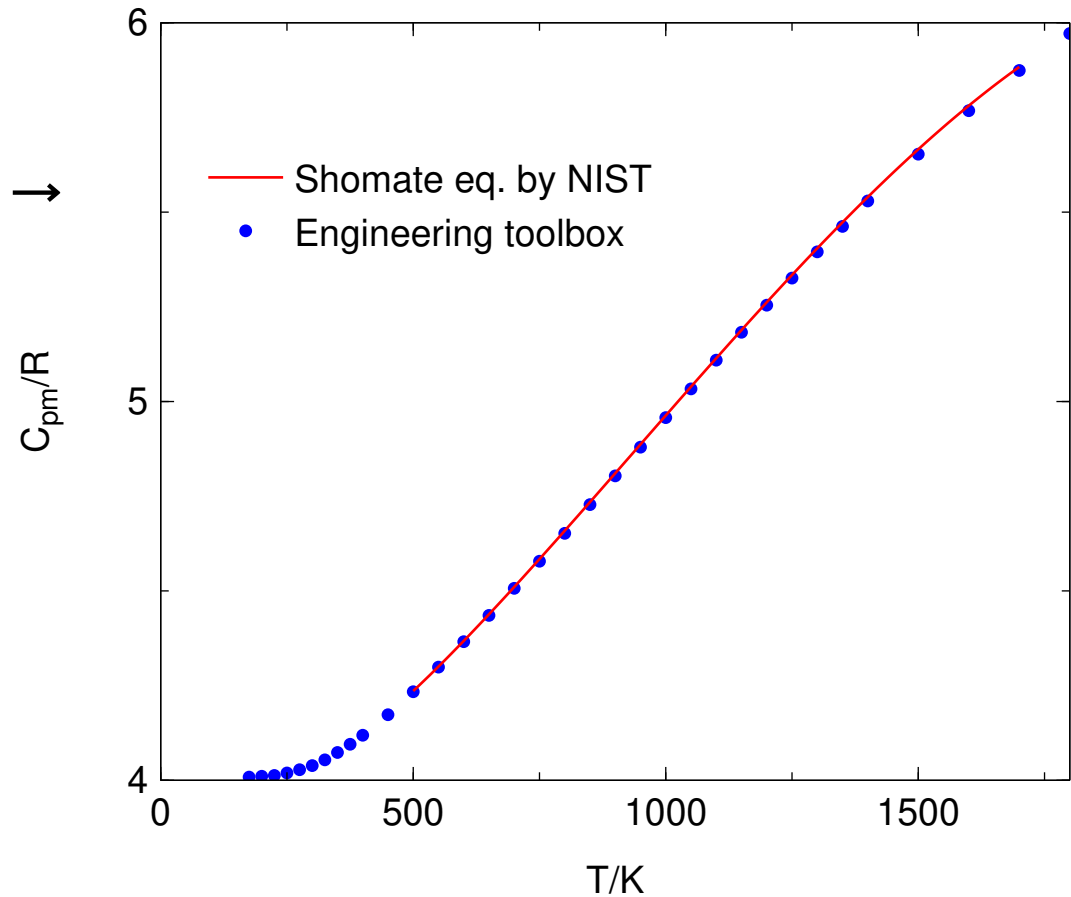
Calculate C_{pm} for a) nitrogen, b) water vapor?

$$3.5R = 29.10 \text{ J K}^{-1} \text{ mol}^{-1}, 4R = 33.26 \text{ J K}^{-1} \text{ mol}^{-1}$$

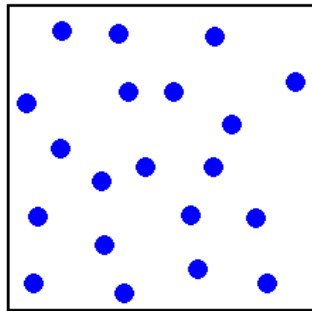
Experiment: N_2 (300 K): $29.12 \text{ J K}^{-1} \text{ mol}^{-1}$

H_2O (500 K): $35.22 \text{ J K}^{-1} \text{ mol}^{-1}$

Isobaric heat capacity of water vapor → → →



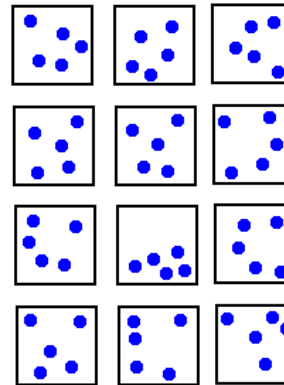
- **microstate** (state, configuration) = instantaneous “snapshot” at given time
quantum description: state = eigenstate (wave function ψ)
classical description: state = positions and velocities* of all particles
at given time, $\psi = (\vec{r}_1, \dots, \vec{r}_N, \vec{v}_1, \dots, \vec{v}_N)$
- **macrostate** = averaged action of all microstates
- **ensemble** = set of all microstates with known probabilities $\pi(\psi)$
- **trajectory** = record of a time development of a microstate



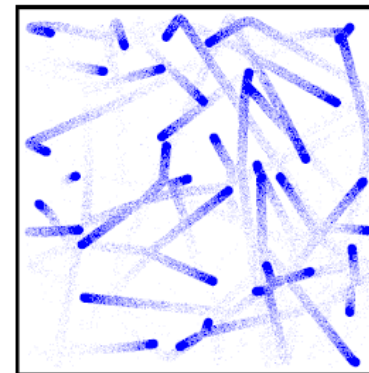
microstate



macrostate



ensemble



trajectory

*in fact, momenta – more later. There are ∞ states, hence we work with their probability density $\rho(\psi) \equiv \rho(\vec{r}_1, \dots, \vec{r}_N, \vec{p}_1, \dots, \vec{p}_N)$.

