PH-107

Quantum Physics and Applications

Elements of Statistical Physics-III

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Recap

We are interested in determining the number of particles ***dN(E)*** in the system with energy between ***E*** and ***E+dE***.

$$N(E)\;dE = g(E)\;f(E)\;dE$$

$N(E)\;dE$ Number of particles per unit volume in the energy range *E* and *E+dE.*

$g(E)\;dE$ Density of states (number of energy states per unit volume) in the energy range *E* and *E+dE.*

$f(E)$ Probability Distribution function: Dependence on Particle Characteristics

Classical Particles and Quantum (Bosons and Fermions) Particles

Recap

We need to optimise $Q(\{N_i\})$ with two constraints

$$\sum_{i=1}^{\infty} N_i = N \quad \text{and} \quad \sum_{i=1}^{\infty} E_i N_i = E$$

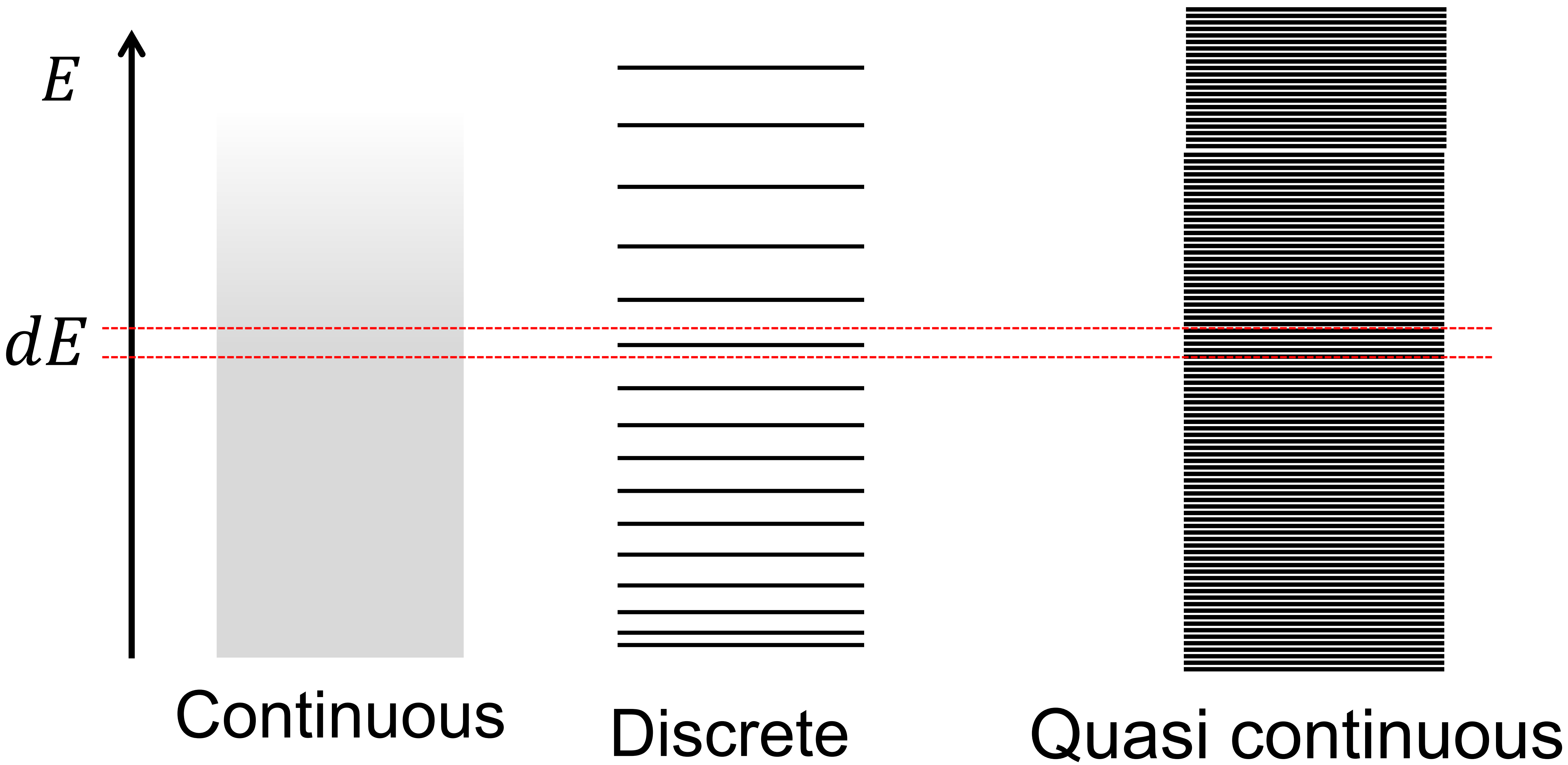
$$f_{\mathrm{MB}}(E) = A\, e^{-\frac{E}{k_B T}}$$

