# Maxwell-Boltzmann Distribution
# (Thermal Physics)

## e-content for B.Sc Physics
## (General and Subsidiary Course)

## B.Sc Part-I
Paper-I

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## Maxwell-Boltzmann Distribution

The Probability Distribution function for an ideal (classical) gas is called the Maxwell-Boltzmann distribution function. It specifies the probability that a single gas particle from a large distribution of particles in equilibrium at some temperature T has a speed v or a momentum p or a kinetic energy E.

## There are many ways to derive the Maxwell-Boltzmann (M-B) Distribution Law:

- Calculate the number of particles with velocities between v and v+dv as a function of energy E. Maxwell velocity distribution results.

- Enumerate all possible ways that N particles can be distributed in energy. Use variational calculus to find the distribution law (number of particles vs. energy) that maximizes the system weight W. The M-B Distribution results (see Appendix GG).

- Maximize the Entropy $S=k_B \ln W$. The M-B Law results.

- Use microscopic reversibility arguments.

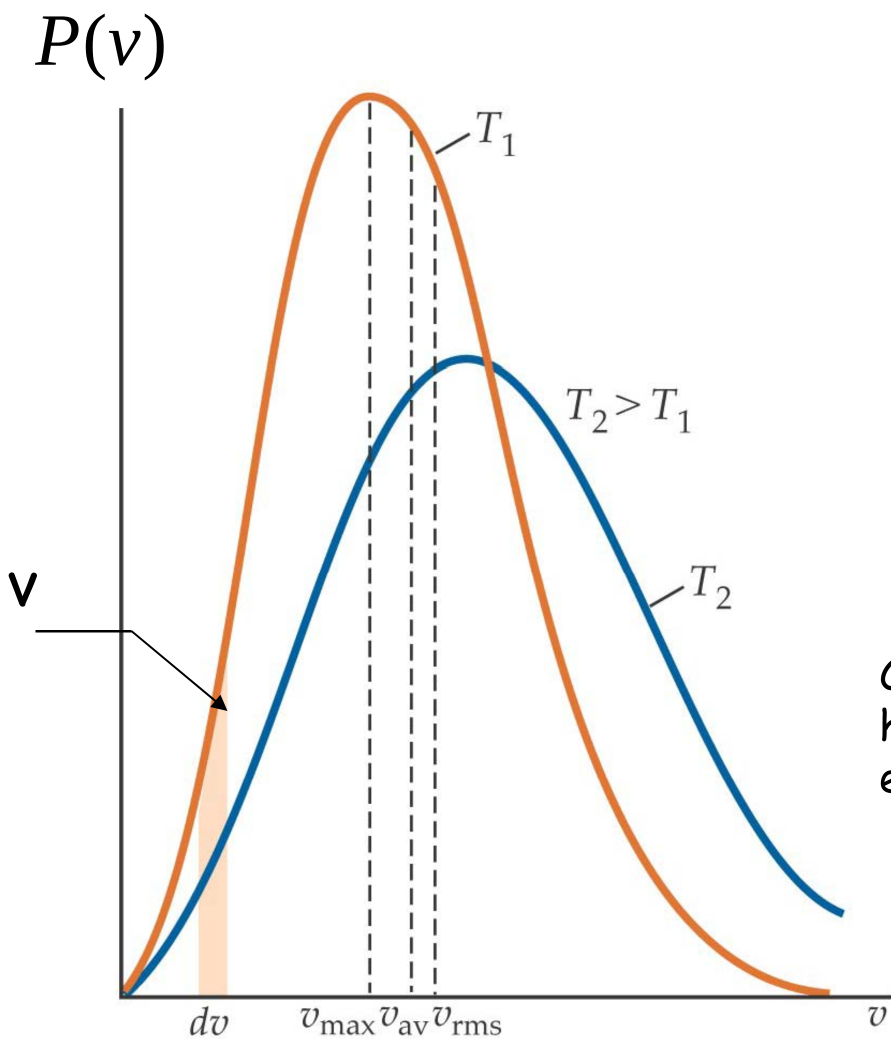
# The Distribution of Molecular Speeds in a Gas

first derived by J.C. Maxwell in 1852

$$P(v)dv = \frac{4}{\sqrt{\pi}}\left(\frac{m}{2k_BT}\right)^{3/2} \underbrace{v^2}_{} \, e^{\underbrace{-mv^2/2k_BT}_{}} dv = \frac{n(v)}{N} dv$$