Microcanonical ensemble and ergodic hypothesis

Microcanonical ensemble = ensemble of microstates in an isolated system (which has developed in time for a long time)

Also denoted as **NVE** ($N = \text{const}$, $V = \text{const}$, $E = \text{const}$)

● **Ergodic hypothesis** (quantum): $\pi(\psi_i) = \text{const} = \frac{1}{W}$
($W = \#$ of states)

● **Ergodic hypothesis** (classical):
trajectory covers the space[†] with uniform probability

for me:
e NVE ensemble
r smaller balls
c trajectory

In other words:

Time average (over a trajectory)

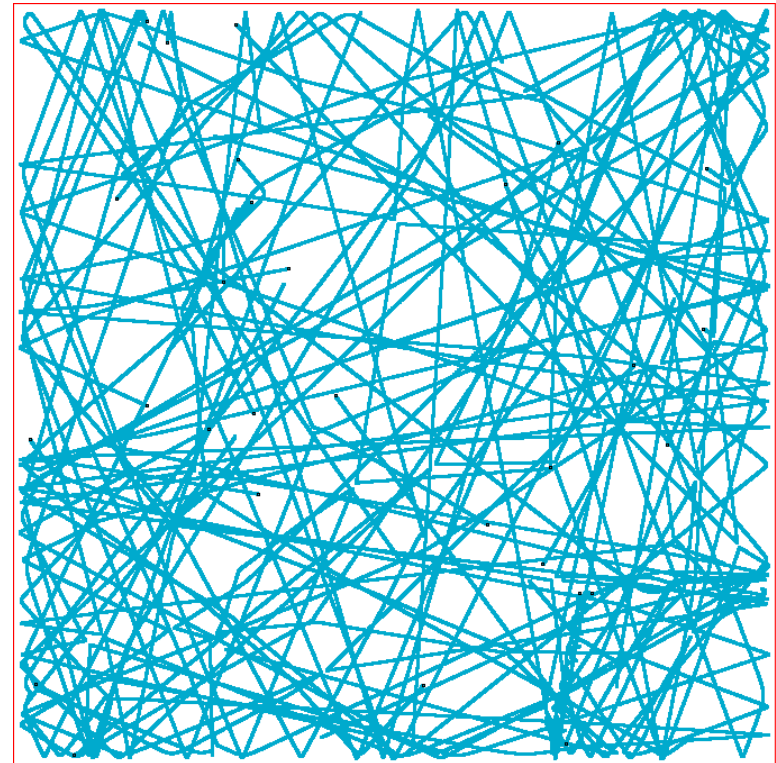
$$= \langle X \rangle_t = \lim_{t \rightarrow \infty} \frac{1}{t} \int_0^t X(t) dt$$

= ensemble average


$$= \langle X \rangle = \frac{1}{W} \sum_{\psi} X(\psi)$$

for any quantity $X = X(\psi)$, where $\psi = \psi(t)$

[†]namely: the phase state of $\{(\vec{r}_1, \dots, \vec{r}_N, \vec{p}_1, \dots, \vec{p}_N)\}$



$$\langle X \rangle = \frac{\sum_{\psi} X(\psi)}{W}$$

Example. You win \$5 if you throw  on a dice, you loose \$1 if you throw anything else. What is your mean (expected) win in this game?

0

Whole thermodynamics can be built on the top of the microcanonical ensemble.
But for $T = \text{const}$ it is much easier.

We want $T = \text{const}$: Canonical ensemble

Also **NVT** ($N = \text{const}$, $V = \text{const}$, $T = \text{const}$)

Ergodic hypothesis: $\pi(\psi) = \pi(\mathcal{E}(\psi))$

$E_1 + E_2 = E_{1+2}$ (do not interact)

$\pi(E)$ = probability of any state with energy E

$$\pi(E_1) \cdot \pi(E_2) = \pi(E_{1+2}) = \pi(E_1 + E_2)$$

$$\Rightarrow \pi(E) = \text{const}^E = \exp(\alpha_i - \beta E)$$

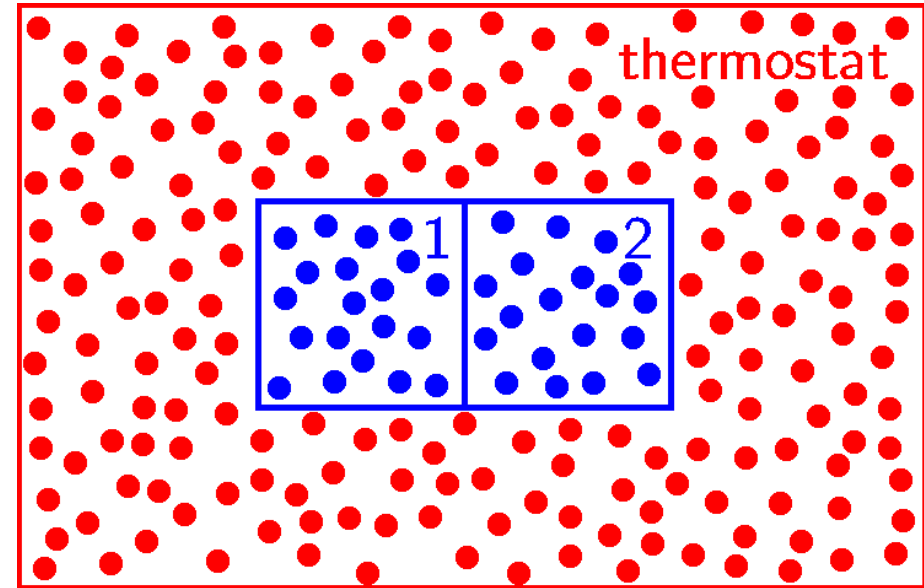
● 0th Law $\Rightarrow \beta$ is empirical temperature

● α_i is system-dependent a normalizing const. so that $\sum_{\psi} \pi(\psi) = 1$

