

### Pressure of ideal gas from the kinetic theory I

[simolant -10 -N100 -Prho=.01] 1/27 s01/2

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

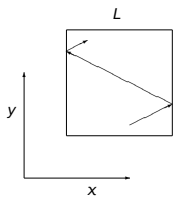
**Averaged** force caused by impacts of one molecule:

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

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

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


### Equipartition principle - example

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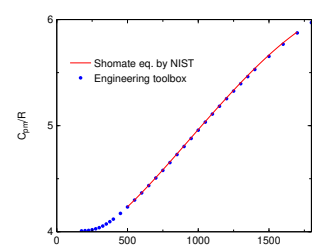
Calculate  $C_{p,m}$  for nitrogen and water vapor.

$N_2$ :  $C_{V,m} = \frac{5}{2}R$ ,  $C_{p,m} = C_{V,m} + R = 3.5R = 29.10 \text{ J K}^{-1} \text{ mol}^{-1}$

$H_2O$ :  $C_{V,m} = \frac{6}{2}R$ ,  $C_{p,m} = C_{V,m} + R = 4R = 33.26 \text{ J K}^{-1} \text{ mol}^{-1}$

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  $\rightarrow \rightarrow \rightarrow$



### Pressure of ideal gas from the kinetic theory II

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Kinetic energy of gas = internal energy (monoatomic gas)

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

$\Rightarrow$

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

In other words

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

Temperature is a measure of kinetic energy

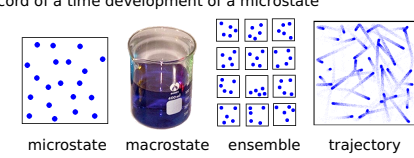
Assumptions:

- Pressure is a result of **averaged** impacts of molecules
- We used the **classical mechanics**
- Quantum effects at low  $T$ :  $p < nRT/V$  for bosons,  $p > nRT/V$  for fermions

### Microstate, macrostate, ensemble, trajectory

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- microstate** (state, configuration) = instantaneous "snapshot" at given time  
 quantum description: state = eigenstate (wave function  $\psi$ )  
 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



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

### Consequences

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Equation of state:  $pV = nRT = Nk_B T$  ( $N = nN_A$ )

also "thermal equation of state"

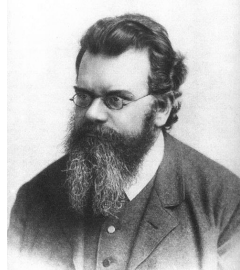
Energy

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

"caloric equation of state" / "internal energy" where the Boltzmann constant is

$$k_B = \frac{R}{N_A}$$

**Defined** since May 5, 2019:  
 $k_B = R/N_A = 1.380649 \times 10^{-23} \text{ J K}^{-1}$ ,  
 $N_A = 6.02214076 \times 10^{23} \text{ mol}^{-1}$ ,  
 hence **exactly**  
 $R = 8.31446261815324 \text{ J mol}^{-1} \text{ K}^{-1}$



Ludwig Eduard Boltzmann (1844-1906)  
credit: scienceworld.wolfram.com/biography/boltzmann.html

(both equations of state are needed to define entropy)

### Microcanonical ensemble and ergodic hypothesis

[tchem/simolant1+2.sh] 8/27 s01/2

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<sup>1</sup> with uniform probability

**In other words:**  
 Time average (over a trajectory)

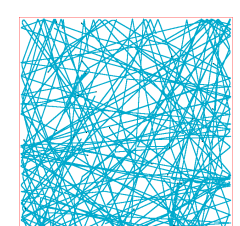
$$\langle X \rangle_t = \lim_{t \rightarrow \infty} \frac{1}{t} \int_0^t X(t) dt$$

= ensemble average

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

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

<sup>1</sup>namely: the phase state of  $\{(\vec{r}_1, \dots, \vec{r}_N, \vec{p}_1, \dots, \vec{p}_N)\}$



for me:  
 e NVE ensemble  
 r smaller balls  
 c trajectory

### Overview of classical thermodynamics

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**0th Law**  $\rightarrow$  id. gas:  $pV = nRT$   $\rightarrow$  id. gas:  $pV^K = \text{const}$  (id., ad.)

