

THE MAXWELL-BOLTZMANN DISTRIBUTION

(Classical Statistical Mechanics)

1. Define the ideal gas as a system of non-interacting point particles.

Then the total energy is the sum of the kinetic energies of the particles:

$$U = \sum_{i=1}^N (p_i^2/2m) = N \left\langle \frac{p^2}{2m} \right\rangle$$

Notation: I use E for the energy of a single particle and U for the energy of a system of N particles.

Then kinetic theory tells us that $PV = (2/3) U$ ideal monatomic gas.

2. We define temperature by the ideal gas thermometer:

$$PV = NkT = \nu RT \quad \text{ideal gas where } N = \text{no. particles, } \nu = \text{no. moles}$$

3. Thus we immediately obtain

$$U = (3/2) NkT = (3/2) \nu RT \quad \text{ideal monatomic gas}$$

4. The Maxwell-Boltzmann distribution is obtained by maximizing the number of ways of obtaining a particular distribution $\{N_{ij}\}$:

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

subject to the constraints

$$N = \sum N_i \quad \text{or} \quad dN = \sum dN_i$$

$$U = \sum N_i E_i \quad \text{or} \quad dU = \sum E_i dN_i$$

(This is done in most statistical physics texts.)

The result is $N_i = A e^{-\beta E_i}$ or $dN = A e^{-\beta E(r,p)} dV dV_p$

5. Application of this to the ideal gas leads to $U = 3N/2 \beta$

6. Therefore we make the identification $\beta = 1/kT$

and we have the Maxwell-Boltzmann distribution:

- a) **For discrete energy levels,** $N_i = A g_i e^{-E_i/kT}$

where g_i (degeneracy) = no. of states with energy E_i .

$$N_i/N = F_i = C g_i e^{-E_i/kT}$$

The normalization condition, $\sum N_i = N$ or $\sum F_i = 1$

tells us that $A/N = C = (\sum g_i e^{-E_i/kT})^{-1} = (\text{partition function})^{-1}$

Note that the total energy of the system U is $U = \sum N_i E_i = N \sum F_i E_i$

The average energy per particle is $\langle E \rangle = U/N = \sum F_i E_i$

The heat capacity of the system is $C_V = \frac{U}{T}$ with N, V held constant

b) For a continuous distribution of energies, $dN = A e^{-E(\mathbf{r}, \mathbf{p})/kT} dV dV_p$

where the single particle Hamiltonian $E(\mathbf{r}, \mathbf{p}) = p^2/2m + U(\mathbf{r})$

This is written in vector notation; it is true in any coordinate system, e.g.,

rectangular coordinates x, y, z $dV = dx dy dz$

spherical coordinates r, θ, φ $dV = r^2 \sin \theta dr d\theta d\varphi$

cylindrical coordinates ρ, φ, z $dV = \rho d\rho d\varphi dz$

7. Let us work out some examples of problems concerning the ideal gas with an assumed continuum of allowed energies in spherical coordinates.

a) Find the normalization constant A .

$$\begin{aligned} N &= \int dN = A \int dV e^{-p^2/2mkT} dV_p \\ &= A V 4\pi \int_0^\infty e^{-p^2/2mkT} p^2 dp = AV(2\pi mkT)^{3/2} \\ A &= (N/V) (2\pi mkT)^{-3/2} \end{aligned}$$

b) Find $F(p)$ where $F(p) dp$ is the fraction of particles with absolute value of momentum between p and $p + dp$.

$$\begin{aligned} F(p) dp &= N^{-1} A \iiint dV \iiint dV_p e^{-p^2/2mkT} p^2 dp \sin \theta d\theta d\varphi \\ &= \frac{1}{N} \frac{N}{V} (2\pi mkT)^{-3/2} V 4\pi e^{-p^2/2mkT} p^2 dp \end{aligned}$$

c) Find $F(E)$ where $F(E) dE$ is the fraction of particles with energy between E and $E + dE$:

$$F(E) dE = F(p) dp \quad E = p^2/2m \quad dE = (p/m) dp$$

$$\begin{aligned} F(E) dE &= \frac{4\pi}{(2\pi mkT)^{3/2}} e^{-E/kT} (2mE)^{1/2} m dE \\ &= 2\pi^{-1/2} (kT)^{-3/2} e^{-E/kT} E^{1/2} dE \end{aligned}$$