Determining β : monoatomic perfect gas, per 1 atom $U_1 = \frac{3}{2}k_B T$

$$\langle U_1 \rangle = \frac{\sum_{\psi} \mathcal{E}(\psi) \pi(\mathcal{E}(\psi))}{\sum_{\psi} \pi(\mathcal{E}(\psi))} = \frac{\int \frac{1}{2} m \vec{v}^2 \pi(\frac{1}{2} m \vec{v}^2) d\vec{v}}{\int \pi(\frac{1}{2} m \vec{v}^2) d\vec{v}}$$

Evaluation gives: $\langle U_1 \rangle = \frac{3}{2} \frac{1}{\beta} \Rightarrow \beta = \frac{1}{k_B T}$



$$\begin{aligned}
 \langle U_1 \rangle &= \frac{\int_{R^3} \frac{1}{2} m \vec{v}^2 \pi(\frac{1}{2} m \vec{v}^2) d\vec{v}}{\int_{R^3} \pi(\frac{1}{2} m \vec{v}^2) d\vec{v}} \\
 &= \frac{\int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \frac{1}{2} m (v_x^2 + v_y^2 + v_z^2) e^{-\frac{1}{2} \beta m v_x^2} dv_x e^{-\frac{1}{2} \beta m v_y^2} dv_y e^{-\frac{1}{2} \beta m v_z^2} dv_z}{\int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} e^{-\frac{1}{2} \beta m v_x^2} dv_x e^{-\frac{1}{2} \beta m v_y^2} dv_y e^{-\frac{1}{2} \beta m v_z^2} dv_z} \\
 &= 3 \frac{\int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \frac{1}{2} m v_x^2 e^{-\frac{1}{2} \beta m v_x^2} dv_x e^{-\frac{1}{2} \beta m v_y^2} dv_y e^{-\frac{1}{2} \beta m v_z^2} dv_z}{\int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} e^{-\frac{1}{2} \beta m v_x^2} dv_x e^{-\frac{1}{2} \beta m v_y^2} dv_y e^{-\frac{1}{2} \beta m v_z^2} dv_z} \\
 &= 3 \frac{\int_{-\infty}^{\infty} \frac{1}{2} m v_x^2 e^{-\frac{1}{2} \beta m v_x^2} dv_x}{\int_{-\infty}^{\infty} e^{-\frac{1}{2} \beta m v_x^2} dv_x} = 3 \frac{\frac{1}{2} m \frac{1}{2 \frac{1}{2} \beta m} \sqrt{\frac{\pi}{\frac{1}{2} \beta m}}}{\sqrt{\frac{\pi}{\frac{1}{2} \beta m}}} = \frac{3}{2} \frac{1}{\beta}
 \end{aligned}$$

We have used the **Gauss integral**: $\int_{-\infty}^{\infty} e^{-ax^2} dx = \sqrt{\frac{\pi}{a}}$ (where $a = \frac{1}{2} \beta m$)
and its derivative by parameter a :

$$\int_{-\infty}^{\infty} x^2 e^{-ax^2} dx = -\frac{d}{da} \int_{-\infty}^{\infty} e^{-ax^2} dx = -\frac{d}{da} \sqrt{\frac{\pi}{a}} = \frac{1}{2a} \sqrt{\frac{\pi}{a}}$$

Determining β

+ 11/32
s01/2

$$\frac{\int_{-\infty}^{\infty} \frac{1}{2} m v_x^2 e^{-\frac{1}{2} \beta m v_x^2} dv_x}{\int_{-\infty}^{\infty} e^{-\frac{1}{2} \beta m v_x^2} dv_x} = \frac{1}{2\beta}$$

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> int(1/2*m*(vx^2)*exp(-beta*m*v_x^2/2), vx=-infinity..infinity) /  
int(exp(-1/2*beta*m*(vx^2)), vx=-infinity..infinity)  
assuming m>0,beta>0;
```

$$\frac{1}{2\beta}$$