**1st Law**  $\rightarrow$  id. gas:  $U = U(T)$

**2nd Law**  $\rightarrow$  Carnot cycle  $\rightarrow$   $\oint \frac{dQ}{T} = 0$   $\rightarrow$   $\exists S, dS = \frac{dQ}{T}$

**3rd Law**  $\rightarrow$   $\lim_{T \rightarrow 0} S = 0$   $\rightarrow$   $\Delta_r G, K, \dots$

### Mean value in the microcanonical ensemble

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

**Example.** You win \$5 if you throw 6 on a dice, you lose \$1 if you throw anything else. What is your mean (expected) win in this game?

$$\langle \text{win} \rangle = \frac{-1 - 1 - 1 - 1 - 1 + 5}{6} = 0$$

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

### Equipartition principle

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

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

$f =$  number of mechanical degrees of freedom.

**Average energy contribution** per one degree of freedom:

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

**Generalization:** any quadratic function in the Hamiltonian

Heat capacity in molar units ( $N = N_A$ ,  $f = 3N_A$ ):

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

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!**)

degrees of freedom per molecule

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

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

Ergodic hypothesis:  $\pi(\psi) = \pi(E(\psi))$

$E_A + E_B = E_{A+B}$  (do not interact)

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

$$\pi(E_A) \cdot \pi(E_B) = \pi(E_{A+B}) = \pi(E_A + E_B)$$

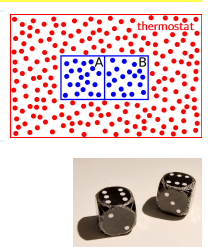
$$\Rightarrow \pi(E) = \text{const}^E = \exp(\alpha_i - \beta E)$$

- 0th Law**  $\Rightarrow \beta$  is empirical temperature
- $\alpha_i$  is system-dependent normalizing const. so that  $\sum_{\psi} \pi(\psi) = 1$

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

$$\langle U_1 \rangle = \frac{\sum_{\psi} E(\psi) \pi(E(\psi))}{\sum_{\psi} \pi(E(\psi))} = \frac{\int \frac{3}{2} m \vec{v}^2 \pi(\frac{3}{2} m \vec{v}^2) d\vec{v}}{\int \pi(\frac{3}{2} m \vec{v}^2) d\vec{v}}$$

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



## Determining $\beta$

[start/home/jiri/vyuka/maple/beta.mw] 11/27 s01/2

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

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 $\beta$

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

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

## Boltzmann probability

[cd tchem; blend -g butane] 16/27 s01/2

**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:** There are two gauche states and one anti state!

$$\pi(\text{gauche}+) = \pi(\text{gauche}-)$$

$$\pi(\text{gauche}) : \pi(\text{anti}) = \exp[-\Delta E/RT] = 0.1899$$

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

$$\pi(\text{anti}) = \frac{1}{2 \exp[-\Delta E/RT] + 1} = \frac{1}{2 \times 0.1899 + 1} = 0.725$$

$$2 \pi(\text{gauche}) = \frac{2 \exp[-\Delta E/RT]}{2 \exp[-\Delta E/RT] + 1} = \frac{2 \times 0.1899}{2 \times 0.1899 + 1} = 0.275$$

Note: we assumed that both minima are well separated and their shapes are identical. Better formula would be with  $\Delta G$  instead of  $\Delta E$ .  $\Delta G$  includes the factor of 2 as well as vibrations which will be a little different in both states. In fact, we solve the equilibrium:

$$\text{anti} \rightarrow \text{gauche}, K = \exp[-\Delta G/RT]$$

$$\pi(\text{gauche}) = 0.1899 \pi(\text{anti})$$

## Mean value in the canonical ensemble

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Generalization of the mean value (= expectation value):

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

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

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

Note:  $5 \times 0.16 + 0.2 = 1$  (normalized)

$$\langle \text{win} \rangle = -1 \cdot 0.16 - 1 \cdot 0.16 - 1 \cdot 0.16 - 1 \cdot 0.16 - 1 \cdot 0.16 + 5 \cdot 0.2 = 0.2$$

## Thermodynamics

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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  $\psi$  changed

