Marwari college Darbhanga

Subject---physics (Hons)

Class--- B.Sc. part 1 (Hons)

Topic—Thermal physics (Maxwell's distribution law for Energy)

Paper--.2 , Group—A

Lacture series---10

By:- Dr. Sony Kumari

Assistant professor

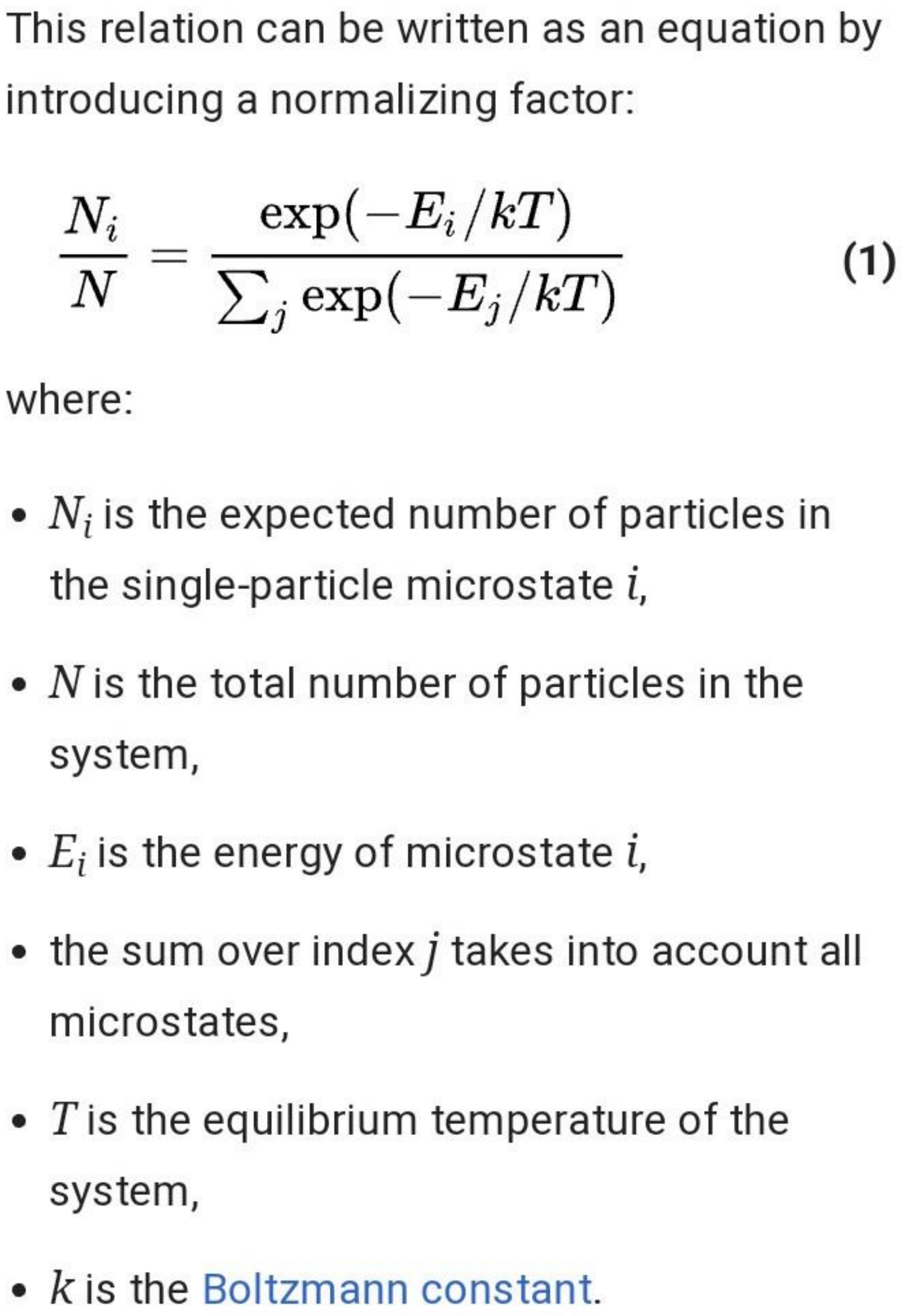
Marwari college Darbhanga

Maxwell's distribution law

Maxwell–Boltzmann statistics gives the average number of particles found in a given single-particle microstate. Under certain assumptions, the logarithm of the fraction of particles in a given microstate is proportional to the ratio of the energy of that state to the temperature of the system:

$$-\log\left(\frac{N_i}{N}\right) \propto \frac{E_i}{T}.$$

The assumptions of this equation are that the particles do not interact, and that they are classical; this means that each particle's state can be considered independently from the other particles' states. Additionally, the particles are assumed to be in thermal equilibrium.



This relation can be written as an equation by introducing a normalizing factor:

$$\frac{N_i}{N} = \frac{\exp(-E_i/kT)}{\sum_j \exp(-E_j/kT)} \qquad (1)$$

where:

- N_i is the expected number of particles in the single-particle microstate i,
- N is the total number of particles in the system,
- E_i is the energy of microstate i,
- the sum over index j takes into account all microstates,
- T is the equilibrium temperature of the system,
- k is the Boltzmann constant.

The denominator in Equation (1) is simply a normalizing factor so that the ratios add up to unity — in other words it is a kind of partition function (for the single-particle system, not the usual partition function of the entire system).

Because velocity and speed are related to energy, Equation (1) can be used to derive relationships between temperature and the speeds of gas particles. All that is needed is to discover the density of microstates in energy, which is determined by dividing up momentum space into equal sized regions.

Distribution for the momentum vector

The potential energy is taken to be zero, so that all energy is in the form of kinetic energy. The relationship between kinetic energy and momentum for massive non-relativisticparticles is

$$E = \frac{p^2}{2m} \tag{2}$$

where p^2 is the square of the momentum vector $\mathbf{p} = [p_x, p_y, p_z]$. We may therefore rewrite Equation (**1**) as:

$$\frac{N_i}{N} = \frac{1}{Z} \exp\left[-\frac{p_{i,x}^2 + p_{i,y}^2 + p_{i,z}^2}{2mkT}\right] \tag{3}$$

where Z is the partition function, corresponding to the denominator in Equation (**1**). Here m is the molecular mass of the gas, T is the thermodynamic temperature and k is the Boltzmann constant. This distribution of $N_i : N$ is proportional to the probability density function $f_\mathbf{p}$ for finding a molecule with these values of momentum components, so:

$$f_\mathbf{p}(p_x, p_y, p_z) \propto \exp\left[-\frac{p_x^2 + p_y^2 + p_z^2}{2mkT}\right] \tag{4}$$

The normalizing constant can be determined by recognizing that the probability of a molecule having *some* momentum must be 1. Integrating the exponential in (**4**) over all p_x, p_y, and p_z yields a factor of

$$\iiint_{-\infty}^{+\infty} \exp\left[-\frac{p_x^2 + p_y^2 + p_z^2}{2mkT}\right] dp_x\, dp_y\, dp_z = (\sqrt{\pi}\sqrt{2mkT})^3$$

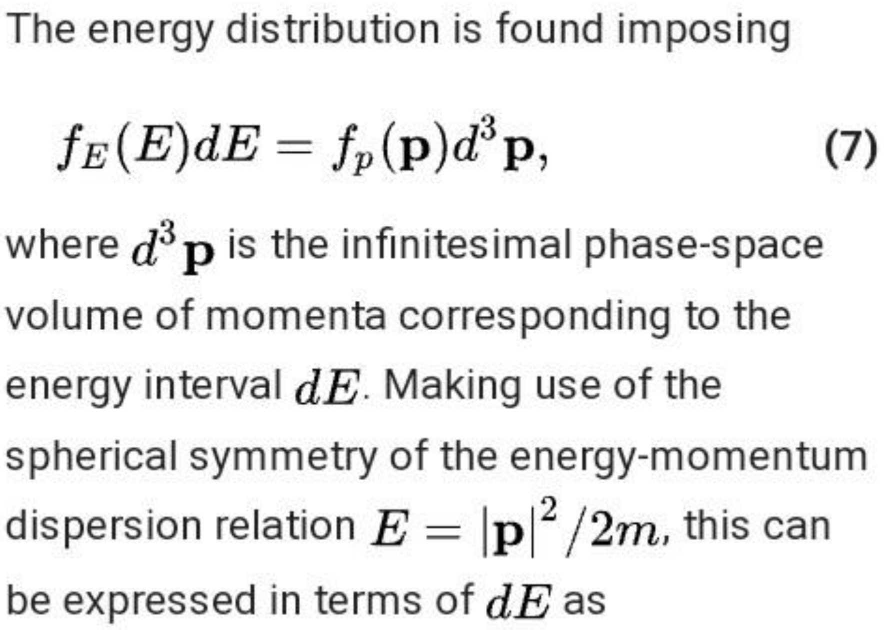
So that the normalized distribution function is:

$$f_{\mathbf{p}}(p_x, p_y, p_z) = (2\pi mkT)^{-3/2} \exp\left[-\frac{p_x^2 + p_y^2 + p_z^2}{2mkT}\right]$$

(6)

The distribution is seen to be the product of three independent normally distributed variables p_x, p_y, and p_z, with variance mkT. Additionally, it can be seen that the magnitude of momentum will be distributed as a Maxwell–Boltzmann distribution, with $a = \sqrt{mkT}$. The Maxwell–Boltzmann distribution for the momentum (or equally for the velocities) can be obtained more fundamentally using the H-theorem at equilibrium within the Kinetic theory of gases framework.

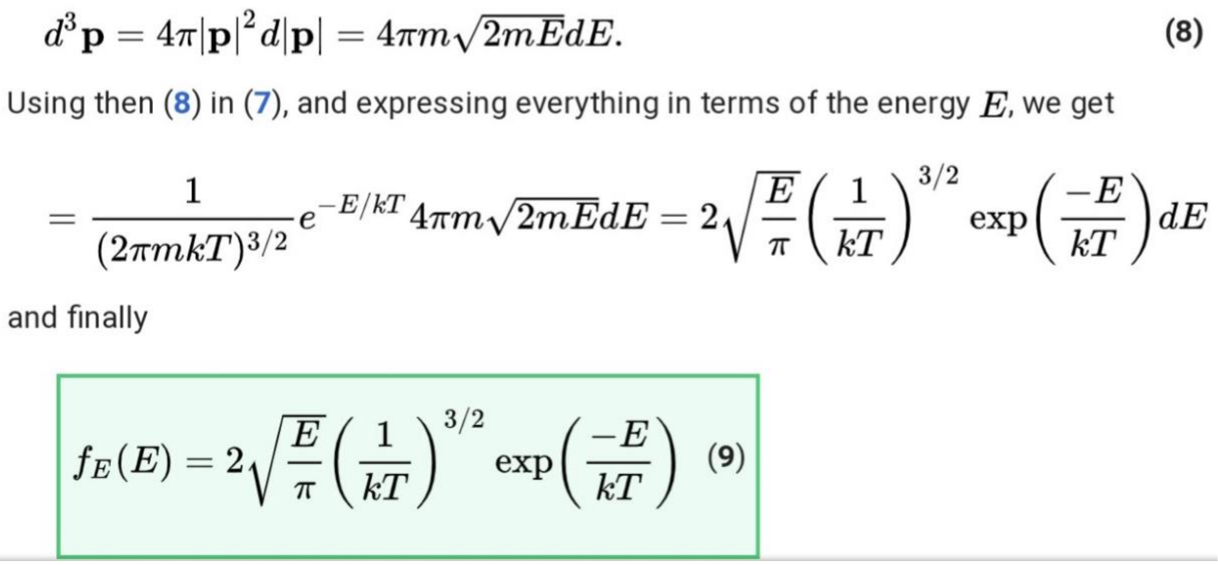
Distribution for Energy



The energy distribution is found imposing

$$f_E(E)dE = f_p(\mathbf{p})d^3\mathbf{p}, \tag{7}$$

where $d^3\mathbf{p}$ is the infinitesimal phase-space volume of momenta corresponding to the energy interval dE. Making use of the spherical symmetry of the energy-momentum dispersion relation $E = |\mathbf{p}|^2/2m$, this can be expressed in terms of dE as



$$d^3\mathbf{p} = 4\pi|\mathbf{p}|^2 d|\mathbf{p}| = 4\pi m\sqrt{2mE}dE. \tag{8}$$

