Pressure of ideal gas from the kinetic theory I

Molecule = point mass

N molecules of masses m_i, $i = 1, .., N$, 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 = $\Delta P_x = 2m_i v_{i,x}$

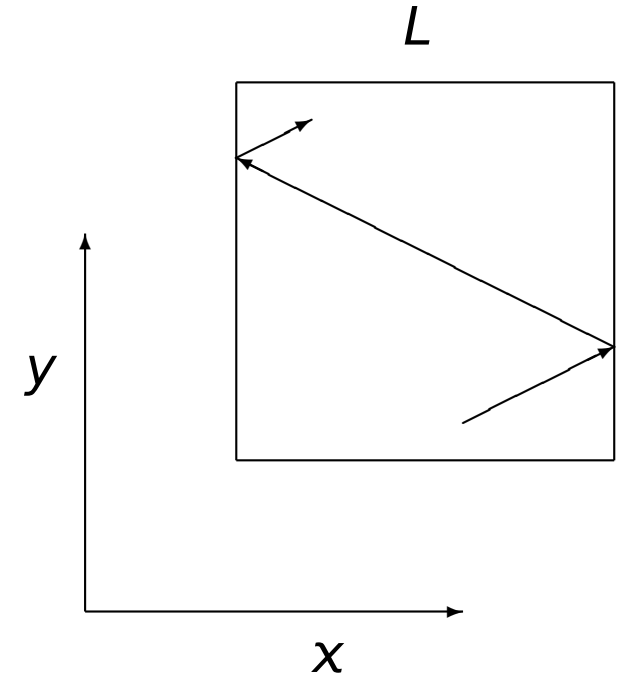**Averaged** force caused by impacts of one molecule:

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

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)

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

$\Rightarrow$

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

In other words

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

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:

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

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

Equation of state:

$$pV = nRT = Nk_BT$$

Internal energy:

$$U \equiv E_\mathrm{kin} = \frac{3n}{2}RT = \frac{3N}{2}k_BT$$

Ludwig Eduard Boltzmann (1844–1906)

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

$$pV = Nk_BT = \frac{f}{3}k_BT = \frac{2}{3}E_{\text{kin}}$$

$f =$ **number of mechanical degrees of freedom**.
Average energy contribution per one degree of freedom:

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

Generalization: any quadratic function in the Hamiltonian

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

degrees of freedom per molec.

$$C_{Vm} = \left(\frac{\partial U}{\partial T}\right)_V = \left(\frac{\partial E_{\text{kin}}}{\partial T}\right)_V = \frac{\frac{1}{2}fk_BT}{N_AT} = \frac{3}{2}R$$

Extension:

- Linear molecules: + 2 rotations, $C_{Vm} = \frac{5}{2}R$ (but: hydrogen)