```
> |
```

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Time: 0.04s

Text Mode

Generalization of the mean value (= expectation value):

$$\langle X \rangle = \sum_{\psi} X(\psi) \pi(\mathcal{E}(\psi)) = \sum_{\psi} X(\psi) e^{\alpha - \beta \mathcal{E}(\psi)} = \frac{\sum_{\psi} X(\psi) e^{-\beta \mathcal{E}(\psi)}}{\sum_{\psi} e^{-\beta \mathcal{E}(\psi)}}$$

Boltzmann factor: $e^{-\mathcal{E}(\psi)/k_B T}$

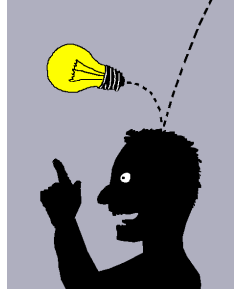
Example. You win \$5 if you throw  on a dice, you lose \$1 if you throw anything else. However, you have drilled a small lead weight under  (opposite to ) so that the probabilities are $\pi(\text{3 dots}) = 0.2$ and $\pi(\text{1 dot}) = \pi(\text{2 dots}) = \pi(\text{4 dots}) = \pi(\text{5 dots}) = \pi(\text{6 dots}) = 0.16$. What is your mean (expected) win in this game?

2.0\$

... or the first half of statistical thermodynamics.

Probability of finding a state with energy \mathcal{E} is proportional to

$$\pi(\mathcal{E}) = \text{const} \cdot \exp\left[-\frac{\mathcal{E}(\psi)}{k_B T}\right] = \text{const} \cdot \exp\left(-\frac{E_m}{RT}\right)$$



Examples:

- a reacting system can overcome the activation energy E^* with probability $\sim \exp\left(-\frac{E^*}{RT}\right) \Rightarrow$ Arrhenius formula

$$k = A \exp\left(-\frac{E^*}{RT}\right)$$

- the energy needed for transferring a molecule from liquid to gas is $\Delta_{\text{vap}}H_m$ (per mole), probability of finding a molecule in vapor is proportional to $\sim \exp\left(-\frac{\Delta_{\text{vap}}H_m}{RT}\right) \Rightarrow$ Clausius–Clapeyron equation (integrated)

$$p = p_0 \exp\left[-\frac{\Delta_{\text{vap}}H_m}{R} \left(\frac{1}{T} - \frac{1}{T_0}\right)\right] = \text{const} \cdot \exp\left(-\frac{\Delta_{\text{vap}}H_m}{RT}\right)$$

... Boltzmann probability once again

Potential energy of a molecule in a homogeneous gravitational field $U_{\text{pot}} = mgh$.
Probability of finding a molecule in height h :

$$\pi \propto \exp\left(-\frac{U_{\text{pot}}}{k_{\text{B}}T}\right) = \exp\left(-\frac{mgh}{k_{\text{B}}T}\right) = \exp\left(-\frac{Mgh}{RT}\right)$$

Probability \propto density \propto pressure:

$$p = p_0 \exp\left(-\frac{Mgh}{RT}\right)$$

The same formula can be derived from the condition of mechanical equilibrium + ideal gas equation of state

$$dp = -dh\rho g, \quad \rho = \frac{Mp}{RT}$$

Which “leads to” the Boltzmann probability

Boltzmann probability

Example Energy of the *gauche* conformation of butane is by $\Delta E = 0.9$ kcal/mol higher than *anti*. Calculate the population of molecules which are in the *gauche* state at temperature 272.6 K (boiling point). (1 cal = 4.184 J).

Solution:

$$\pi(\textit{gauche}) : \pi(\textit{anti}) = \exp\left(-\frac{\Delta E}{RT}\right) = 0.190$$

Don't forget that there are **two** *gauche* states!

$$2\pi(\textit{gauche}) + \pi(\textit{anti}) = 1$$

⇒

$$\pi = \frac{2 \exp(-\Delta E/RT)}{2 \exp(-\Delta E/RT) + 1} = \frac{2 \times 0.190}{2 \times 0.190 + 1} = 0.275$$