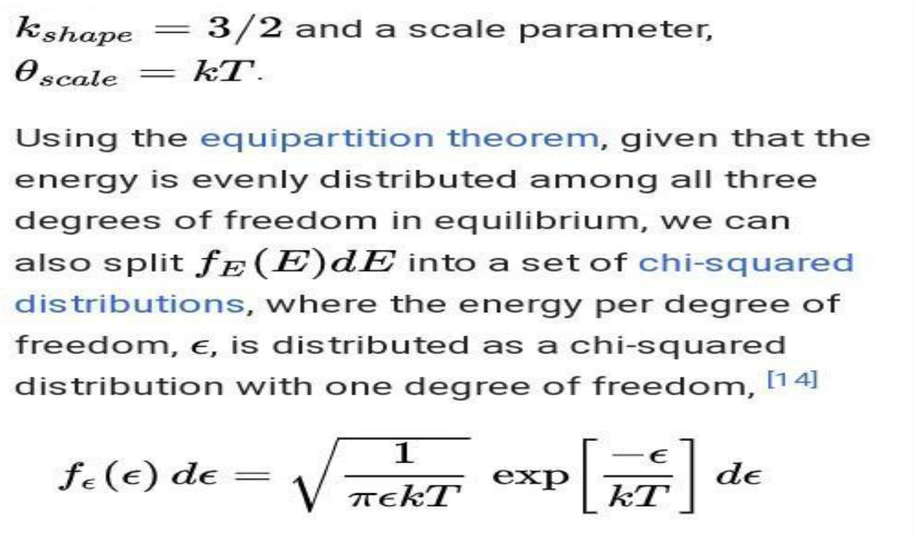
Using then (8) in (7), and expressing everything in terms of the energy E, we get

$$= \frac{1}{(2\pi mkT)^{3/2}} e^{-E/kT} 4\pi m\sqrt{2mE}dE = 2\sqrt{\frac{E}{\pi}}\left(\frac{1}{kT}\right)^{3/2} \exp\left(\frac{-E}{kT}\right)dE$$

and finally

$$\boxed{f_E(E) = 2\sqrt{\frac{E}{\pi}}\left(\frac{1}{kT}\right)^{3/2} \exp\left(\frac{-E}{kT}\right) \quad (9)}$$

Since the energy is proportional to the sum of the squares of the three normally distributed momentum components, this energy distribution can be written equivalently as a gamma distribution, using a shape parameter,



$k_{shape} = 3/2$ and a scale parameter,
$\theta_{scale} = kT$.

Using the equipartition theorem, given that the energy is evenly distributed among all three degrees of freedom in equilibrium, we can also split $f_E(E)dE$ into a set of chi-squared distributions, where the energy per degree of freedom, ϵ, is distributed as a chi-squared distribution with one degree of freedom,[14]

$$f_\epsilon(\epsilon)\,d\epsilon = \sqrt{\frac{1}{\pi\epsilon kT}}\ \exp\left[\frac{-\epsilon}{kT}\right] d\epsilon$$

At equilibrium, this distribution will hold true for any number of degrees of freedom. For example, if the particles are rigid mass dipoles of fixed dipole moment, they will have three translational degrees of freedom and two additional rotational degrees of freedom. The energy in each degree of freedom will be described according to the above chi-squared distribution with one degree of freedom, and the total energy will be distributed according to a chi-squared distribution with five degrees of freedom. This has implications in the theory of the specific heat of a gas.

The Maxwell–Boltzmann distribution can also be obtained by considering the gas to be a type of quantum gas for which the approximation $\varepsilon >> kT$ may be made.