- Normalized
- $v \equiv \sqrt{v_x^2 + v_y^2 + v_z^2}$
- Probability that molecule has speed v $\propto e^{-mv^2/2k_BT}$
- Number of molecules with speed v $\propto v^2$
- Note that P(v) is a continuous probability distribution function
- Note that only $v^2$ appears, not the components of velocity
- Connects macroscopic Thermodynamic properties with microscopic models

# Maxwell Speed Distribution Function




Shaded area represents probability that molecule will have a speed v ± dv/2

Note asymmetry – there are more ways to get a large speed than a small one.

The inherent asymmetry gives rise to different values for $v_{max}$, $v_{av}$, and $v_{rms}$.

Check out: http://www.chm.davidson.edu/ChemistryApplets/KineticMolecularTheory/Maxwell.html

# The Average Speed

$$v_{avg} \equiv \int_0^\infty v\, P(v)dv = \frac{4}{\sqrt{\pi}}\left(\frac{m}{2k_BT}\right)^{3/2}\int_0^\infty v^3 e^{-mv^2/2k_BT}dv$$

$$\int_0^\infty x^{2n+1}e^{-ax^2}dx = \frac{n!}{2a^{n+1}}; \quad n=1;\, a=\frac{m}{2k_BT}$$

$$v_{avg} = \sqrt{\frac{8k_BT}{\pi m}}$$ (mean speed)

On earth, T=300K, atmosphere is mostly $N_2$. Mass of $N_2$ molecule is $4.7\times10^{-26}$ kg. What is $v_{avg}$?

$$v_{avg} = \sqrt{\frac{8k_BT}{\pi m}} = \sqrt{\frac{8(1.38\times10^{-23})(300)}{3.14(4.7\times10^{-26})}} = 474\, m/s$$

# Most Probable Speed

$$v_{most\ probable} \Rightarrow \frac{dP(v)}{dv} = 0$$

$$2ve^{-mv^2/2k_BT} + v^2\left(-\frac{2mv}{2k_BT}\right)e^{-mv^2/2k_BT} = 0$$

$$v^2 = \frac{2k_BT}{m}$$

$$v_{most\ probable} = \sqrt{\frac{2k_BT}{m}}$$

# Square Root of the Mean Squared Speed

$$(v_{avg})^2 \equiv \int_0^\infty v^2\, P(v)\, dv = \frac{4}{\sqrt{\pi}}\left(\frac{m}{2k_BT}\right)^{3/2}\int_0^\infty v^4 e^{-mv^2/2k_BT}\, dv$$

$$\int_0^\infty x^{2n} e^{-ax^2}\, dx = \frac{1\cdot 3\cdot 5\cdots(2n-1)}{2^{n+1}a^n}\sqrt{\frac{\pi}{a}}; \quad n=2;\, a=\frac{m}{2k_BT}$$