Note: we assumed that both minima are well separated and their shapes are identical. Better formula would be with ΔG instead of ΔE

Internal energy

$$U = \sum_{\psi} \mathcal{E}(\psi) \pi(\psi)$$

Its small change is

$$dU = \sum_{\psi} \pi(\psi) \cdot d\mathcal{E}(\psi) + \sum_{\psi} d\pi(\psi) \cdot \mathcal{E}(\psi)$$

$d\mathcal{E}(\psi)$: energy level changed

$d\pi(\psi)$: probability of state ψ changed

Thermodynamics:

$$dU = -p dV + TdS$$

- $-p dV$: A “piston” moved by dx . Change in energy = $d\mathcal{E}(\psi)$ = **mechanical work**
= $-Fdx = -F/A \cdot d(Ax) = -p(\psi) dV$
 $p(\psi)$ = “pressure of state ψ ”, pressure = $p = \sum_{\psi} \pi(\psi) p(\psi)$.
- TdS : Change $\pi(\psi)$ [V] = change of the population of states with varying energies
= **heat**

Boltzmann equation for entropy

... or the 2nd half of the statistical thermodynamics

$$\pi(E) = \exp(\alpha_i - \beta E) \Rightarrow \mathcal{E}(\psi) = \frac{1}{\beta} [\alpha_i - \ln \pi(\psi)]$$

$$\sum_{\psi} d\pi(\psi) \mathcal{E}(\psi) = \sum_{\psi} d\pi(\psi) \frac{1}{\beta} [\alpha_i - \ln \pi(\psi)] = -\frac{1}{\beta} \sum_{\psi} d\pi(\psi) \cdot \ln \pi(\psi)$$

$$= -k_B T d \left[\sum_{\psi} \pi(\psi) \ln \pi(\psi) \right]$$

On comparing with TdS :

$$S = -k_B \sum_{\psi} \pi(\psi) \ln \pi(\psi)$$

Microcanonical ensemble: $\pi(\psi) = \begin{cases} 1/W & \text{for } E = \mathcal{E}(\psi) \\ 0 & \text{for } E \neq \mathcal{E}(\psi) \end{cases}$

Boltzmann equation: $S = k_B \ln W$

Property: $S_{1+2} = S_1 + S_2 = k_B \ln(W_1 W_2) = k_B \ln(W_{1+2})$



Example: Ideal solution

Energies of neighbors: $\bullet-\bullet = \bullet-\circ = \circ-\circ$

All configurations have the same energy

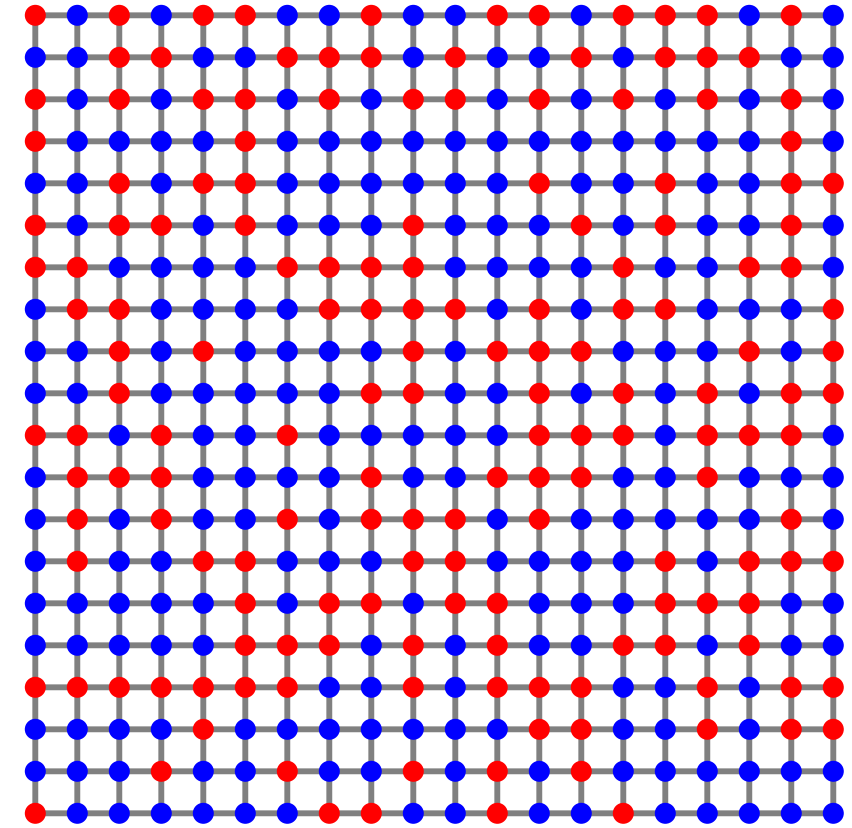
Mix N_1 molecules of 1 + N_2 molecules of 2:

$$W = \binom{N}{N_1} = \frac{N!}{N_1!N_2!}$$

$$S = k_B \ln W \approx -k_B \left(N_1 \ln \frac{N_1}{N} + N_2 \ln \frac{N_2}{N} \right)$$

$$S_m = -R (x_1 \ln x_1 + x_2 \ln x_2)$$

cf. $S = -k_B \sum_{\psi} \pi(\psi) \ln \pi(\psi)$



We used the Stirling formula, $\ln N! \approx N \ln N - N$:

$$\ln N! = \sum_{i=1}^N \ln i \approx \int_0^N \ln x \, dx \stackrel{\text{by parts}}{=} [x \ln x - x]_0^N = N \ln N - N$$

More accurately:

$$\ln N! \stackrel{\text{asympt.}}{=} N \ln N - N + \ln \sqrt{2\pi N} + \frac{1}{12N} - \frac{1}{360N^3} + \frac{1}{1260N^5} - + \dots$$

Example: Residual entropy of crystals at $T \rightarrow 0$

Crystal: 1 microstate $\Rightarrow S = k_B \ln 1 = 0$ (3rd Law)

3rd Law violation: CO, N₂O, H₂O.

Not in the true equilibrium, but “frozen”
because of high barriers

Example 1: Entropy of a crystal of CO at 0 K

$$S_m = k_B \ln 2^{N_A} = R \ln 2$$

Example 2: Entropy of ice at 0 K

$$S_m = k_B \ln 1.507^{N_A} = 3.41 \text{ J K}^{-1} \text{ mol}^{-1}$$

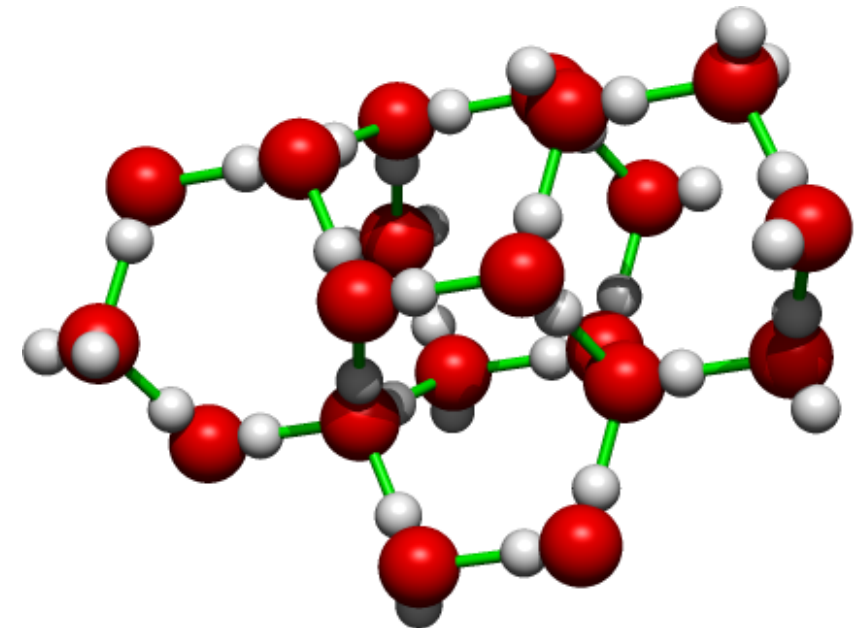
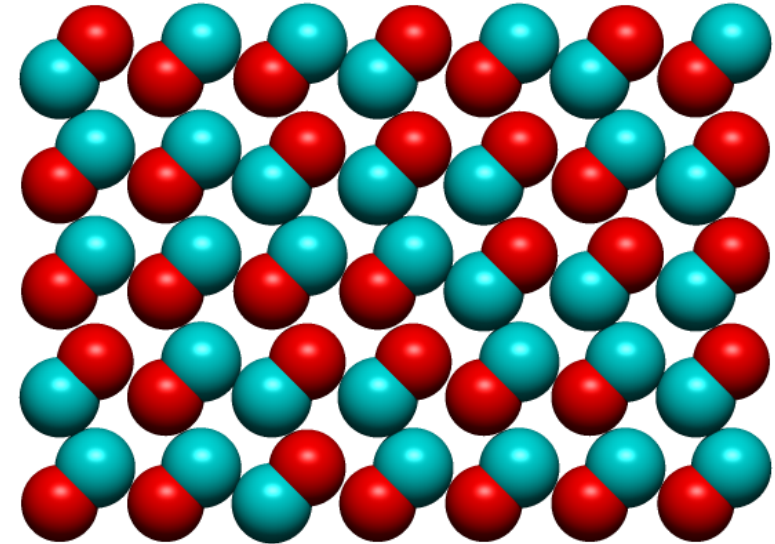
Pauling's derivation:

● 6 = $\binom{4}{2}$ orientations of a water molecule

● then an H-bond is wrong with prob. = $\frac{1}{2}$

● $2N_A$ bonds in a mole

● $\Rightarrow S_m = k_B \ln \left(\frac{6^{N_A}}{2^{2N_A}} \right) = 3.37 \text{ J K}^{-1} \text{ mol}^{-1}$



Example: Information entropy of DNA

20/32
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Assuming random and equal distribution of base pairs.

Per one base pair: $S = k_B \ln 4$, per mole: $S_m = R \ln 4$.

Corresponding Gibbs energy (at 37 °C):

$$\Delta G_m = -RT \ln 4 = -3.6 \text{ kJ mol}^{-1}$$

To be compared to: $\text{ATP} \rightarrow \text{ADP}$

– standard: $\Delta_r G_m^\ominus = -31 \text{ kJ mol}^{-1}$

– in usual conditions in a cell: $\Delta_r G_m = -57 \text{ kJ mol}^{-1}$



Fermi golden rule for the transition probability $\phi \rightarrow \psi$ caused by a perturbing Hamiltonian $\mathcal{H}_{\text{pert}}$ (in an isolated system):

$$\frac{d\pi(\phi \rightarrow \psi)}{dt} \equiv W(\phi \rightarrow \psi) = \frac{2\pi}{\hbar} |\langle \phi | \mathcal{H}_{\text{pert}} | \psi \rangle|^2 \rho_{\text{final}} = W(\psi \rightarrow \phi) = W_{\psi\phi}$$

Change of the population of state ψ (**master equation**):

$$\frac{d\pi(\psi)}{dt} = \sum_{\phi} \pi(\phi) W(\phi \rightarrow \psi) - \pi(\psi) \sum_{\phi} W(\psi \rightarrow \phi) = \sum_{\phi} W_{\phi\psi} [\pi(\phi) - \pi(\psi)]$$

Rate of entropy change:

$$\frac{dS}{dt} = -k \frac{d}{dt} \sum_{\psi} \pi(\psi) \ln \pi(\psi) = -k \sum_{\psi} \ln \pi(\psi) \sum_{\phi} W_{\phi\psi} [\pi(\phi) - \pi(\psi)]$$

Trick: swap $\phi \leftrightarrow \psi$ and sum:

$$\frac{dS}{dt} = \frac{1}{2} k \sum_{\psi, \phi} W_{\psi\phi} [\ln \pi(\phi) - \ln \pi(\psi)] [\pi(\phi) - \pi(\psi)] \geq 0$$

The entropy of an isolated system never decreases

Loschmidt paradox: Irreversibility from reversible microscopic laws

The probability that a molecule is found in:

- a tiny box $dx dy dz$ with coordinates in intervals $[x, x + dx)$, $[y, y + dy)$ a $[z, z + dz)$
AND
 - with velocities in intervals $[v_x, v_x + dv_x)$, $[v_y, v_y + dv_y)$, $[v_z, v_z + dv_z)$,
- is proportional to the Boltzmann factor

$$\begin{aligned} & \exp\left(-\frac{E_{\text{pot}} + E_{\text{kin}}}{k_B T}\right) \\ &= \exp\left(\frac{-E_{\text{pot}}}{k_B T}\right) \exp\left(\frac{-\frac{1}{2} m v_x^2}{k_B T}\right) \exp\left(\frac{-\frac{1}{2} m v_y^2}{k_B T}\right) \exp\left(\frac{-\frac{1}{2} m v_z^2}{k_B T}\right) \end{aligned}$$

The probability that a molecule is found with velocities in intervals $[v_x, v_x + dv_x)$, $[v_y, v_y + dv_y)$, $[v_z, v_z + dv_z)$ (irrespective of E_{pot}) is proportional to

$$\exp\left(\frac{-\frac{1}{2} m v_x^2}{k_B T}\right) \exp\left(\frac{-\frac{1}{2} m v_y^2}{k_B T}\right) \exp\left(\frac{-\frac{1}{2} m v_z^2}{k_B T}\right)$$

● Assumptions:

- π is isotropic
- π is composed of independent contributions of coordinates,

$$\pi(v_x, v_y, v_z) = \pi(v_x)\pi(v_y)\pi(v_z)$$

- $\lim_{v \rightarrow \infty} \pi(v_x, v_y, v_z) = 0$