$$f_{\mathrm{FD}}(E) = \frac{1}{1 + e^{(E-E_F)/k_B T}}$$

$$f_{\mathrm{BE}}(E) = \frac{1}{e^{(E/k_B T)} - 1}$$

Density of State

Energy Spectrum



$g(E)dE$: No. of states in the interval dE (about E)

Density of State

Calculation of *g*(*E*): Infinite 3D Box

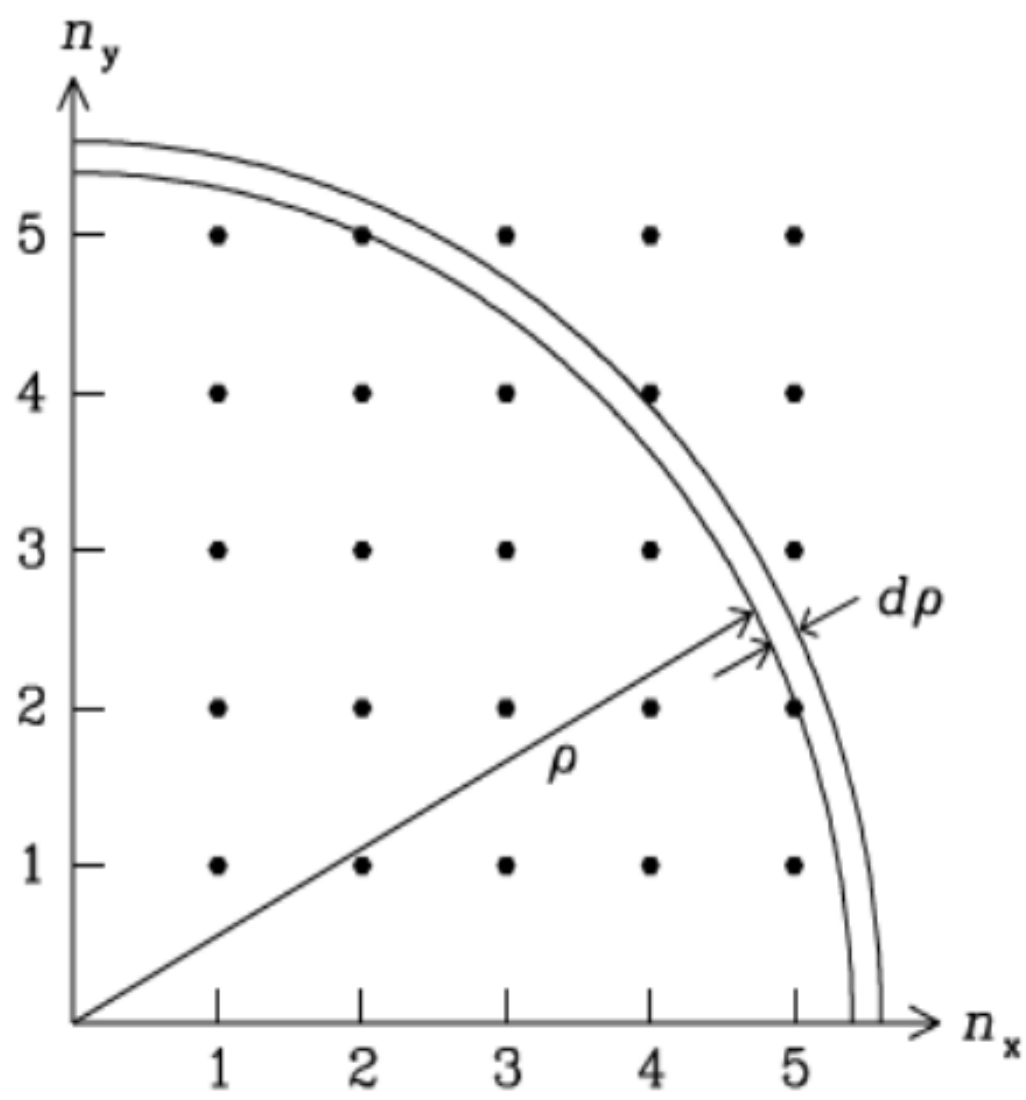
$$E = \frac{\pi^2 \hbar^2}{2mL^2}(n_x^2 + n_y^2 + n_z^2)$$