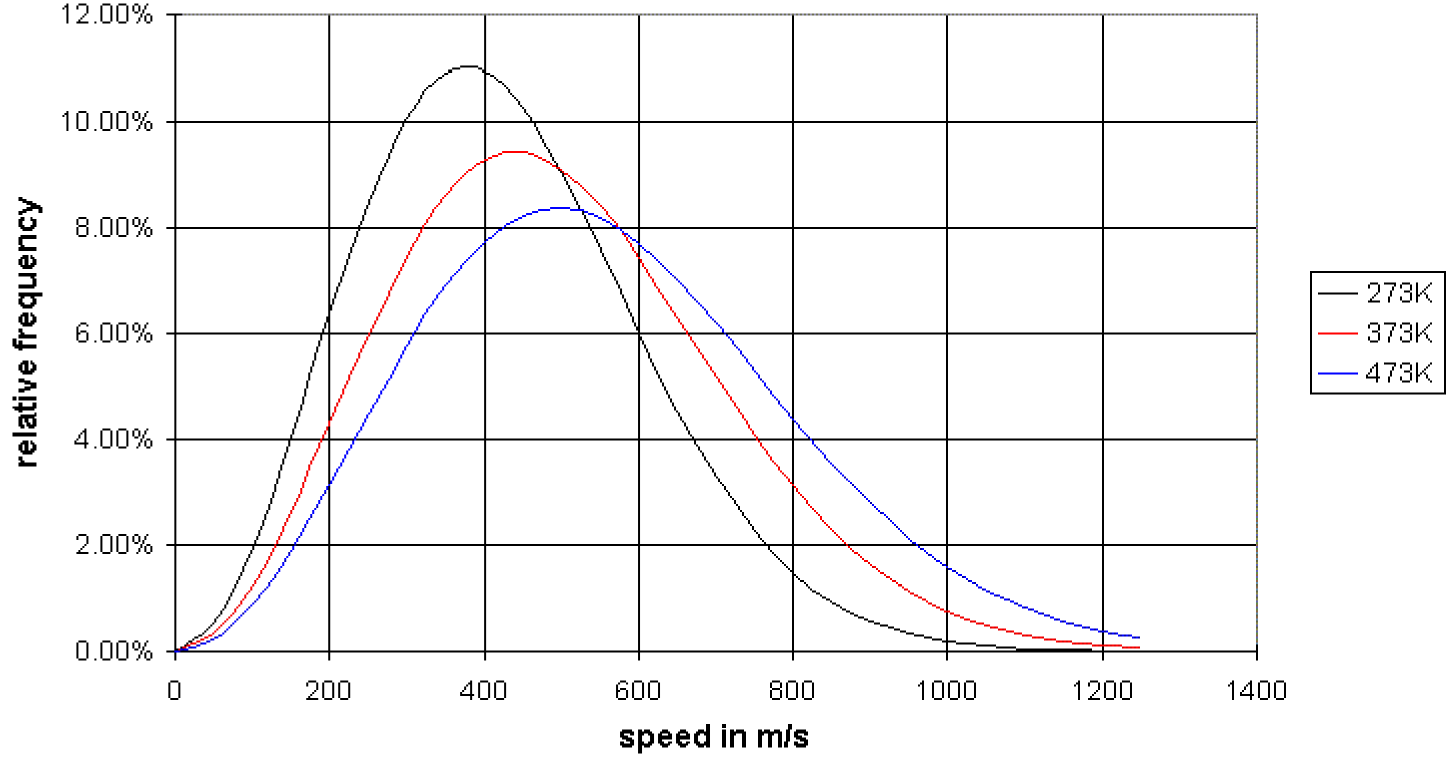
$$(v_{avg})^2 = \frac{3k_BT}{m}$$

$$v_{rms} = \sqrt{(v_{avg})^2} = \sqrt{\frac{3k_BT}{m}}$$

$$\frac{1}{2}mv_{rms}^2 = \frac{1}{2}m\cdot\frac{3k_BT}{m} = \frac{3}{2}k_BT$$

(equipartition theorem)