The only function satisfying these conditions is

$$\pi(v_x) = \text{const} \times \exp(-\text{const} \cdot v_x^2)$$

Examples of functions:

1. $x^2 + y^2$ – is isotropic, but is not a product, bad limit
2. $x^2 y^2$ – is a product, is not isotropic, bad limit
3. $\frac{3}{(1+x^2)(1+y^2)}$ – is a product, is not isotropic, good limit
4. $3 \exp(-x^2/2 - y^2/2)$ – good!

● Assumption:

- velocity is a sum of many small random “hits”
Central limit theorem \Rightarrow Gauss distribution

Doppler broadening of spectral lines

$$\frac{\lambda - \lambda_0}{\lambda} = \frac{v_x}{c}$$

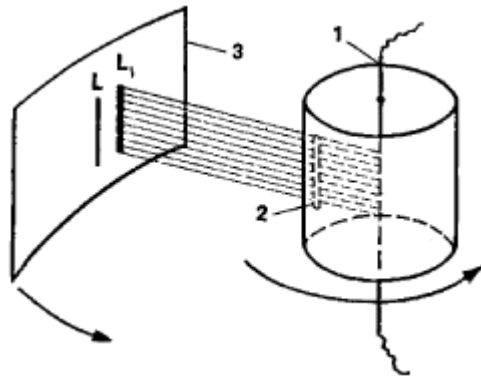
molecular beam:

Stern, Zartman (1920):

1 = Pt wire covered by Ag^a

2 = slit

3 = screen

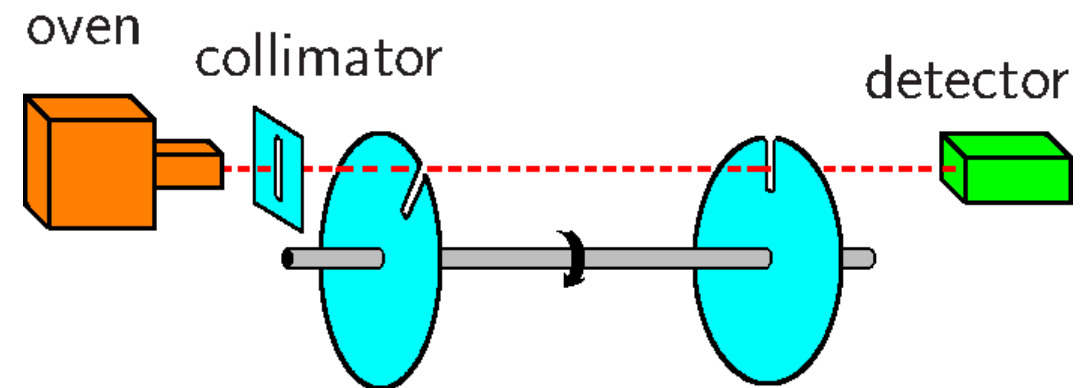


credit: <http://encyclopedia2.thefreedictionary.com/Stern-Zartman+Experiment>

^aother literature: Sn oven

Lammert (1929)

vapor of Bi or Hg (?)



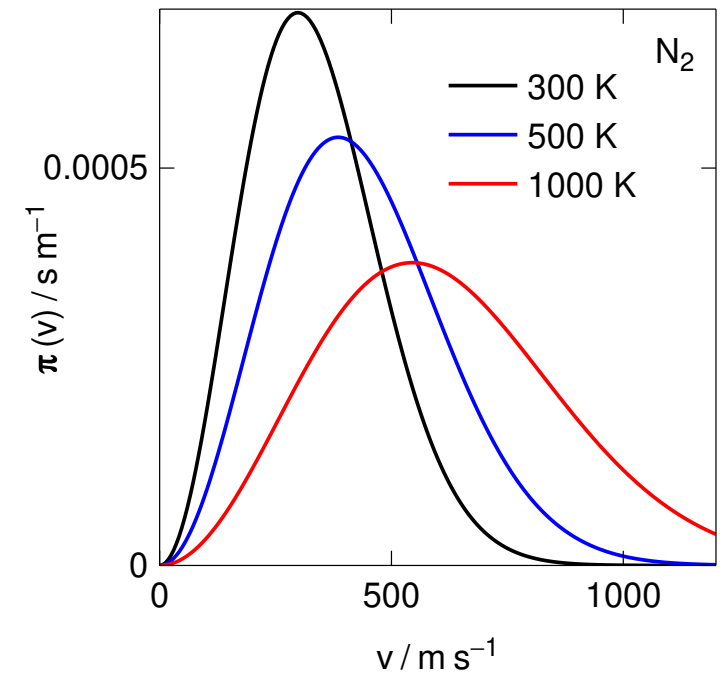
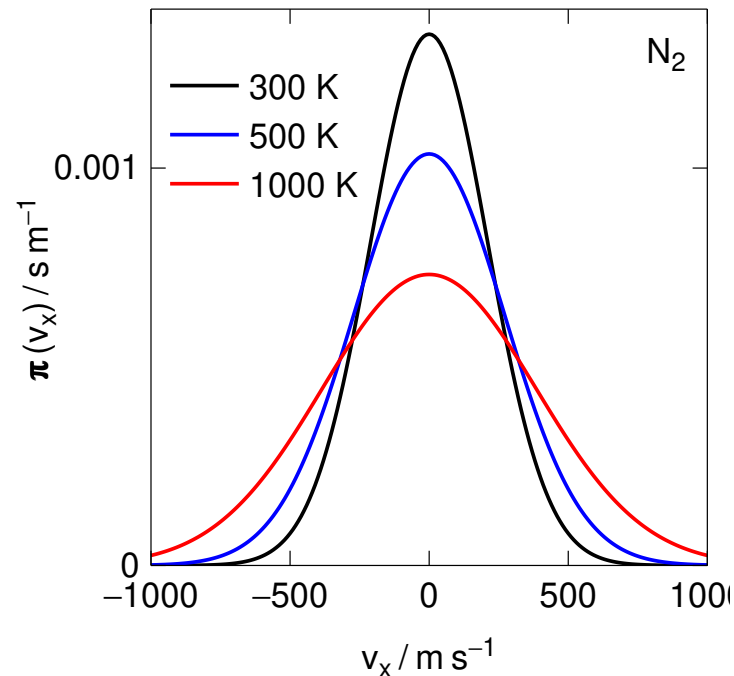
Pseudoexperimental verification and consequences

Normalized distribution in one coordinate:

$$\pi(v_x) = \frac{1}{\sigma_v \sqrt{2\pi}} \exp\left(\frac{-v_x^2}{2\sigma_v^2}\right), \quad \sigma_v^2 = \langle v_x^2 \rangle = \frac{k_B T}{m} = \frac{RT}{M}$$

Distribution of velocities, i.e., probability density that a particle is found with $v = |\vec{v}|$ in interval $[v, v + dv)$:

$$\pi(v) = 4\pi v^2 \pi(v_x) \pi(v_y) \pi(v_z) = \sqrt{\frac{2}{\pi}} \frac{v^2}{\sigma_v^3} \exp\left(\frac{-v^2}{2\sigma_v^2}\right)$$



for me (tchem/MBexpE.sh):

e switch to NVE
F record
F stop recording
ESC ESC quit

Mean velocity

$$\bar{v} = \int_0^{\infty} v \pi(v) dv = \sqrt{\frac{8}{\pi}} \sigma_v = \sqrt{\frac{8RT}{\pi M}} = \sqrt{\frac{8k_B T}{\pi m}}$$

Mean quadratic velocity

$$\bar{v}_q = \sqrt{\int_0^{\infty} v^2 \pi(v) dv} = \sqrt{\frac{3RT}{M}} = \sqrt{\frac{3k_B T}{m}}$$

Most probable velocity

$$\frac{d\pi}{dv} = 0 \Rightarrow v_{\max} = \sqrt{\frac{2RT}{M}} = \sqrt{\frac{2k_B T}{m}}$$

Speed of sound ($\kappa = C_p/C_V$)

$$v_{\text{sound}} = \sqrt{\frac{\kappa RT}{M}} = \sqrt{\frac{\kappa k_B T}{m}}$$

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> restart; assume(s>0);
> p := x -> 1/s/sqrt(2*Pi)*exp(-x^2/s^2/2);
p := x -> \frac{e^{-\frac{1}{2} \frac{x^2}{s^2}}}{s \sqrt{2 \pi}}
> int(p(x), x=-infinity..infinity);
1
> ppp := x -> sqrt(2/Pi)*x^2/s^3*exp(-x^2/s^2/2);
ppp := x -> \frac{\sqrt{\frac{2}{\pi}} x^2 e^{-\frac{1}{2} \frac{x^2}{s^2}}}{s^3}
> simplify(int(ppp(x), x=0..infinity));
1
mean velocity
> int(v*ppp(v), v=0..infinity);
\frac{2 \sqrt{2} s \sim}{\sqrt{\pi}}
mean quadratic velocity
> sqrt(simplify(int(v^2*ppp(v), v=0..infinity)));
\sqrt{3} s \sim
most probable velocity
> eq:=diff(ppp(v),v)=0; solve({eq,v>0},v);
eq := \frac{2 \sqrt{2} v e^{-\frac{1}{2} \frac{v^2}{s^2}}}{\sqrt{\pi} s^3} - \frac{\sqrt{2} v^3 e^{-\frac{1}{2} \frac{v^2}{s^2}}}{\sqrt{\pi} s^5} = 0
{v = \sqrt{2} s \sim}