Note that we can label the states as (n_x, n_y, n_z) and arrange them in a (imaginary) 3D space defined by the axes, n_x, n_y, and n_z.

Density of State

Integer Space

This is how we invoke the concept of a integer space (space defined by axes, n_x, n_y, and n_z)



$$\rho_{2\mathrm{D}} = \sqrt{n_x^2 + n_y^2}$$

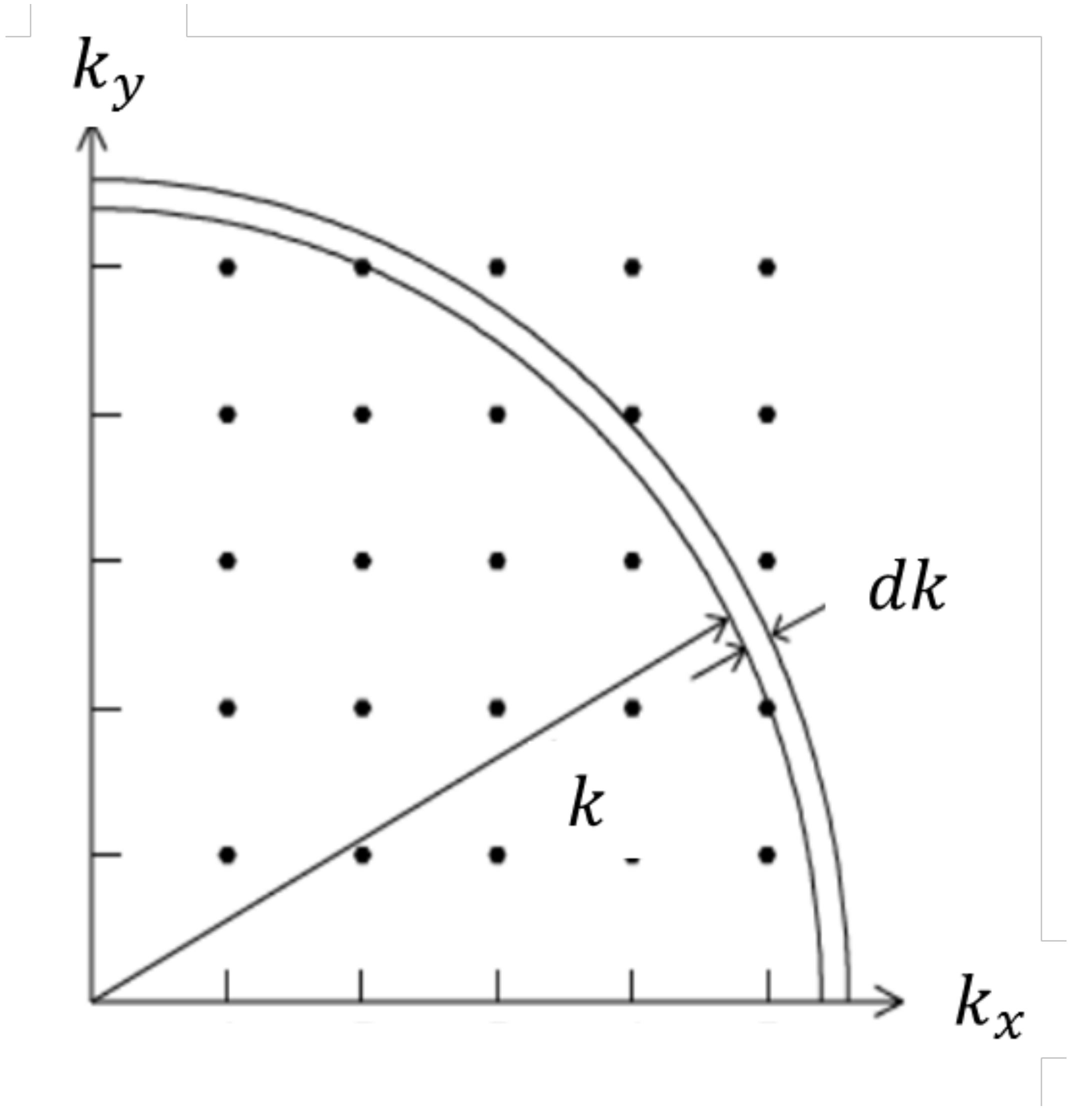
$$\rho_{3\mathrm{D}} = \sqrt{n_x^2 + n_y^2 + n_z^2}$$