# Maxwell Boltzmann Speed Distribution for different T




$N_2$ molecule

## What is the probability that a gas atom with mass m has a momentum between p and p+dp at temperature T?

$$P(v)dv = \frac{4}{\sqrt{\pi}}\left(\frac{m}{2k_B T}\right)^{3/2} v^2 e^{-mv^2/2k_BT}dv = 4\pi v^2\left(\frac{m}{2\pi k_B T}\right)^{3/2} e^{-mv^2/2k_BT}dv$$

$$\frac{1}{2}mv^2 = \frac{p^2}{2m} \quad \Rightarrow \quad mvdv = \frac{pdp}{m} \quad \Rightarrow \quad dv = \frac{1}{mv}\frac{pdp}{m} = \frac{dp}{m}$$

$$= \frac{4\pi m^2 v^2}{m^2}\left(\frac{m}{2\pi k_B T}\right)^{3/2} e^{-p^2/2mk_BT}\frac{dp}{m}$$

$$= \frac{4\pi p^2}{m^3}\left(\frac{m}{2\pi k_B T}\right)^{3/2} e^{-p^2/2mk_BT}dp = 4\pi p^2\left(\frac{1}{m^2}\frac{m}{2\pi k_B T}\right)^{3/2} e^{-p^2/2mk_BT}dp$$

$$P(p)dp \equiv \frac{4\pi p^2}{(2\pi m k_B T)^{3/2}} e^{-p^2/2mk_BT}dp \equiv \frac{n(p)}{N}dp$$

# What is the probability that a gas atom with mass m has an energy between E and E+dE at temperature T?

Change Variables:

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

$$p^2 = 2mE$$

$$2p\,dp = 2m\,dE$$

$$p^2 dp = p \cdot p dp = \sqrt{2mE} \cdot m dE$$

$$= \frac{1}{2}(2m)^{3/2} E^{1/2} dE$$

$$\frac{n(p)}{N} dp = \frac{4\pi p^2}{(2\pi m k_B T)^{3/2}} e^{-p^2/2mk_BT} dp$$

$$= \frac{4\pi}{(2\pi m k_B T)^{3/2}} e^{-p^2/2mk_BT} p^2 dp$$

$$= \frac{4\pi}{(2\pi m k_B T)^{3/2}} e^{-E/k_BT} \cdot \frac{1}{2}(2m)^{3/2} E^{1/2} dE$$

$$P(E)dE \equiv \frac{n(E)}{N} dE = \frac{2}{\sqrt{\pi}} \frac{E^{1/2}}{(k_B T)^{3/2}} e^{-E/k_BT} dE$$

# What is the Average Energy of Gas Atom at Temperature T?

$$E_{avg} = \int_0^\infty E \times P(E)dE = \frac{2}{\sqrt{\pi}} \int_0^\infty E \frac{E^{1/2}}{(k_B T)^{3/2}} e^{-E/k_B T} dE$$