1st + 2nd Law:

$$dU = -p dV + T dS$$

●  $-p dV$ : A "piston" moved by  $dx$ . Change in energy =  $d\mathcal{E}(\psi) = \text{mechanical work} = -F dx = -F/A \cdot d(Ax) = -p(\psi) dV$

●  $T dS$ : Change  $\pi(\psi)$  [V] = change of the population of states with varying energies = **heat**

## Boltzmann equation for entropy

[jkv pic/BoltzmannTomb.jpg] 18/27 s01/2

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

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

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

On comparing with  $T dS$ :

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

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



If we consider transitions between states, we can derive  $\frac{dS}{dt} \geq 0$  (H-theorem)

## Boltzmann probability

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... 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)

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

## Example: 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:

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

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

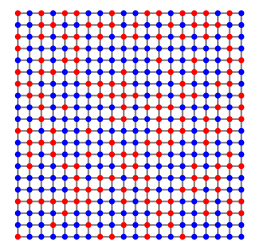
$$S_m = -R (x_1 \ln x_1 + x_2 \ln x_2)$$

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

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

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

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



## Case study: Barometric formula

[simulant-12] 15/27 s01/2

... 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  $h$ :

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

Probability  $\propto$  density  $\propto$  pressure:

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

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

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

$$\int_{p_0}^p \frac{dp}{p} = - \int_0^h \frac{Mg}{RT} dh \Rightarrow \ln \frac{p}{p_0} = -h \frac{Mg}{RT}$$

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

[traj/ice.sh] 20/27 s01/2

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

3rd Law violation: CO, N<sub>2</sub>O, H<sub>2</sub>O.

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

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

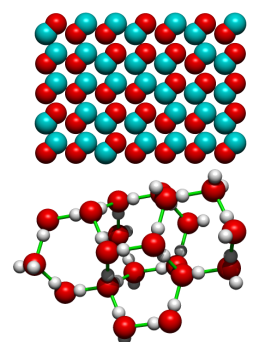
**Pauling's derivation:**

●  $6 = \binom{4}{2}$  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

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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: ATP → ADP

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

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



credit: www.pbs.org/wgbh/nova/sciencenow/321401-coll-04.html

### Thermal de Broglie wavelength

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s01/2

#### Example

a) Calculate  $\Lambda$  for helium at  $T = 2 \text{ K}$ .

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

a) 6.2 Å, b) 3.8 Å

a)

$$\begin{aligned} \Lambda &= \frac{h}{\sqrt{2\pi m k_B T}} \\ &= \frac{6.6 \times 10^{-34}}{\sqrt{2 \times \pi \times \frac{0.004}{6 \times 10^{23}} \times 1.38 \times 10^{-23} \times 2}} \\ &= 6.2 \times 10^{-10} \text{ m} \end{aligned}$$



credit: high3ch.com/superfluid-liquid-helium

b)

$$l = \sqrt[3]{V_1} = \sqrt[3]{\frac{M}{N_A \rho}} = \sqrt[3]{\frac{0.004}{6 \times 10^{23} \times 125}} = 3.8 \times 10^{-10} \text{ m}$$

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

### Thermodynamics finished

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s01/2

$\alpha = ?$

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

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

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

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

[...] = **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:

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

$$\begin{aligned} p &= -\frac{\partial F}{\partial V} & U &= F + TS \\ S &= -\frac{\partial F}{\partial T} & H &= U + pV \\ & & G &= F + pV \end{aligned}$$

### Semiclassical monoatomic ideal gas

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

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

$$p = -\left(\frac{\partial F}{\partial V}\right)_T = \frac{k_B T N}{V} = \frac{nRT}{V} \quad \begin{aligned} e &= \text{Euler number} \\ e &= \text{elementary charge} \end{aligned}$$

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

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

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

And verification:

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

### Semiclassical partition function

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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 (classical mechanics needed):

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

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

● Fails if quantum effects are important (vide infra)

### 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:

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

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

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

### Semiclassical partition function

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#### Integrals over positions and momenta are separated

Integrals over momenta can be evaluated:  $\int \exp\left(-\frac{p_{1,x}^2/2m}{k_B T}\right) dp_{1,x} = \sqrt{2\pi k_B T m}$  After  $3N$  integrations we get:

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

$\Lambda$  = 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):

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