- Nonlinear molecules: + 3 rotations, $C_{Vm} = 3R$

- (Vibrations classically: + 2 for each (incl. E_{pot}) – imprecise!)
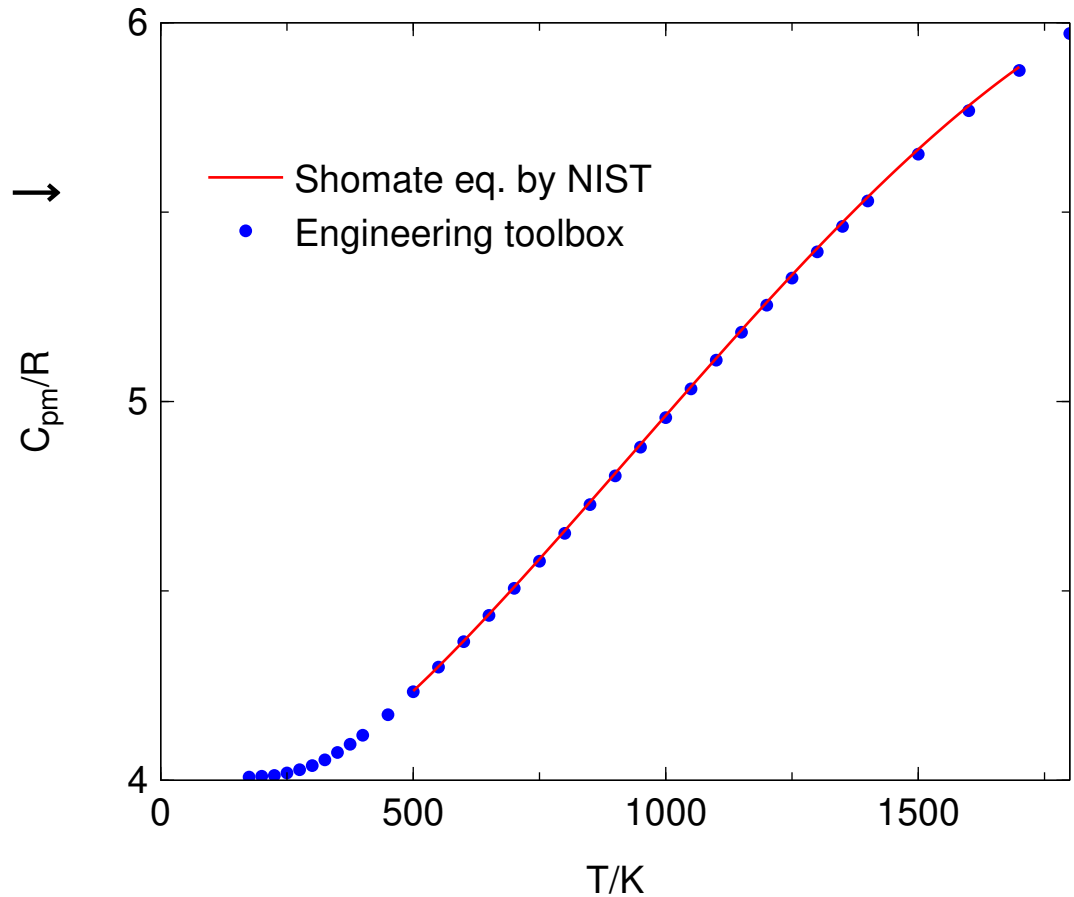
Calculate $C_{p\text{m}}$ for a) nitrogen, b) water vapor?

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

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

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

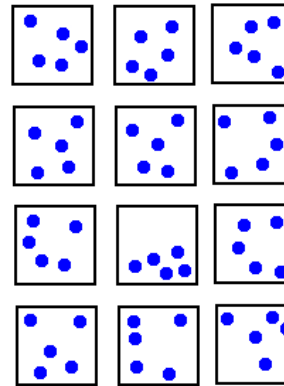Isobaric heat capacity of water vapor → → →

🔴 **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, $\psi = (\vec{r}_1, \ldots, \vec{r}_N, \vec{v}_1 \ldots, \vec{v}_N)$

🔴 **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
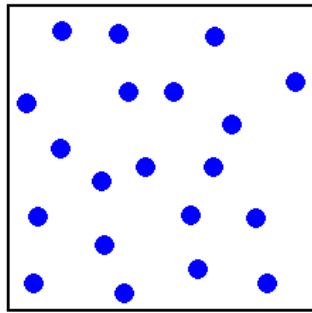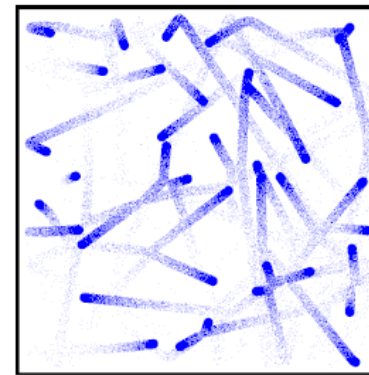
| microstate | macrostate | ensemble | trajectory |

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

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 = $ const, $V = $ const, $E = $ const)

for me:
e NVE ensemble
r smaller balls
c trajectory

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

- **Ergodic hypothesis** (classical):
  trajectory covers the space† with uniform probability

In other words:

Time average (over a trajectory)

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

= 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 $\{(\vec{r}_1, \ldots, \vec{r}_N, \vec{p}_1 \ldots, \vec{p}_N)\}$

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

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 = const: Canonical ensemble

Also **NVT** (N = const, V = const, T = const)