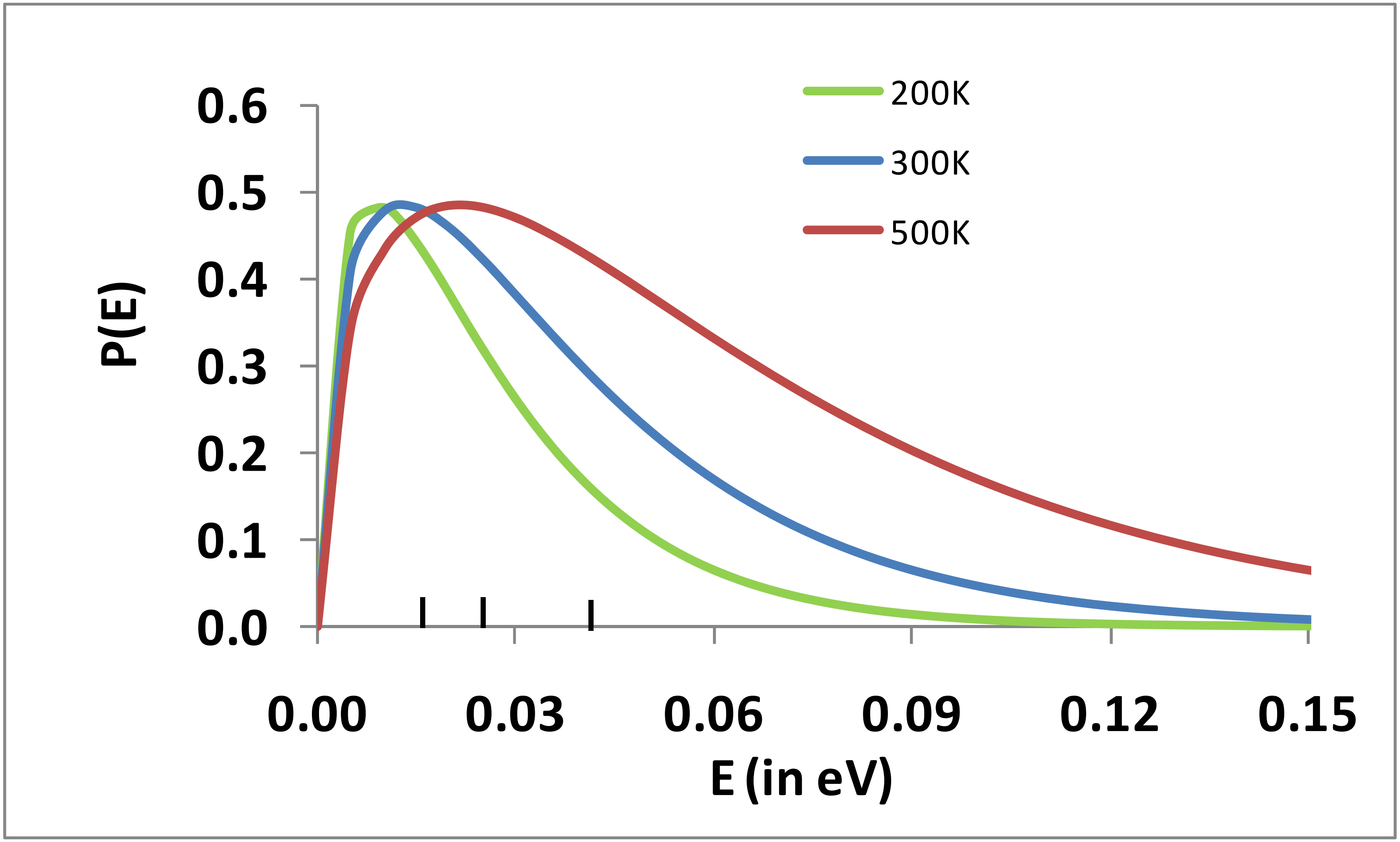
$$= \frac{2}{\sqrt{\pi}} \frac{1}{(k_B T)^{3/2}} \int_0^\infty E^{3/2} e^{-E/k_B T} dE$$

$$a = \frac{1}{k_B T} \quad \Rightarrow \int_0^\infty E^{3/2} e^{-E/k_B T} dE = \int_0^\infty E^n e^{-aE} dE; \quad n = 3/2$$

