PHY215-01: Maxwell-Boltzmann distribution

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1 How to derive the Maxwell-Boltzmann distribution for an ideal gas?

The Maxwell-Boltzmann distribution describes the distribution of speeds of particles in an ideal gas at a given temperature. Here is a step-by-step derivation of the Maxwell-Boltzmann speed distribution function:

1.1 Assumptions:

- The gas consists of a large number of identical non-interacting particles (ideal gas assumption), moving with a speed much less than the speed of light.

- The motion of the particles is random, and the system is in thermal equilibrium at temperature T.

- The gas is in a three - dimensional space.

1.2 Probability in momentum space

We start with the principle of statistical mechanics. The probability P of a particle having a certain energy E in a system at temperature T is given by the Boltzmann factor: $P \propto e^{-\frac{E}{kT}}$

For a particle of mass m with momentum $\vec{p} = (p_x, p_y, p_z)$, the kinetic energy $E = \frac{p^2}{2m} = \frac{p_x^2 + p_y^2 + p_z^2}{2m}$, where $p = |\vec{p}|$.

The probability density function $f(p_x, p_y, p_z)$ of a particle having momentum components p_x, p_y, and p_z is proportional to the Boltzmann factor:

$f(p_x, p_y, p_z) = Ce^{-\frac{p_x^2+p_y^2+p_z^2}{2mkT}}$

where C is a normalization constant.

1.3 Normalization

To find the normalization constant C, we use the fact that the total probability of finding a particle with any momentum must be equal to 1. That is,

$\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} f(p_x, p_y, p_z) dp_x dp_y dp_z = 1$

Substituting $f(p_x, p_y, p_z) = Ce^{-\frac{p_x^2+p_y^2+p_z^2}{2mkT}}$ into the above integral, we get:

$C\int_{-\infty}^{\infty} e^{-\frac{p_x^2}{2mkT}} dp_x \int_{-\infty}^{\infty} e^{-\frac{p_y^2}{2mkT}} dp_y \int_{-\infty}^{\infty} e^{-\frac{p_z^2}{2mkT}} dp_z = 1$

We know that the Gaussian integral is $\int_{-\infty}^{\infty} e^{-ax^2} dx = \sqrt{\frac{\pi}{a}}$. In our case, $a = \frac{1}{2mkT}$, so $\int_{-\infty}^{\infty} e^{-\frac{p_i^2}{2mkT}} dp_i = \sqrt{2\pi mkT}$ for $i = x, y, z$

Then $C(2\pi mkT)^{\frac{3}{2}} = 1$, and $C = \left(\frac{1}{2\pi mkT}\right)^{\frac{3}{2}}$

1.4 Transformation to speed distribution

The speed v of a particle is related to its momentum by $p = mv$. The volume element in momentum space $dp_x dp_y dp_z$ can be transformed into a volume element in speed space. In spherical coordinates in momentum space, $dp_x dp_y dp_z = p^2 \sin\theta dp d\theta d\varphi$, and $p = mv$. As a side remark, we note that the phase space factor $p^2 dp = m^3 v^2 dv$ accounts for the fact that there are more states available at higher momentum or speed in three-dimensional space.

The probability density function of speed $f(v)$ is obtained by integrating the angular variables θ and φ (since we are only interested in speed, not direction of motion).

$\int_0^{2\pi} d\varphi \int_0^{\pi} \sin\theta d\theta = 4\pi$, and $\int p^2 dp = m^3 \int v^2 dv$.

The probability density function of speed $f(v)$ is given by:

$f(v)dv = 4\pi \left(\frac{m}{2\pi kT}\right)^{\frac{3}{2}} v^2 e^{-\frac{mv^2}{2kT}} dv$

This is the Maxwell-Boltzmann speed distribution function, which gives the fraction of gas particles with speeds between v and $v + dv$ in an ideal gas at temperature T.

1.5 The Boltzmann factor in statistical mechanics

In statistical mechanics, the Boltzmann factor is a crucial concept and is expressed as $e^{-\frac{E}{kT}}$, where:

- E represents the energy of a particular state of a system.

- k is the Boltzmann constant, which has a value of approximately $1.38 \times 10^{-23} J/K$.

- T is the absolute temperature of the system in Kelvin.