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

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

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

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

$$\Rightarrow \boldsymbol{\pi}(E) = \text{const}^E = \exp(\alpha_i - \beta E)$$
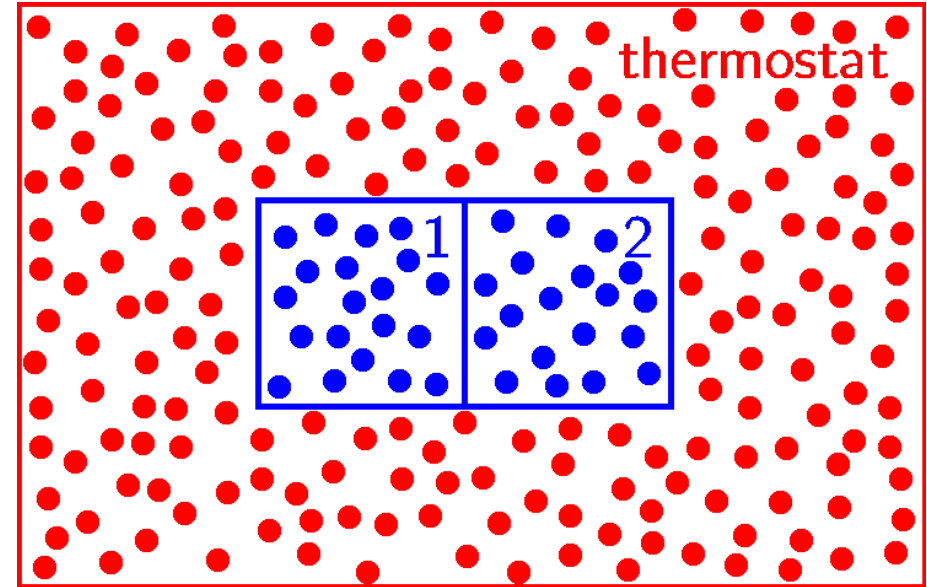
⬤ 0th Law $\Rightarrow \beta$ is empirical temperature

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

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

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

Evaluation gives: $\langle U_1 \rangle = \frac{3}{2}\frac{1}{\beta} \quad \Rightarrow \quad \beta = \frac{1}{k_\text{B}T}$

Determining β

$$\langle U_1 \rangle = \frac{\int_{R^3} \frac{1}{2}m\vec{v}^2 \, \pi(\frac{1}{2}m\vec{v}^2) \, d\vec{v}}{\int_{R^3} \pi(\frac{1}{2}m\vec{v}^2) \, d\vec{v}}$$

$$= \frac{\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} \frac{1}{2}m(v_x^2 + v_y^2 + v_z^2)\, e^{-\frac{1}{2}\beta m v_x^2} dv_x \, e^{-\frac{1}{2}\beta m v_y^2} dv_y \, e^{-\frac{1}{2}\beta m v_z^2} dv_z}{\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} e^{-\frac{1}{2}\beta m v_x^2} dv_x \, e^{-\frac{1}{2}\beta m v_y^2} dv_y \, e^{-\frac{1}{2}\beta m v_z^2} dv_z}$$

$$= 3 \frac{\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} \frac{1}{2}m v_x^2 \, e^{-\frac{1}{2}\beta m v_x^2} dv_x \, e^{-\frac{1}{2}\beta m v_y^2} dv_y \, e^{-\frac{1}{2}\beta m v_z^2} dv_z}{\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} e^{-\frac{1}{2}\beta m v_x^2} dv_x \, e^{-\frac{1}{2}\beta m v_y^2} dv_y \, e^{-\frac{1}{2}\beta m v_z^2} dv_z}$$

$$= 3 \boxed{\frac{\int_{-\infty}^{\infty} \frac{1}{2}m v_x^2 \, e^{-\frac{1}{2}\beta m v_x^2} dv_x}{\int_{-\infty}^{\infty} e^{-\frac{1}{2}\beta m v_x^2} dv_x}} = 3 \frac{\frac{1}{2}m \frac{1}{2\frac{1}{2}\beta m}\sqrt{\frac{\pi}{\frac{1}{2}\beta m}}}{\sqrt{\frac{\pi}{\frac{1}{2}\beta m}}} = \frac{3}{2}\frac{1}{\beta}$$

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 derivate by parameter a:

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

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

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```
> int(1/2*m*(vx^2)*exp(-beta*m*vx^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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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 loose \$1 if you throw anything else. However, you have drilled a small lead weight under ⚀ (opposite to ⚅) so that the probabilities are $\pi(⚅) = 0.2$ and $\pi(⚀) = \pi(⚁) = \pi(⚂) = \pi(⚃) = \pi(⚄) = 0.16$. What is your mean (expected) win in this game?

