

Macroscopic quantities are a consequence of averaged behavior of many particles



Pressure of ideal gas from kinetic theory I

Molecule = mass point

N molecules of mass m_i in a cube of edge length L

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

After reflection from the wall: $v_{i,x} \rightarrow -v_{i,x}$

Next time it hits the wall after $\tau = 2L/v_{i,x}$

Force = change in momentum per unit time

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

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

Averaged force by impacts of one molecule:

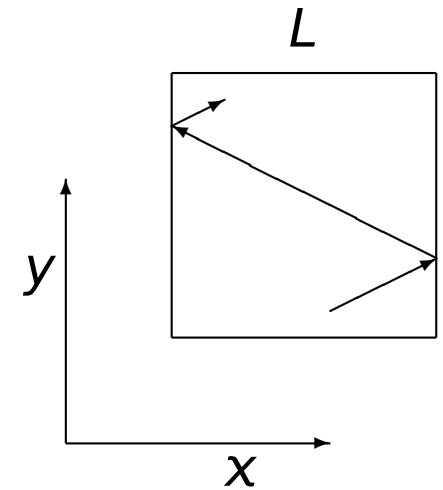
$$F_{i,x} = \frac{\Delta P_x}{\tau} = \frac{2m_i v_{i,x}}{2L/v_{i,x}} = \frac{m_i v_{i,x}^2}{L}$$

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 = internal energy (monoatomic gas)

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

⇒

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

Or

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

Summary:

- **Temperature is a measure of the kinetic energy** (~ 0th Law)
- Pressure = **averaged** impacts of molecules
- We needed the **classical mechanics**

Once more:

$$n = \frac{N}{N_A}, \quad k_B = \frac{R}{N_A} \quad \Rightarrow \quad U \equiv E_{\text{kin}} = \frac{3n}{2} RT = \frac{3N}{2} k_B T, \quad C_{V,m} = \frac{3}{2} R$$

$$pV = nRT = Nk_B T$$

$$N = nN_A$$

$$k_B = \frac{R}{N_A} = 1.380649 \times 10^{-23} \text{ J K}^{-1}$$

Note:

since May 20, 2019 it is *defined*:

$$k_B = 1.380649 \times 10^{-23} \text{ J K}^{-1},$$

$$N_A = 6.02214076 \times 10^{23} \text{ mol}^{-1},$$

therefore, *exactly*:

$$R = 8.31446261815324 \text{ J mol}^{-1} \text{ K}^{-1}$$



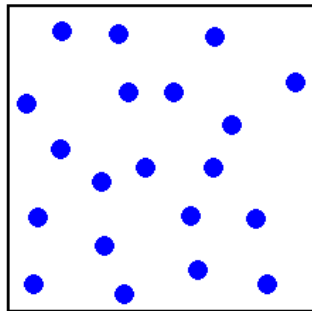
Ludwig Eduard Boltzmann (1844–1906)

- microstate (state, configuration) = instantaneous quantum description: wave function, ψ
classical description: positions and velocities of all particles (better momenta...)

$$\psi = (\vec{r}_1, \dots, \vec{r}_N, \vec{v}_1, \dots, \vec{v}_N)$$

- macrostate = averaged microstates

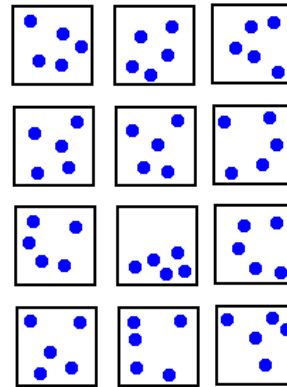
- ensemble = set of all microstates with their respective probabilities $\pi(\psi)$,



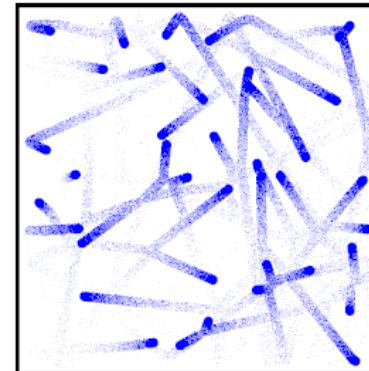
microstate



macrostate



ensemble



trajectory

Microcanonical ensemble and the ergodic hypothesis

Microcanonical ensemble = set of microstates in an isolated system

Denoted: **NVE** ($N = \text{const}$, $V = \text{const}$, $E = \text{const}$)