The Boltzmann factor is used to describe the relative probability of a system being in a particular energy state at a given temperature. For a system in thermal equilibrium, the probability P_i of the system being in a state i with energy E_i is proportional to the Boltzmann factor:

$P_i = \frac{e^{-\frac{E_i}{kT}}}{Z}$

where Z is the partition function, which is given by the sum of the Boltzmann factors over all possible states of the system:

$Z = \sum_i e^{-\frac{E_i}{kT}}$

The partition function Z serves to normalize the probabilities so that $\sum_i P_i = 1$.

When relating probability to the number of states, the number of systems in a state n_i is related to the total number of systems N by $n_i = N\frac{e^{-\frac{E_i}{kT}}}{\sum_j e^{-\frac{E_j}{kT}}}$. The probability P_i of a system being in state i

can also be expressed as $P_i = \frac{n_i}{N}$. Hence, the Boltzmann distribution is $P_i = \frac{e^{-\frac{E_i}{kT}}}{\sum_j e^{-\frac{E_j}{kT}}}$,
and
$-\ln\left(\frac{n_i}{N}\right) = \frac{E_i}{kT} + c$,
where c is a normalization constant.

The Boltzmann factor plays a vital role in various aspects of statistical mechanics, such as in calculating thermodynamic properties like the internal energy U and entropy S of a system.

We note that the Boltzmann distribution is the distribution that maximizes the entropy

1.5.1 The Boltzmann Entropy S in Statistical Mechanics

In statistical mechanics, the Boltzmann entropy, denoted by S, is a fundamental concept that connects the microscopic details of a system to its macroscopic thermodynamic properties, particularly its disorder or randomness.

- **Define entropy in terms of probability:**
Entropy S is a measure of the uncertainty or randomness of a system. It can be defined in terms of the probabilities p_i of the microstates as
$S = -k \sum_i P_i \ln P_i$,

where the sum is taken over all possible microstates. This is the general form of the entropy in information theory and statistical mechanics.

- **Substitute the probability for equally likely microstates:** For a system where all microstates are equally likely, $P_i = \frac{1}{\Omega}$ for all i corresponding to the macrostate. (Hence, this does not follow Boltzmann distribution.) Then the entropy becomes:

$$\begin{aligned} S &= -k \sum_i \frac{1}{\Omega} \ln \left(\frac{1}{\Omega} \right) && (1) \\ &= -k \times \Omega \times \frac{1}{\Omega} \ln \left(\frac{1}{\Omega} \right) && (2) \\ &= k \ln \Omega && (3) \end{aligned}$$

The probability of a system being in a particular macrostate is directly proportional to the number of microstates that correspond to that macrostate. A macrostate with more microstates is more probable and thus has higher entropy. Some examples are:

- **Coin Toss:**

Consider tossing a coin multiple times. The most probable outcome is a roughly equal number of heads and tails, as this macrostate corresponds to the largest number of microstates (combinations of heads and tails).

- **Gas Expansion:**

When a gas expands into a larger volume, the number of possible positions for the gas molecules increases dramatically, leading to a greater number of microstates and a higher entropy.

1.5.2 The Boltzmann constant (k)

- The Boltzmann constant (k) is a universal physical constant, meaning its value is the same for all substances and does not change depending on the type of gas or material being considered.
- It relates the average (linear) kinetic energy of particles in a gas to the temperature of the gas, as in the equation $\overline{E}_k = \frac{3}{2}kT$. This relationship holds true for all ideal gases and is a cornerstone of the kinetic theory of gases.
- It relates the average (linear) kinetic energy of particles in a system to the absolute temperature, acting as a conversion factor between these two quantities.
- It is based on the principles of statistical mechanics, which assume that the microscopic behavior of particles is governed by certain fundamental laws that are independent of the specific type of particle or gas.

1.6 Speed versus velocity dependence

In the case of an ideal gas, the Maxwell-Boltzmann distribution does not depend on the direction of the particle velocity in a strict sense, but the full description of the distribution does consider the velocity direction in a way. The details are as follows:

1.6.1 Speed Distribution

- The Maxwell-Boltzmann speed distribution function $f(v) = 4\pi \left(\frac{m}{2\pi kT}\right)^{\frac{3}{2}} v^2 e^{-\frac{mv^2}{2kT}}$ depends only on the magnitude of the velocity, that is, the speed v. It gives the probability distribution of particles that have a particular speed regardless of the direction in which the particles are moving. This is because in an ideal gas in thermal equilibrium, the gas is isotropic, meaning that on average there is no preferred direction of motion. The distribution is spherically symmetric in velocity space, and all directions are equally likely for a particle to move in.