\$0.2

... or the first half of statistical thermodynamics.

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

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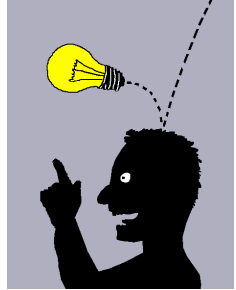
Examples:

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

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

Barometric formula

... 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:

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

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

$$\mathrm{d}p = -\mathrm{d}h\rho g, \quad \rho = \frac{Mp}{RT}$$

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:

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

Don't forget that there are two gauche states!

$$2\pi(gauche) + \pi(anti) = 1$$

$\Rightarrow$

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

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

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

Its small change is

$$\mathrm{d}U = \sum_\psi \boldsymbol{\pi}(\psi) \cdot \mathrm{d}\mathcal{E}(\psi) + \sum_\psi \mathrm{d}\boldsymbol{\pi}(\psi) \cdot \mathcal{E}(\psi)$$

$\mathrm{d}\mathcal{E}(\psi)$: energy level changed
$\mathrm{d}\boldsymbol{\pi}(\psi)$: probability of state ψ changed

Thermodynamics:

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

● $-p\,\mathrm{d}V$: A "piston" moved by dx. Change in energy = $\mathrm{d}\mathcal{E}(\psi)$ **= mechanical work**
   $= -F\mathrm{d}x = -F/\mathcal{A} \cdot \mathrm{d}(\mathcal{A}x) = -p(\psi)\,\mathrm{d}V$
   $p(\psi)$ = "pressure of state ψ", pressure = $p = \sum_\psi \boldsymbol{\pi}(\psi)p(\psi)$.

● $T\mathrm{d}S$: Change $\boldsymbol{\pi}(\psi)\,[V]$ = change of the population of states with varying energies
   = heat

Boltzmann equation for entropy

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

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

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

$$= -k_\mathrm{B}T \,\mathrm{d}\left[\sum_\psi \pi(\psi)\ln \pi(\psi)\right]$$

On comparing with $T\mathrm{d}S$:

$$S = -k_\mathrm{B}\sum_\psi \pi(\psi)\ln \pi(\psi)$$

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: $S = k_\mathrm{B}\ln W$

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

Example: Ideal solution

Energies of neighbors: ●─● = ●─● = ●─●

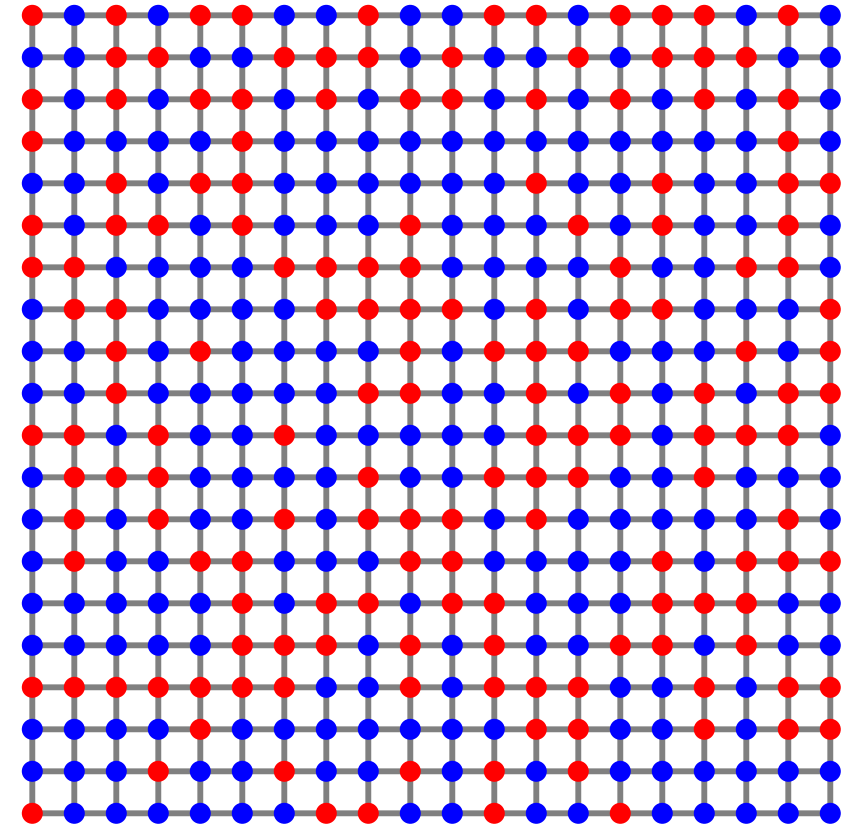All configurations have the same energy

Mix N_1 molecules of 1 + N_2 molecules of 2:

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

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

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

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

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

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

More accurately:

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

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

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

3rd Law violation: CO, N_2O, H_2O.
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

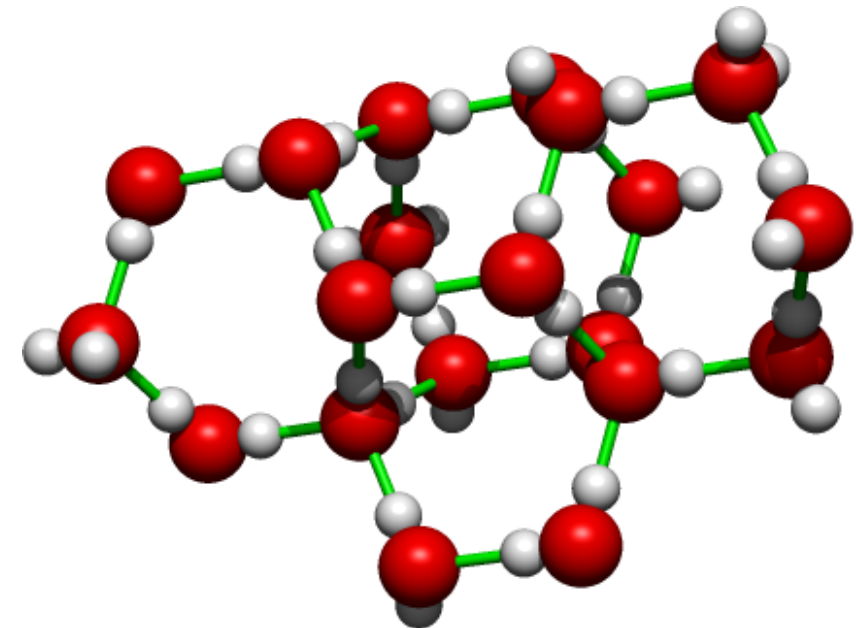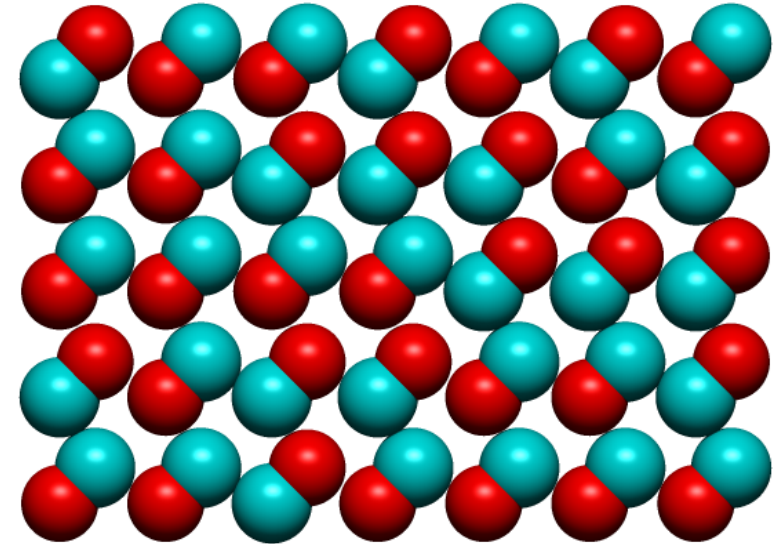$$S_m = k_B \ln 1.507^{N_A} = 3.41 \, J \, K^{-1} \, mol^{-1}$$

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

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

Assuming random and equal distribution of base pairs.