- Ergodic hypothesis (quantum): $\pi(\psi_i) = \text{const} = \frac{1}{W}$
($W = \text{number of all states}$)
- Ergodic hypothesis (classical):
trajectories fill the (phase) space uniformly

In other words:

Time averaged (mean) value =

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

= ensemble mean value =

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

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

... but $T = \text{const}$ is more practical



is the ensemble with a constant temperature.

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

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

$E_1 + E_2 = E_{1+2}$ (small influence)

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

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

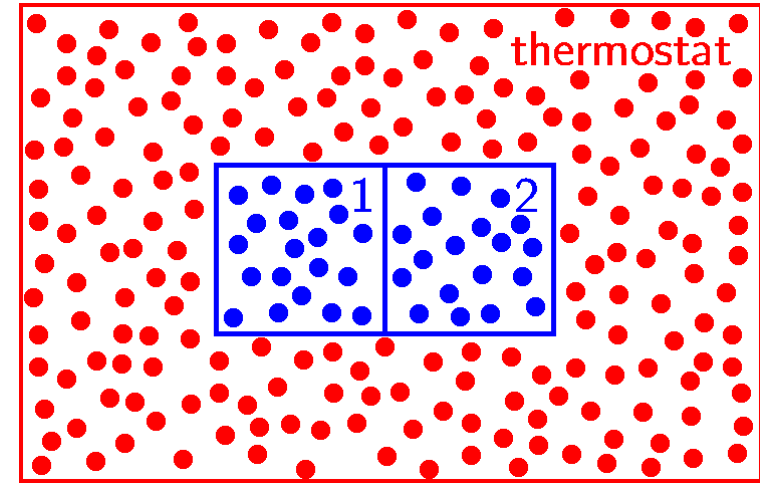
$$\Rightarrow \pi(E) = \text{const}^E = \exp(\alpha_i - \beta E)$$

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

● α_i is the normalization constant, so that $\sum_{\psi} \pi(\psi) = 1$, depends on the system

Determine β : monoatomic ideal gas, energy per atom = $U_1 = \frac{3}{2}k_B T$

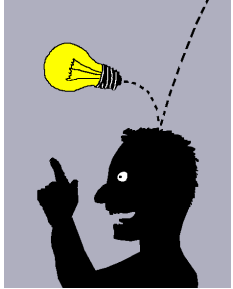
$$\langle U_1 \rangle = \frac{\sum_{\psi} \mathcal{E}(\psi) \pi(\mathcal{E}(\psi))}{\sum_{\psi} \pi(\mathcal{E}(\psi))} = \frac{\int \frac{1}{2} m \vec{v}^2 \pi(\frac{1}{2} m \vec{v}^2) d\vec{v}}{\int \pi(\frac{1}{2} m \vec{v}^2) d\vec{v}} = \dots = \langle U_1 \rangle = \frac{3}{2} \frac{1}{\beta} \Rightarrow \beta = \frac{1}{k_B T}$$



... or the first half of the statistical thermodynamics.

Probability of finding a state of 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 barrier (activation energy) E_a is overcome by $\sim \exp\left(-\frac{E_a}{RT}\right)$ molecules
⇒ Arrhenius formula

$$k = A \exp\left(-\frac{E_a}{RT}\right)$$

- energy needed to transfer a molecule from liquid to vapor is $\Delta_{\text{vap}}H$, probability of finding a molecule in the vapor is proportional to $\sim \exp\left(-\frac{\Delta_{\text{vap}}H}{RT}\right)$ ⇒ Clausius-Clapeyron equation (integrated)

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

Barometric formula: particle in a gravitational field

... once again.

Potential energy of a molecule in a homogeneous gravitational field:

$$U = mgh$$

Probability of finding a molecule at height h :

$$\pi \propto \exp\left(-\frac{U}{k_B T}\right) = \exp\left(-\frac{mgh}{k_B T}\right) = \exp\left(-\frac{Mgh}{RT}\right)$$

Probability \propto density \propto pressure:

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

The same formula can be obtained from the mechanical equilibrium + ideal gas EOS:

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

(" \Rightarrow " 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).