All states which lie within the shell of thickness dρ about ρ are being assigned the energy

$$E = \frac{\pi^2 \hbar^2}{2mL^2} \rho^2$$

Density of State

Since $n_{x,y,z} = \dfrac{k_{x,y,z}\ L}{\pi}$, we could define an equivalent space with axes $k_x = \dfrac{n_x\pi}{L}, k_y = \dfrac{n_y\pi}{L}$, and $k_z = \dfrac{n_z\pi}{L}$

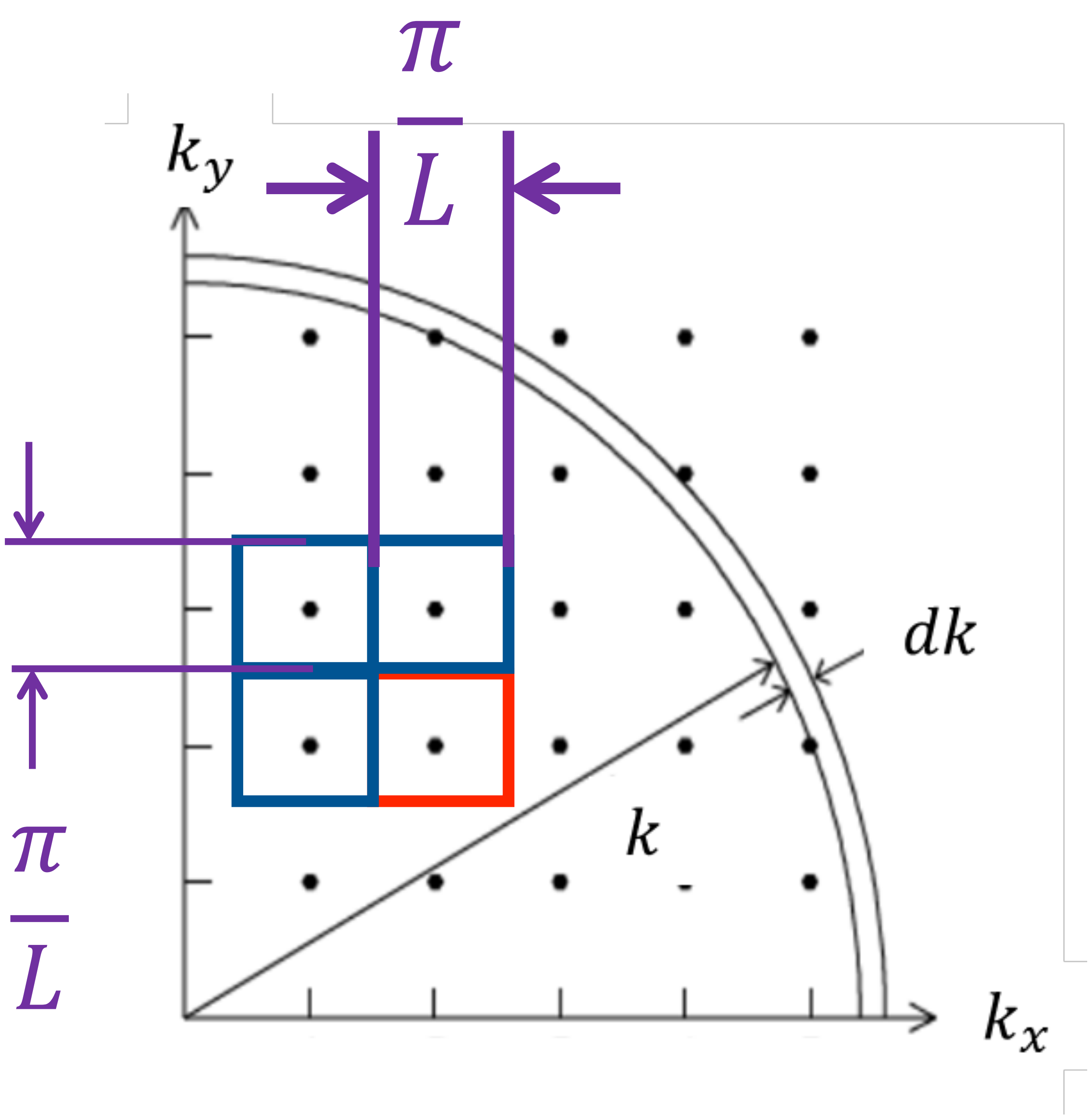


$$k_{2\mathrm{D}} = \sqrt{k_x^2 + k_y^2}$$