Per one base pair: $S = k_\text{B} \ln 4$, per mole: $S_m = R \ln 4$.

Corresponding Gibbs energy (at 37 °C):

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

To be compared to: ATP → ADP
– standard: $\Delta_\text{r}G_\text{m}^{\ominus} = -31\,\text{kJ}\,\text{mol}^{-1}$
– in usual conditions in a cell: $\Delta_\text{r}G_\text{m} = -57\,\text{kJ}\,\text{mol}^{-1}$

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

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

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

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

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 $\phi \longleftrightarrow \psi$ 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

$$\exp\left(-\frac{E_{pot} + E_{kin}}{k_B T}\right)$$

$$= \exp\left(\frac{-E_{pot}}{k_B T}\right) \exp\left(\frac{-\frac{1}{2}mv_x^2}{k_B T}\right) \exp\left(\frac{-\frac{1}{2}mv_y^2}{k_B T}\right) \exp\left(\frac{-\frac{1}{2}mv_z^2}{k_B T}\right)$$

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

$$\exp\left(\frac{-\frac{1}{2}mv_x^2}{k_B T}\right) \exp\left(\frac{-\frac{1}{2}mv_y^2}{k_B T}\right) \exp\left(\frac{-\frac{1}{2}mv_z^2}{k_B T}\right)$$

[tchem/MBfunkce.sh]
Maxwell distribution – historical approach
23/32
s01/2

⬤ Assumptions:

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

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

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

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. $\dfrac{3}{(1 + x^2)(1 + y^2)}$ – 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

$$\frac{\lambda - \lambda_0}{\lambda} = \frac{v_x}{c}$$
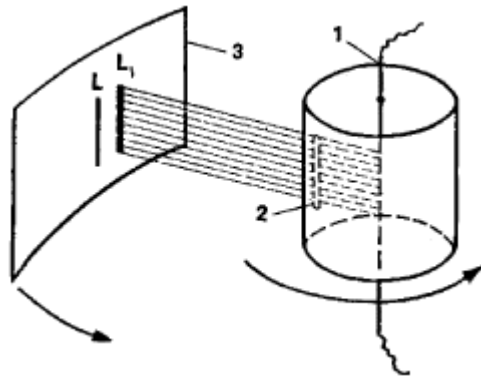
🟣 molecular beam:

Stern, Zartman (1920):

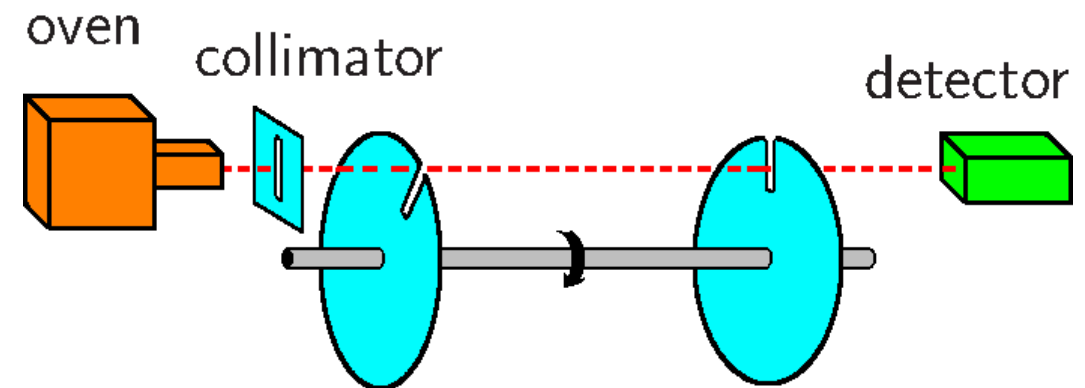1 = Pt wire covered by Ag[a]

2 = slit

3 = screen

Lammert (1929)

vapor of Bi or Hg (?)

