Stochastic description of the ideal gas

Ideal gas in a box: \( N \) independent particles in a volume \( V \)

Each particle has a velocity \( \vec{v} \)
- \( \vec{v} \) change all the time by interaction with other particles and the wall

\( N \) large \( \Rightarrow \) number of particles with given velocity \( \vec{v} \) constant

\( \Rightarrow \) probability distribution for velocity

\[ p_{\vec{v}}(\vec{v}) \text{ time independent} \]

Calculate pressure on a wall:

Look at particles with velocity \( \vec{v} \):

- Within time \( dt \) all particles will velocity \( \vec{v} \) within the shaded volume \( dV \) hit the wall.

\[ dV = A \Delta v \, dt \]

- Each particle exchange momentum \( 2m \Delta v \)

\[ \Rightarrow \] the number of particles with velocity \( \vec{v} \) within \( dV \) is

\[ dN = \frac{3}{2} \rho \Delta v \, p_{\vec{v}}(\vec{v}) \, dt \]
Total momentum transfer on area A in time $dt$:

$$\sum_{\nu>0} N_v u_v^2 P_v(\nu) dt d^3\Omega$$

Total force on area $A$:

$$F = \sum_{\nu>0} N_v u_v^2 P_v(\nu) d^3\Omega$$

Total pressure

$$P = \frac{N}{V} \sum_{\nu>0} u_v^2 P_v(\nu) d^3\Omega$$

Since $N$ is isotropic:

$$\int u_v^2 P_v(\nu) d^3\Omega = \int u_x^2 P_v(\nu) d^3\Omega = \int u_y^2 P_v(\nu) d^3\Omega$$

$$\Rightarrow \int u_v^2 P_v(\nu) d^3\Omega = \frac{1}{3} \int \nabla^2 P_v(\nu) d^3\Omega$$

$$\Rightarrow PV = N \frac{m}{3} \langle \vec{V}^2 \rangle = \frac{2}{3} N \frac{1}{2} m \langle \vec{V}^2 \rangle = \frac{2}{3} N \langle E_{\text{kin}} \rangle = \frac{2}{3} \frac{N}{N_A} k_B T$$

Compare with $PV = nRT$

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

"Temperature is average kinetic energy of the particle"
System with discrete states

\[ N: \text{number of states} \]

system completely described by \( \gamma_i \): \( \gamma_i \) is probability of system to be in state \( i \) for \( i = 1, \ldots, N \)

\[ \sum_{i=1}^{N} \gamma_i = 1 \]

Entropy describes "amount of disorder" 
\( \Rightarrow \) entropy depends only on \( \gamma_i \).

Define

\[ S = -k_B \sum_{i=1}^{N} \gamma_i \ln \gamma_i \]

This entropy is an extensive variable:

\[
\begin{array}{c|c|c}
\gamma_i^{(1)} & \gamma_0^{(2)} & \text{state of total system } (1,2) , \ N_1 N_2 = N \\
N_1 S^{(1)} & N_2 S^{(2)} & \end{array}
\]

\[
S_{\text{total}} = -k_B \sum_{i=1}^{N} \gamma_i^{(1)} \ln \gamma_i^{(1)}
\]

\[
= -k_B \sum_{i=1}^{N} \gamma_i^{(2)} \ln \gamma_i^{(2)}
\]

\[
= -k_B \sum_{i=1}^{N} \gamma_i^{(1)} \gamma_i^{(2)} \ln \gamma_i^{(1)} - k_B \sum_{i=1}^{N} \gamma_i^{(2)} \ln \gamma_i^{(2)}
\]

\[ = S^{(1)} + S^{(2)} \]
Classical N-particle system

\( \vec{Q}_i \): generalized position of particle
\( \vec{p}_i \): generalized momentum of particle

System described by

\[ S(\vec{Q}_1, ..., \vec{Q}_N, \vec{p}_1, ..., \vec{p}_N) = \mathcal{P}(\vec{Q}_1, ..., \vec{Q}_N, \vec{p}_1, ..., \vec{p}_N) \]

notation: \( \vec{X}^N = (\vec{Q}_1, ..., \vec{Q}_N, \vec{p}_1, ..., \vec{p}_N) \) “point in phase space”

\[ S = S(\vec{X}^N) \]

Analogous definition of entropy

\[ S = -k_B \int d\vec{X}^N g(\vec{X}^N) \ln [g_N(\vec{X}^N)] \]

\( k_B \): dimensionful constant
III.4 Summary

- Concepts:
  - probability
  - stochastic variable
  - distribution function, probability density
  - characteristic function
  - moment
  - cumulant
  - correlation function
  - independent variable
  - Boltzmann constant
  - microscopic definition of entropy

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

- Tools:
  - handling expectation values
  - Gaussian integrals