$$k_{3\mathrm{D}} = \sqrt{k_x^2 + k_y^2 + k_z^2}$$

Density of State

What is the area (volume) of the 2D (3D) k-space occupied by each point ?



This area is $\Delta k_x \times \Delta k_y = \left(\frac{\pi}{L}\right)^2$

In 3D, this volume is $\left(\frac{\pi}{L}\right)^3$

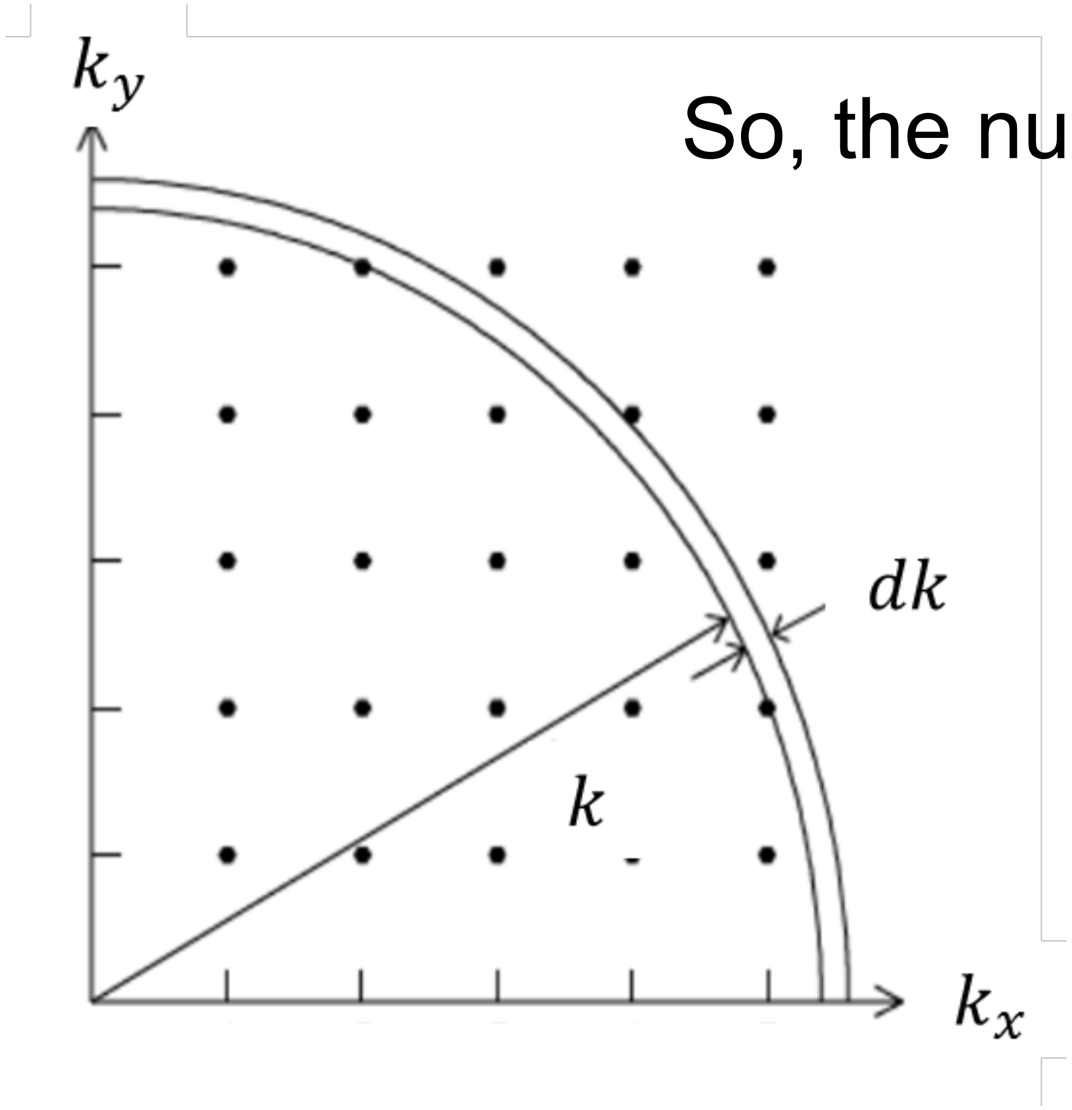
So, the density of points in the k-space is 1 state per $\left(\frac{\pi}{L}\right)^2$ area