1.6.2 Velocity Distribution Consideration

- When considering the full velocity distribution (not just speed), the direction is implicitly taken into account. In three - dimensional space, the velocity of a particle is a vector $\vec{v} = (v_x, v_y, v_z)$. The probability density function in velocity space $f(v_x, v_y, v_z) =$

$\left(\frac{m}{2\pi kT}\right)^{\frac{3}{2}} e^{-\frac{m(v_x^2+v_y^2+v_z^2)}{2kT}}$ shows that the probability depends on the components of the velocity vector. However, when we integrate this function over all possible directions (using spherical coordinates and integrating over the angular variables), we get the speed distribution function that is independent of direction. So, while the basic form of the Maxwell-Boltzmann distribution is often presented in terms of speed and is direction independent in that sense, the underlying velocity distribution in three-dimensional space does account for direction in the way the velocities are decomposed into components.

1.7 The three characteristic Velocities and Speeds

In addition to the average speed and the most probable speed, the root-mean-square velocity can also be derived from the Maxwell-Boltzmann distribution. We note that “velocity” implies direction, while “speed” only refers to magnitude.

Below is a detailed explanation of how to obtain these three velocities or speeds, associated with the translational kinetic energies of the ideal gas molecules.

The Maxwell-Boltzmann speed distribution function is given by:

$$f(v) = 4\pi \left(\frac{m}{2\pi kT}\right)^{\frac{3}{2}} e^{-\frac{mv^2}{2kT}} v^2$$

where m is the mass of a gas molecule, k is the Boltzmann constant, T is the absolute temperature, and v is the speed of the molecule.

1.7.1 Average speed($\langle v \rangle$)

The average velocity vector of gas molecules in thermal equilibrium is zero due to the randomness of their motion. The average speed is given by:

$$\langle v \rangle = \int_0^\infty v \cdot f(v) dv$$

Substituting the Maxwell-Boltzmann distribution function $f(v)$ and performing the integration, we get

$$\langle v \rangle = \sqrt{\frac{8kT}{\pi m}}$$

1.7.2 Most Probable Speed (v_p)

The most probable speed is the speed at which the distribution function $f(v)$ has a maximum. To find it, we take the derivative of $f(v)$ with respect to v, set it equal to zero, and solve for v.

Differentiating $f(v)$ and setting $\frac{df(v)}{dv} = 0$, we get

$$v_p = \sqrt{\frac{2kT}{m}}$$

1.7.3 Root-Mean-Square Velocity (v_{rms})

The correct term is "root-mean-square velocity" (or RMS velocity), as it refers to the square root of the average of the squared velocities, which is a measure of speed with a direction component, making it a velocity rather than just a speed.

The root-mean-square velocity is defined as:

$$v_{rms} = \sqrt{\langle v^2 \rangle}$$

where $\langle v^2 \rangle = \int_0^\infty v^2 \cdot f(v) dv$

Substituting $f(v)$ and performing the integration, we get

$$\langle v^2 \rangle = \frac{3kT}{m}$$

So,

$$v_{rms} = \sqrt{\frac{3kT}{m}}$$

We note that this is the relationship between the root-mean-square velocity and the average translational kinetic energy per molecule of an ideal gas is $\langle E \rangle = \frac{1}{2} m v_{rms}^2$, in the three-dimensional case with $v^2 = \sqrt{v_x^2 + v_y^2 + v_z^2}$.

In the case of one-dimensional linear motion,

$$\frac{1}{2} m \langle v_x^2 \rangle = \frac{1}{2} kT,$$

which is expected based on the Equipartition Theorem in thermodynamics.

The Equipartition Theorem states that each quadratic degree of freedom in a thermal equilibrium system contributes, on average, $\frac{1}{2}kT$ to the total internal energy of the system.