Solution:

$$1 \text{ cal}_{\text{th}} = 4.184 \text{ J}$$

$$\pi(\textit{gauche}) : \pi(\textit{anti}) = \exp[-\Delta E/RT] = 0.190$$

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.

Internal energy

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

Small change of U :

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

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

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

1st Law of Thermodynamics: $dU = -p dV + TdS$

● $-p dV$

“Piston” moved. Energy changes by $d\mathcal{E}(\psi) = \mathbf{mechanical\ work} = -Fdx = -F/\mathcal{A} \cdot$

$d(\mathcal{A}x) = -p(\psi) dV$

$p(\psi) =$ “pressure of state ψ ”, (mean) pressure $= p = \sum_{\psi} \pi(\psi) p(\psi)$.

● TdS

Change of $\pi(\psi)$ at constant $[V] =$ change of probabilities of states of different energies $= \mathbf{heat}$

Boltzmann equation for entropy

... the second half of the statistical thermodynamics

$$\pi(E) = \exp(\alpha_i - \beta E) \quad \beta = 1/k_B T \quad \Rightarrow \quad \mathcal{E}(\psi) = k_B T [\alpha_i - \ln \pi(\psi)], \quad \sum_{\psi} d\pi(\psi) = 0$$

$$\begin{aligned} \sum_{\psi} d\pi(\psi) \mathcal{E}(\psi) &= \sum_{\psi} d\pi(\psi) k_B T [\alpha_i - \ln \pi(\psi)] = -k_B T \sum_{\psi} d\pi(\psi) \cdot \ln \pi(\psi) \\ &= -k_B T d \left[\sum_{\psi} \pi(\psi) \ln \pi(\psi) \right] \end{aligned}$$

On comparison with TdS :

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

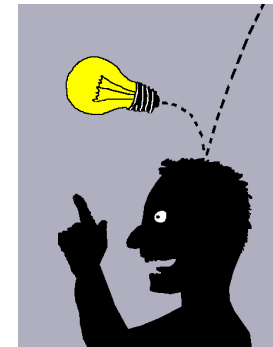
Microcanonical ensemble: $\pi(\psi) = \begin{cases} 1/W & \text{for } E = \mathcal{E}(\psi) \\ 0 & \text{for } E \neq \mathcal{E}(\psi) \end{cases}$

Boltzmann equation: $S = k_B \ln W$

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



credit: schneider.ncifcrf.gov/images/boltzmann/boltzmann-tomb-8.html



Transitions between states \Rightarrow
 $dS/dt \geq 0$
(H-theorem)

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

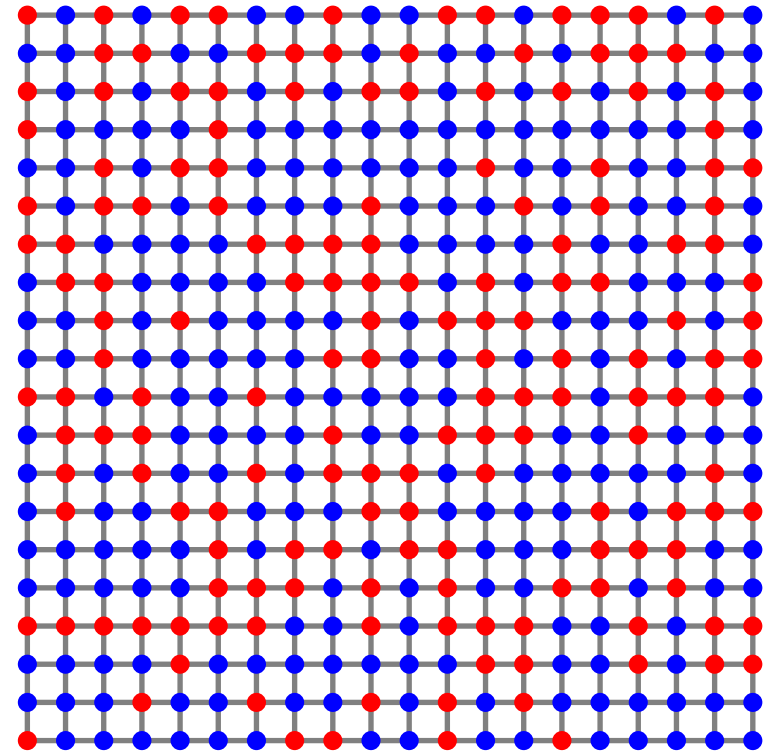
All configurations have the same energy

Mix N_1 molecules of 1 + N_2 molecules of 2:

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

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

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



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

$$\ln N! = \sum_{i=1}^N \ln i \approx \int_1^N \ln x \, dx \stackrel{\text{by parts}}{=} [x \ln x - x]_1^N = N \ln N - N + 1 \approx N \ln N - N$$

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

Residual entropy of crystals at $T \rightarrow 0$

Crystal: 1 microstate $\Rightarrow S = k \ln 1 = 0$ (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

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

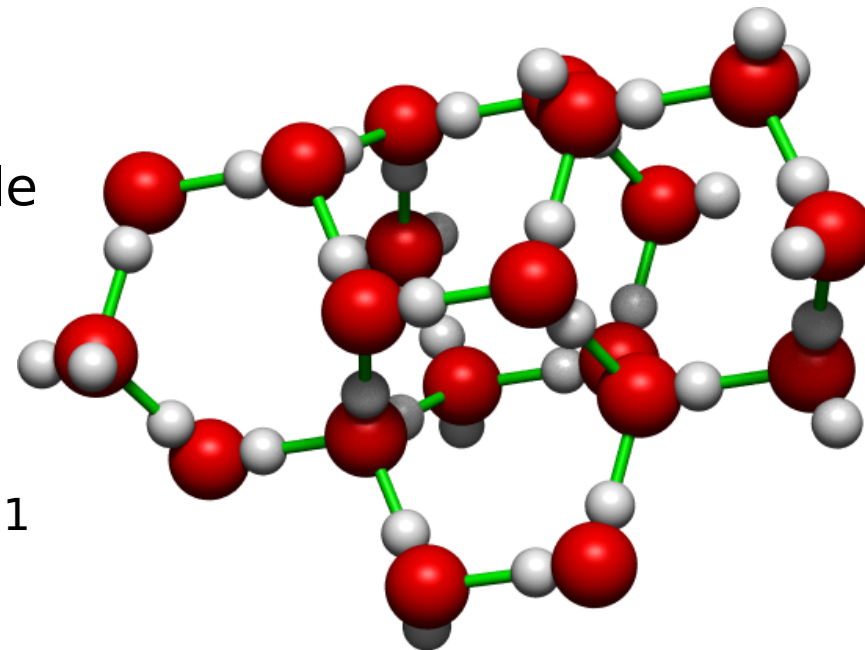
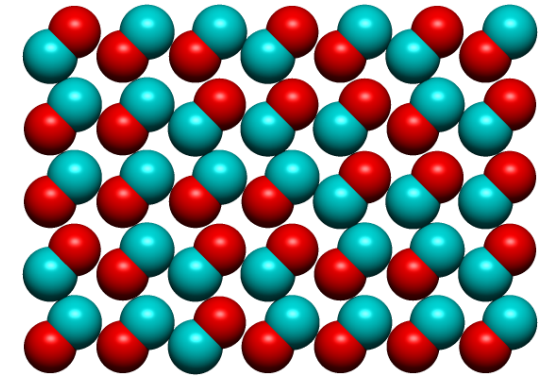
Pauling derivation:

● 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

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



Assuming random and equal distribution of base pairs.

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

Corresponding Gibbs energy (at 37 °C):

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

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: $\Delta_r G_m = -57 \text{ kJ mol}^{-1}$



$\alpha = ?$

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

Helmholtz energy:

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

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

Interpretation: number of “available” states
(low-energy easily, high-energy difficult)

All equilibrium quantities can be calculated from F ($dF = -pdV - SdT$):

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

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

$$U = F + TS$$

$$H = U + pV$$

$$G = F + pV$$