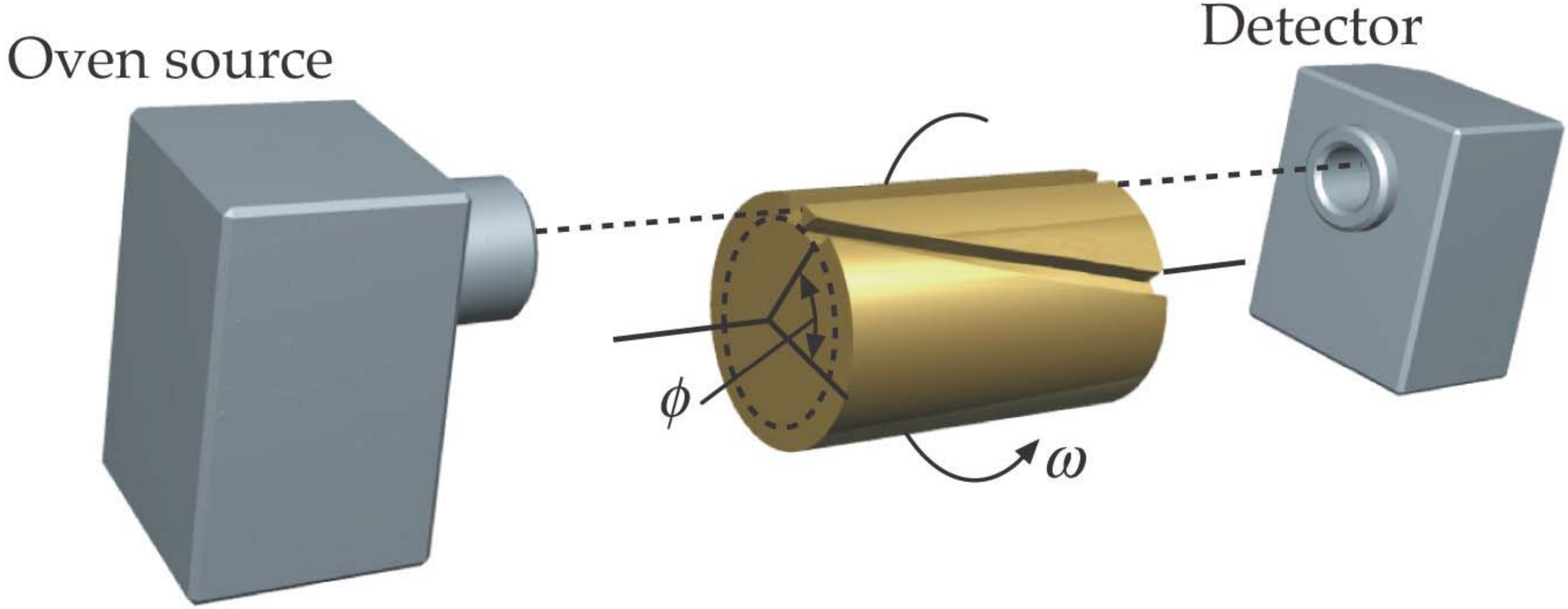
$$= \frac{\Gamma(n+1)}{a^{n+1}} = \frac{3\sqrt{\pi}}{4} \frac{1}{\left[ 1/k_B T \right]^{5/2}} = \frac{3\sqrt{\pi}}{4} (k_B T)^{5/2}$$

$$E_{avg} = \frac{2}{\sqrt{\pi}} \frac{1}{(k_B T)^{3/2}} \frac{3\sqrt{\pi}}{4} (k_B T)^{5/2} = \frac{6}{4} k_B T = \frac{3}{2} k_B T$$

## Probability of finding gas atom with energy between E and E+dE



# Experimental Verification of Maxwellian Distribution Function




## APPLICATION

The Maxwell speed distribution serves as the basic input for computer calculations of molecular dynamic (MD) simulations of gas flow, gas cooling, gas heating, flames, etc.

## Summary

Velocity distribution

$$P(v)dv = \frac{n(v)}{N}dv = \frac{4}{\sqrt{\pi}}\left(\frac{m}{2k_BT}\right)^{3/2} v^2 \, e^{-mv^2/2k_BT} dv$$

Momentum distribution

$$P(p)dp = \frac{n(p)}{N}dp = \frac{4\pi p^2}{\left(2\pi m k_B T\right)^{3/2}} e^{-p^2/2mk_BT} dp$$

Energy distribution

$$P(E)dE = \frac{n(E)}{N}dE = \frac{2}{\sqrt{\pi}} \frac{E^{1/2}}{\left(k_B T\right)^{3/2}} e^{-E/k_BT} dE$$