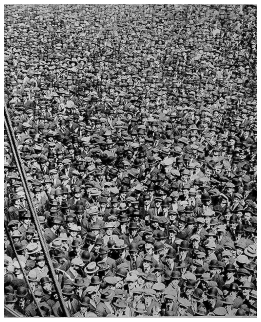
Statistical thermodynamics (mechanics)

Macroscopic quantities are a consequence of averaged behavior of many particles



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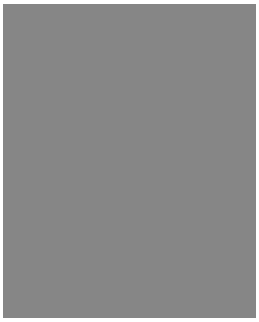
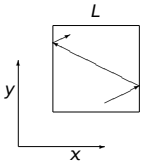


Pressure of ideal gas from kinetic theory I

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: $v_{i,x} \to -v_{i,x}$
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:

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

Pressure of ideal gas from kinetic theory II

Kinetic energy = internal energy (monoatomic gas)

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

⇒

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

Or

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

Summary:

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

Once more:

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

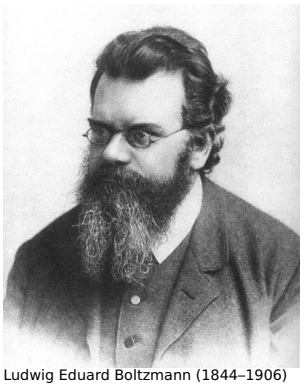
Boltzmann constant

$$pV = nRT = Nk_B T$$

$$N = nN_A$$

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

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

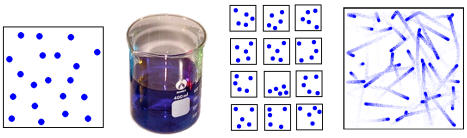


Ludwig Eduard Boltzmann (1844–1906)

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

Microstate, macrostate, ensemble, trajectory

- microstate (state, configuration) = instantaneous
  quantum description: wave function, ψ
  classical description: positions and velocities of all particles (better momenta...)
  $\psi = (\vec{r}_1, \ldots, \vec{r}_N, \vec{v}_1 \ldots, \vec{v}_N)$
- macrostate = averaged microstates
- ensemble = set of all microstates with their respective probabilities $\boldsymbol{\pi}(\psi)$,

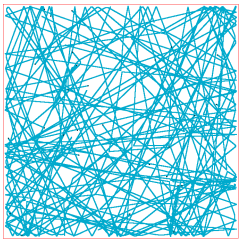


microstate macrostate ensemble trajectory

Microcanonical ensemble and the ergodic hypothesis

Microcanonical ensemble = set of microstates in an isolated system
Denoted: **NVE** (N = const, V = const, E = const)

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



In other words:
Time averaged (mean) value =

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

= ensemble mean value =

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

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

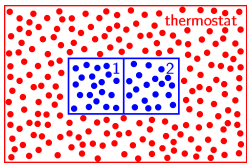
. . . but T = const is more practical

Canonical ensemble

is the ensemble with a constant temperature.
Denoted: **NVT** (N = const, V = const, T = const)
Ergodic hypothesis: $\boldsymbol{\pi}(\psi) = \boldsymbol{\pi}(\mathcal{E}(\psi))$
$E_1 + E_2 = E_{1+2}$ (small influence)
$\boldsymbol{\pi}(E)$ = probability of any state of 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 ⇒ β is the empirical temperature
- α_i is the normalization constant, so that $\sum_\psi \boldsymbol{\pi}(\psi) = 1$, depends on the system

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

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

Boltzmann probability

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

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

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

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

[simolant -l2] 9/16 col05

. . . 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 ∝ density ∝ pressure:

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

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

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

("⇒" Boltzmann probability.)

Boltzmann probability

[cd ../simul/nmf/; blend -g butane] 10/16 col05

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 $\mathrm{cal_{th}}$ = 4.184 J

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

Don't forget that there are two gauche states!

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

⇒

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

Note: we assumed that both minima are well separated and their shapes are identical.

Thermodynamics

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Internal energy

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

Small change of U:

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

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

1st Law of Thermodynamics: $\mathrm{d}U = -p\,\mathrm{d}V + T\mathrm{d}S$

- $-p\,\mathrm{d}V$
  "Piston" moved. Enegy changes by $\mathrm{d}\mathcal{E}(\psi)$ **= 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", (mean) pressure $= p = \sum_\psi \pi(\psi)p(\psi)$.
- $T\mathrm{d}S$
  Change of $\pi(\psi)$ at constant $[V]$ = change of probabilities of states of different energies **= heat**

Boltzmann equation for entropy

[jkv pic/BoltzmannTomb.jpg] 12/16 col05

. . . the second half of the statistical thermodynamics

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

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

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

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

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

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

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

Transitions between states ⇒ $\mathrm{d}S/\mathrm{d}t \geq 0$ (H-theorem)

Ideal solution

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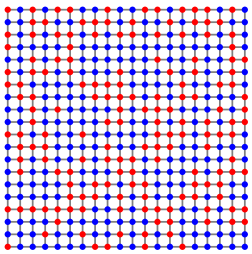
Energies of neighbors: ●–● = ●–● = ●–●
All configurations have the same energy



Mix N_1 molecules of 1 + N_2 molecules of 2:

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

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

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

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

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

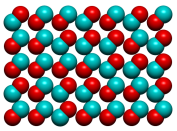
More accurate: $\ln N! \overset{\text{asympt.}}{=} N\ln N - N + \ln\sqrt{2\pi N} + \frac{1}{12N} - \frac{1}{360N^3} + -\cdots$

Residual entropy of crystals at $T \to 0$

[traj/ice.sh] 14/16 col05

Crystal: 1 microstate ⇒ $S = k\ln 1 = 0$ (3rd Law)

3rd Law violation: CO, N_2O, H_2O.
Not in the true equilibrium, but "frozen" because of high barriers



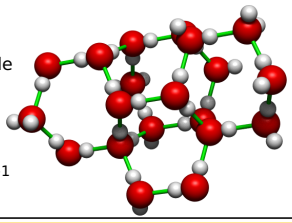
Example 1: Entropy of a crystal of CO at 0 K

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

Example 2: Entropy of ice at 0 K

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

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

Information entropy of DNA

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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):

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

To be compared to: ATP → ADP
– standard: $\Delta_r G_m^\ominus = -31\,\mathrm{kJ\,mol^{-1}}$
– in usual conditions in a cell: $\Delta_r G_m = -57\,\mathrm{kJ\,mol^{-1}}$

credit: www.pbs.org/wgbh/nova/sciencenow/3214/01-coll-04.html

Finishing the story

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α = ?

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

Helmholtz energy:

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

$[\ldots]$ = **canonical partition function** = **statistical sum** (Q or Z)

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

All equilibrium quantites can be calculated from F ($\mathrm{d}F = -p\mathrm{d}V - S\mathrm{d}T$):

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