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$$\alpha = ?$$

$$\pi(\psi) = \exp[\alpha - \beta\mathcal{E}(\psi)]$$

$$\sum \pi(\psi) = 1 \Rightarrow \sum d\pi(\psi) = 0$$

$$S = -k_B \sum_{\psi} \pi(\psi) \ln \pi(\psi) = -k_B \sum_{\psi} \pi(\psi) [\alpha - \beta\mathcal{E}(\psi)] = - \left(k_B \alpha - \frac{U}{T} \right)$$

$$\Rightarrow \alpha = \frac{U - TS}{k_B T} = \frac{F}{k_B T} \Rightarrow F = -k_B T \ln \left[\sum_{\psi} e^{-\beta\mathcal{E}(\psi)} \right]$$

[...] = **canonical partition function** = **statistical sum** (Q or Z)

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:

$$dF = -pdV - SdT$$

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

$$U = F + TS$$

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

$$H = U + pV$$

$$G = F + pV$$

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

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

Sum over states replaced by integrals:

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

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

Why the factorial?

- Particles are indistinguishable ... but 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 (vide infra)

Integrals over positions and momenta are separated

Integrals over momenta can be evaluated:

$$\int \exp(-p_{1,x}^2/2k_B T m) = \sqrt{2\pi k_B T m}$$

After $3N$ integrations we get:

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

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:

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

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

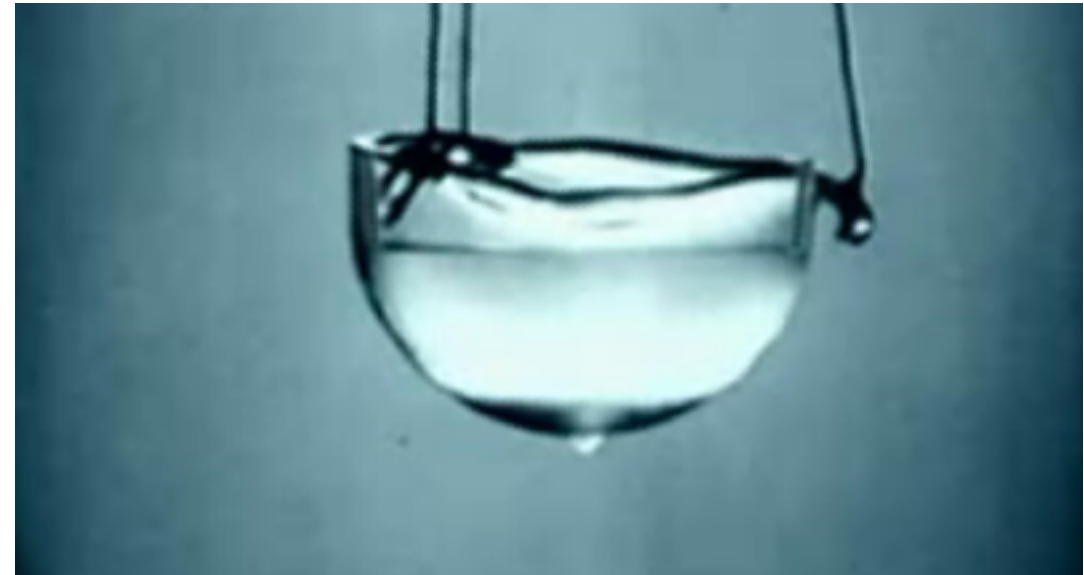
Mean value of a **static** quantity (observable):

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

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 \AA ; b) 3.8 \AA



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

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

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

$$p = - \left(\frac{\partial F}{\partial V} \right)_T = \frac{k_B T N}{V} = \frac{n R T}{V}$$

e = Euler number
e = elementary charge

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

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

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

And verification:

$$G = F + pV = k_B T N \ln \frac{N \Lambda^3}{V e} + N k_B T = N \mu$$

Or quantum calculation of the translational partition function:

Eigenvalues of energy of a point mass in a $a \times b \times c$ box:

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

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:

$$Z_1 = \sum_{n_x=1}^{\infty} \sum_{n_y=1}^{\infty} \sum_{n_z=1}^{\infty} \exp(-\beta\varepsilon) \stackrel{\Sigma \rightarrow \int}{\approx} \int_0^{\infty} \int_0^{\infty} \int_0^{\infty} \exp(-\beta\varepsilon) dn_x dn_y dn_z = \frac{V}{\Lambda^3}$$

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

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