credit: *http://encyclopedia2.thefreedictionary.com/Stern-Zartman+Experiment*
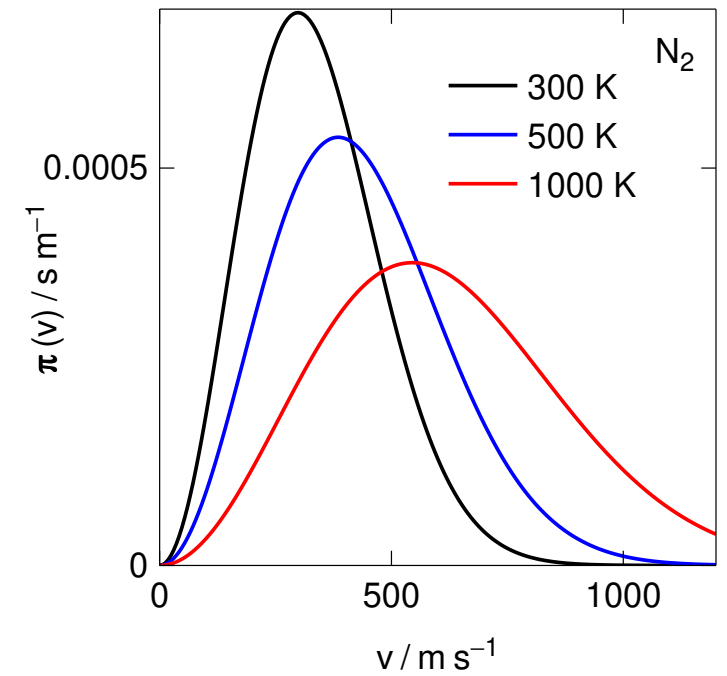
[a]other literature: Sn oven

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 $[v, v + dv)$:

$$\pi(v) = 4\pi v^2 \pi(v_x)\pi(v_y)\pi(v_z) = \sqrt{\frac{2}{\pi}} \frac{v^2}{\sigma_v^3} \exp\left(\frac{-v^2}{2\sigma_v^2}\right)$$
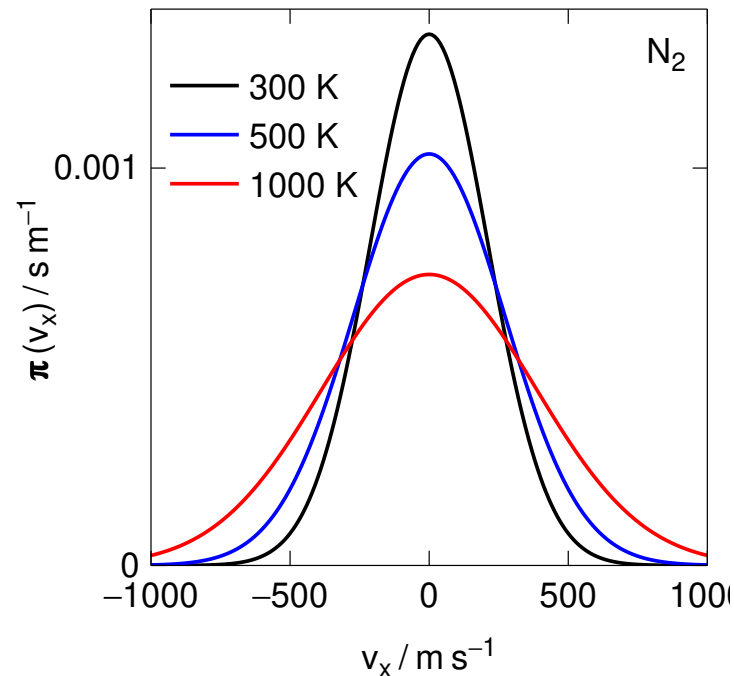
for me (tchem/MBexpE.sh):

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

Consequences

Mean velocity

$$\overline{v} = \int_0^\infty v\,\boldsymbol{\pi}(v)\mathrm{d}v = \sqrt{\frac{8}{\pi}}\,\sigma_V = \sqrt{\frac{8RT}{\pi M}} = \sqrt{\frac{8k_{\mathrm{B}}T}{\pi m}}$$

Mean quadratic velocity

$$\overline{v}_q = \sqrt{\int_0^\infty v^2\boldsymbol{\pi}(v)\mathrm{d}v} = \sqrt{\frac{3RT}{M}} = \sqrt{\frac{3k_{\mathrm{B}}T}{m}}$$

