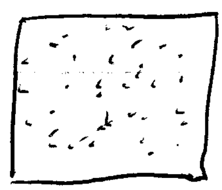
II.2 Stochastic description of the ideal gas

ideal gas in a box: N independent particles in a volume V.

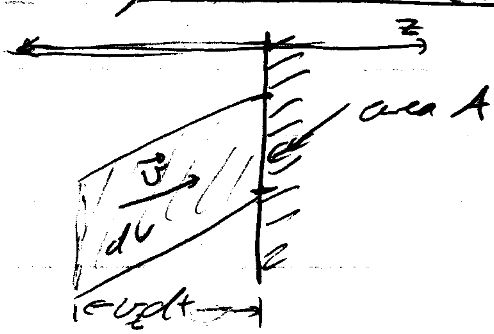


each particle has a velocity $\vec{v}$
- $\vec{v}$ changes all the time by interactions with other particles and the wall

N large $\Rightarrow$ ~~number of~~ particles with given velocity $\vec{v}$ constant
$\Rightarrow$ probability distribution for velocity

$P_{\vec{V}}(\vec{v})$ time independent.

<u>Calculate pressure on a wall:</u>



look at particles with velocity $\vec{v}$:

- within time dt all particles with velocity $\vec{v}$ within the shaded volume dV hit the wall. $dV = A\, v_z\, dt$
- each particle transfers momentum $p = 2 m v_z$
- the number of particles with velocity $\vec{v}$ within dV is
$$dN = \rho\, dV\, P_{\vec{V}}(\vec{v})\, d^3v = \frac{N}{V} A v_z P_{\vec{V}}(\vec{v})\, dt\, d^3\vec{v}$$

$\Rightarrow$ total momentum transfer on area A in time dt

$$\int\limits_{\vec{v},\, v_z>0} \frac{N}{V} 2mA\, v_z^2\, P_{\vec{V}}(\vec{v})\, dt\, d^3\vec{v}$$

$\Rightarrow$ total force on area A: $\quad F = \int\limits_{v_z>0} \frac{N}{V} 2mA\, v_z^2\, P_{\vec{V}}(\vec{v})\, d^3\vec{v}$

$\Rightarrow$ total pressure

$$P = \frac{N}{V} 2m \int\limits_{v_z>0} v_z^2\, P_{\vec{V}}(\vec{v})\, d^3\vec{v}$$

$$\underset{P_{\vec{V}}(\vec{v}) = P_{\vec{V}}(-\vec{v})}{=} \frac{N}{V} m \int v_z^2\, P_{\vec{V}}(\vec{v})\, d^3\vec{v}$$

space is isotropic $\Rightarrow \int v_z^2 P_{\vec{V}}(\vec{v})\, d^3\vec{v} = \int v_x^2 P_{\vec{V}}(\vec{v})\, d^3\vec{v} = \int v_y^2 P_{\vec{V}}(\vec{v})\, d^3\vec{v}$

$$\Rightarrow \int v_z^2 P_{\vec{V}}(\vec{v})\, d^3\vec{v} = \frac{1}{3} \int \vec{v}^2 P_{\vec{V}}(\vec{v})\, d^3\vec{v}$$

$$\Rightarrow \quad PV = N \frac{m}{3} \langle \vec{V}^2 \rangle = \frac{2}{3} N \; \frac{1}{2} m \langle \vec{V}^2 \rangle = \frac{2}{3} N \langle E_{kin} \rangle = \frac{2}{3} n N_A \langle E_{kin} \rangle$$

Compare with $\quad PV = nRT$

$$\Rightarrow \quad \langle E_{kin} \rangle = \frac{3}{2} \frac{R}{N_A} T \equiv \frac{3}{2} k_B T$$

"temperature is average kinetic energy of the particles"

$k_B = \frac{R}{N_A} \approx 1.38062 \cdot 10^{-23} \frac{J}{K}$ "Boltzmann constant"

$$k_B \cdot T_{room} \approx \frac{1}{40}\, eV$$

III.3 Microscopic definition of entropy

System with discrete states

$\mathcal{N}$: number of states
system completely described by
p_i : probability for system to be in state i
for $i = 1, \dots, \mathcal{N}$

$$\sum_{i=1}^{\mathcal{N}} p_i = 1$$

Entropy describes "amount of disorder"
$\Rightarrow$ entropy depends only on p_i

Define $$\boxed{S = -k_B \sum_{i=1}^{\mathcal{N}} p_i \ln p_i}$$

This entropy is an extensive variable:

$p_i^{(1)}$	$p_j^{(2)}$
1	2
$\mathcal{N}_1$ $S^{(1)}$	$\mathcal{N}_2$ $S^{(2)}$

state of total system (i,j), $\mathcal{N}_1 \mathcal{N}_2 = \mathcal{N}$
$$p_{(i,j)} = p_i^{(1)} p_j^{(2)}$$

$$\begin{aligned}
S_{tot} &= -k_B \sum_{i=1}^{\mathcal{N}_1} \sum_{j=1}^{\mathcal{N}_2} p_{(i,j)} \ln p_{(i,j)} \\
&= -k_B \sum_{i=1}^{\mathcal{N}_1} \sum_{j=1}^{\mathcal{N}_2} p_i^{(1)} p_j^{(2)} \ln\left[p_i^{(1)} p_j^{(2)}\right] \\
&= -k_B \sum_{i=1}^{\mathcal{N}_1} \sum_{j=1}^{\mathcal{N}_2} p_i^{(1)} p_j^{(2)} \left[\ln p_i^{(1)} + \ln p_j^{(2)}\right] \\
&= -k_B \sum_{i=1}^{\mathcal{N}_1} \sum_{j=1}^{\mathcal{N}_2} p_i^{(1)} p_j^{(2)} \ln p_i^{(1)} - k_B \sum_{i=1}^{\mathcal{N}_1} \sum_{j=1}^{\mathcal{N}_2} p_i^{(1)} p_j^{(2)} \ln p_j^{(2)} \\
&= -k_B \sum_{i=1}^{\mathcal{N}_1} p_i^{(1)} \ln p_i^{(1)} - k_B \sum_{j=1}^{\mathcal{N}_2} p_j^{(2)} \ln p_j^{(2)} \\
&= S^{(1)} + S^{(2)}
\end{aligned}$$

Classical N-particle system

$\vec{q}_i$: generalized position of particle i
$\vec{p}_i$: generalized momentum of particle i
$i=1,\ldots,N$

System described by

$$\rho(\vec{q}_1,\ldots,\vec{q}_N,\vec{p}_1,\ldots,\vec{p}_N) = P_{\vec{Q}_1,\ldots,\vec{Q}_N,\vec{P}_1,\ldots,\vec{P}_N}(\vec{q}_1,\ldots,\vec{q}_N,\vec{p}_1,\ldots,\vec{p}_N)$$

notation: $\vec{x}^N = (\vec{q}_1,\ldots,\vec{q}_N,\vec{p}_1,\ldots,\vec{p}_N)$ "point in phase space"

$$\rightarrow \rho = \rho(\vec{x}^N)$$

Analogous definition of entropy

$$S = -k_B \int d\vec{x}^N \rho(\vec{x}^N) \ln[C_N \rho(\vec{x}^N)]$$

dimensionful constant

III.4 Summary

concepts:

probability
stochastic variable
distribution function / probability density
characteristic function
moments
cumulants
correlation function
independent variables
Boltzmann constant
microscopic definitions of entropy

facts:

central limit theorem
law of large numbers
temperature as average kinetic energy
Maxwell distribution

tools:

handling expectation values
Gaussian integrals

11/25