1.7.4 Summary

In summary, for gas molecules described by the Maxwell-Boltzmann distribution, the three characteristic velocities or speeds are:

- The average speed: $\langle v \rangle = \sqrt{\frac{8kT}{\pi m}}$
- The most probable speed: $v_p = \sqrt{\frac{2kT}{m}}$
- The root-mean-square velocity: $v_{rms} = \sqrt{\frac{3kT}{m}}$

And the relationship among them is $v_p < \langle v \rangle < v_{rms}$.

2 Equipartition Theorem

2.1 Statement

The Equipartition Theorem in thermodynamics can be derived from statistical mechanics based on the canonical ensemble:

1. Consider a system of N particles in thermal equilibrium with a heat bath at temperature T.
- The Hamiltonian of the system H is a function of the positions q_i and momenta p_i of the particles, $H = H(\{q_i\}, \{p_i\})$.
- The partition function Z is given by $Z = \int e^{-\beta H(\{q_i\},\{p_i\})} d\Gamma$, where $\beta = \frac{1}{kT}$, k is the Boltzmann constant, and $d\Gamma = \prod_{i=1}^{N} dq_i dp_i$ is the phase space volume element.

2. - The average energy $\langle E \rangle$ of the system is given by $\langle E \rangle = -\frac{\partial \ln Z}{\partial \beta}$

3. For every quadratic degree of freedom in the Hamiltonian of the system H, the average energy contribution is $\frac{1}{2}kT$.

4. Generalize to multiple degrees of freedom - If the Hamiltonian has f quadratic degrees of freedom, $H = \sum_{i=1}^{f} \frac{1}{2} a_i x_i^2 + H''$, where x_i can be either momenta or coordinates and a_i are constants, the average energy is $\langle E \rangle = \frac{f}{2}kT$

This is the Equipartition Theorem, which states that each quadratic degree of freedom in a thermal equilibrium system contributes, on average, $\frac{1}{2}kT$ to the total internal energy of the system.

2.2 Example: One-dimensional Harmonic Oscillator

The Hamiltonian of a one-dimensional harmonic oscillator is a key concept in both classical and quantum mechanics. Here is an explanation for each case:

2.2.1 Classical Mechanics

In classical mechanics, the Hamiltonian H of a one-dimensional harmonic oscillator is the sum of its kinetic energy K and potential energy U.

- The kinetic energy of a particle of mass m moving with momentum p is given by $K = \frac{p^2}{2m}$.
- The potential energy of a harmonic oscillator is $U = \frac{1}{2}kx^2$, where k is the force constant and x is the displacement from the equilibrium position.

The Hamiltonian H is then: $H = \frac{p^2}{2m} + \frac{1}{2}kx^2$

Using the relation $\omega = \sqrt{\frac{k}{m}}$, where ω is the angular frequency, we can rewrite the Hamiltonian as: $H = \frac{p^2}{2m} + \frac{1}{2}m\omega^2x^2$

2.2.2 Quantum Mechanics

In quantum mechanics, the Hamiltonian is an operator. For a one - dimensional harmonic oscillator, we replace the classical momentum

p and position x with their corresponding operators.

- The momentum operator is $\hat{p} = -i\hbar\frac{\partial}{\partial x}$, where $\hbar$ is the reduced Planck's constant.

- The position operator is $\hat{x} = x$ (in the position representation)

The Hamiltonian operator $\hat{H}$ is then: $\hat{H} = \frac{\hat{p}^2}{2m} + \frac{1}{2}m\omega^2\hat{x}^2$

Substituting the momentum operator, we get: $\hat{H} = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + \frac{1}{2}m\omega^2x^2$

The eigenvalues of the Hamiltonian operator $\hat{H}$ give the allowed energy levels of the quantum harmonic oscillator, which are $E_n = \left(n + \frac{1}{2}\right)\hbar\omega$, where $n = 0, 1, 2, \cdots$ is the quantum number.

2.2.3 Equipartition Theorem and average energy

The Equipartition Theorem states that each quadratic degree of freedom in a thermal equilibrium system contributes, on average, $\frac{1}{2}kT$ to the total internal energy of the system.

Since there are two quadratic degrees of freedom, one for kinetic energy and another for vibration energy, the average energy of the one-dimensional harmonic oscillator is $2 \times \frac{1}{2}kT = kT$.