Most probable velocity

$$\frac{\mathrm{d}\boldsymbol{\pi}}{\mathrm{d}v} = 0 \quad \Rightarrow v_{\max} = \sqrt{\frac{2RT}{M}} = \sqrt{\frac{2k_{\mathrm{B}}T}{m}}$$

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

$$v_{\mathrm{sound}} = \sqrt{\frac{\kappa RT}{M}} = \sqrt{\frac{\kappa k_{\mathrm{B}}T}{m}}$$

```
> restart; assume(s>0);
> p := x -> 1/s/sqrt(2*Pi)*exp(-x^2/s^2/2);
```

$$p := x \rightarrow \frac{e^{-\frac{1}{2}\frac{x^2}{s^2}}}{s\sqrt{2\pi}}$$

```
> int(p(x),x=-infinity..infinity);
```
$$1$$

```
> ppp := x -> sqrt(2/Pi)*x^2/s^3*exp(-x^2/s^2/2);
```

$$ppp := x \rightarrow \frac{\sqrt{\frac{2}{\pi}}\,x^2\,e^{-\frac{1}{2}\frac{x^2}{s^2}}}{s^3}$$

```
> 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);
```
$$eq := \frac{2\sqrt{2}\,v\,e^{-\frac{1}{2}\frac{v^2}{s\sim^2}}}{\sqrt{\pi}\,s\sim^3} - \frac{\sqrt{2}\,v^3\,e^{-\frac{1}{2}\frac{v^2}{s\sim^2}}}{\sqrt{\pi}\,s\sim^5} = 0$$

$$\{v = \sqrt{2}\,s\sim\}$$

$\alpha = ?$

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

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

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

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

$[\ldots]$ = **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:

$$dF = -p\,dV - S\,dT$$

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

$$U = F + TS$$

$$H = U + pV$$

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

$$G = F + pV$$

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:

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

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:

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

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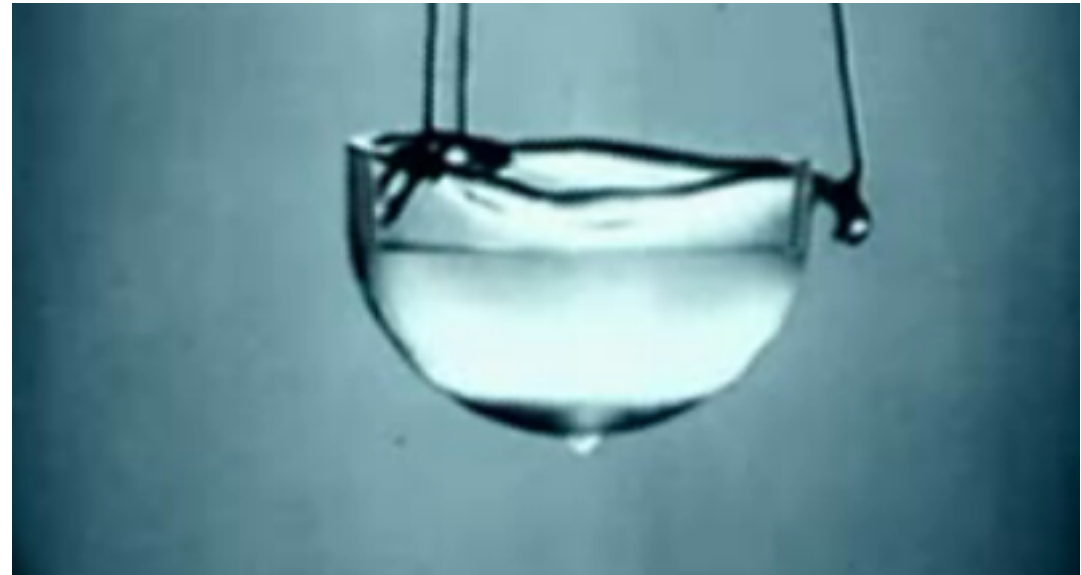$U(\vec{r}_1, \ldots)$ = potential

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

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

Example

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

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

a) 6.2 Å; b) 3.8 Å

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

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

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

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

e = Euler number
e = elementary charge

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

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

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

And verification:

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

Or quantum calculation of the translational partition function:

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

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

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:

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

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

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