Statistical Independence of Momenta and Coordinates

- Consider classical distribution function in cartesian coordinates:

\[ \rho(p, q) = Z^{-1} \exp[-E(p, q)/T] \]

Here

\[ E(p, q) = K(p) + U(q) \]  \hfill (1)

and

\[ p \equiv \{p_{1x}, p_{1y}, p_{1z}, \ldots, p_{Nx}, p_{Ny}, p_{Nz}\} \]
\[ q \equiv \{q_{1x}, q_{1y}, q_{1z}, \ldots, q_{Nx}, q_{Ny}, q_{Nz}\} \]

- By virtue of Eq. (1) the distribution function can be expressed as

\[ dw(p, q) = \rho(p, q)dp \cdot dq = dw_p \cdot dw_q \]

\[ dw_p = A \exp[-K(p)]dp \quad \text{and} \quad dw_q = B \exp[-U(q)]dq \]

Distribution functions of momenta and coordinates are statistically independent for any classical gas (not just for ideal gases!)
Distribution of Momenta and Velocities

- Momenta of different particles are statistically independent as well. Indeed, the kinetic energy:

\[
K(p) = \frac{1}{2m} \sum_{i=1}^{N} (p_{ix}^2 + p_{iy}^2 + p_{iz}^2)
\] (2)

Using Eq. (2) we can calculate the \(dw_p\):

\[
dw_p = A \exp \left[ -\frac{1}{2mT} \sum_{i=1}^{N} (p_{ix}^2 + p_{iy}^2 + p_{iz}^2) \right] \prod_{i=1}^{N} dp_{ix} dp_{iy} dp_{iz} = \prod_{i=1}^{N} dw_i(p),
\]

where (omitting index \(i\))

\[
dw(p) = a \exp \left[ -\frac{1}{2mT} (p_x^2 + p_y^2 + p_z^2) \right] dp_x dp_y dp_z
\]
Distribution of Momenta and Velocities

- The constant $a$ can be calculated from the normalization condition $\int dw(p) = 1$:

$$1 = a \int \exp \left[ -\frac{1}{2mT} (p_x^2 + p_y^2 + p_z^2) \right] dp_x dp_y dp_z$$

$$= a \left[ \int_{-\infty}^{\infty} \exp \left( -\frac{p_x^2}{2mT} \right) dp_x \right]^3$$

$$= a (2mT)^{3/2} \left[ \int_{-\infty}^{\infty} \exp (-u^2) du \right]^3 = a (2\pi mT)^{3/2} = a (\hbar/\lambda_{th})^3$$

- Thus

$$a = \left( \frac{\lambda_{th}}{\hbar} \right)^3 \rightarrow A = \left( \frac{\lambda_{th}}{\hbar} \right)^{3N} \quad \text{where} \quad \lambda_{th} = \frac{\hbar}{\sqrt{2\pi mT}}$$
Distribution of Momenta and Velocities

Finally

\[ dw(p) = \frac{\lambda_{th}^3}{\hbar^3} \exp \left[ -\frac{1}{2mT} (p_x^2 + p_y^2 + p_z^2) \right] dp_x dp_y dp_z \]

One can also write the distribution of velocities \( v = p/m \)

\[ dw(v) = \left( \frac{m}{2\pi T} \right)^{3/2} \exp \left[ -\frac{m}{2T} (v_x^2 + v_y^2 + v_z^2) \right] dv_x dv_y dv_z, \]

which is called the Maxwellian distribution or velocity distribution, which is valid for any gas (not only ideal).

Again, the Maxwell distribution consists of three independent factors, i.e. distributions for different components of the velocity of the particles are statistically independent:

\[ dw(v_i) = \left( \frac{m}{2\pi T} \right)^{1/2} \exp \left( -\frac{mv_i^2}{2T} \right) dv_i, \quad i = x, y, z \]
Maxwell-Boltzmann Distribution

- Maxwell distribution allows us to calculate averages $\langle f(v) \rangle$ of arbitrary functions of $v$
- The configuration probability $dw_q = B \exp(-U(q)/T)dq$ cannot be factorized because, in general $U(q) \neq \sum_{i=1}^{N} U(q_i)$. This is the case only when a system is subject to an external field:

$$U(q) = \sum_{i=1}^{N} U(x_i, y_i, z_i)$$

Then

$$dw_q = \prod_{i=1}^{N} dw(r_i),$$

where one-particle distribution reads:

$$dw(r) = b \exp \left[ -U(x, y, z)/T \right] dx dy dz$$

This is the Boltzmann formula
In a gravitational field

\[ U(x, y, z) = mgz \]

and therefore the number of particle in a volume \( dV \) near \( r = (x, y, z) \):

\[ dN(r) = n(0) \exp\left(-\frac{mgz}{T}\right)dV \]

Therefore

\[ n(r) = \frac{dN(r)}{dV} = n(0) \exp \left( -\frac{mgz}{T} \right), \]

which is again the barometric formula.
Finally let us write down a formal expression for the partition function of a classical monoatomic gas. Combining both the Maxwellian and many-body potential energy parts we obtain:

\[
Z = \frac{Z_1^N Q_N}{N!}
\]

where

\[
Z_1 = \frac{V}{\lambda_{th}^3}
\]

and

\[
Q_N = \int \ldots \int \exp[-U(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N)/T] \, d\mathbf{r}_1 d\mathbf{r}_2 \ldots d\mathbf{r}_N
\]

is called a configuration integral. Most of the effort in statistical mechanics of classical gases and liquids is devoted to computing the configuration integral \(Q_N\).