or 1 state per $\left(\frac{\pi}{L}\right)^3$ volume

Density of State

We get the density of states in the k space, *F*(*k*), as

$$F(k) = \frac{1}{\left(\frac{\pi}{L}\right)^3} = \frac{V}{\pi^3}$$



So, the number of states in the octant of the shell is

$$F(k)\ d\mathbf{k} = \frac{V}{\pi^3}\left(\frac{1}{8}\right)\ 4\pi k^2\ dk$$

Here $\quad d\mathbf{k} = dk_x dk_y dk_z$

Density of State

Reciprocal Space

But the number of states between ***k*** and ***k***+*d**k*** should be the same as the number of states between *E* and *E*+*dE*.

So,
$$F(k)d\mathbf{k} = G(E)dE$$

i.e.,
$$F(k)d\mathbf{k} = \left(\frac{L}{\pi}\right)^3 d\mathbf{k} = G(E)dE$$

This implies
$$\frac{F(k)d\mathbf{k}}{L^3} = \frac{F(k)d\mathbf{k}}{V} = \left(\frac{1}{\pi}\right)^3 d\mathbf{k} = \frac{G(E)}{V}dE = g(E)dE$$

i.e.,
$$f(k)d\mathbf{k} = \frac{1}{\pi^3}\left(\frac{1}{8}\right)4\pi k^2 dk = g(E)dE$$

Density of State

Reciprocal Space

Now, let us recall $E = \dfrac{\hbar^2 k^2}{2m}$

And make use of it in

$$\frac{1}{\pi^3}\left(\frac{1}{8}\right)4\pi k^2 dk = g(E)dE$$

to get the expression for the density of states in terms of energy as

$$g(E) = \frac{1}{4\pi^2}\left(\frac{2m}{\hbar^2}\right)^{\frac{3}{2}}\sqrt{E}$$

Density of State

Reciprocal Space

If there are other degeneracies of each k-state (for example the spin-degeneracy of Fermions), we need to multiply $g(E)$ with the degeneracy factor, (let's say) λ.

So,

$$g(E) = \boxed{\lambda} \times \frac{1}{4\pi^2}\left(\frac{2m}{\hbar^2}\right)^{\frac{3}{2}}\sqrt{E}$$

So, in case of electrons (Fermions) bound to the 3D potential well, we have

$$g(E) = \frac{1}{2\pi^2}\left(\frac{2m}{\hbar^2}\right)^{\frac{3}{2}}\sqrt{E}$$

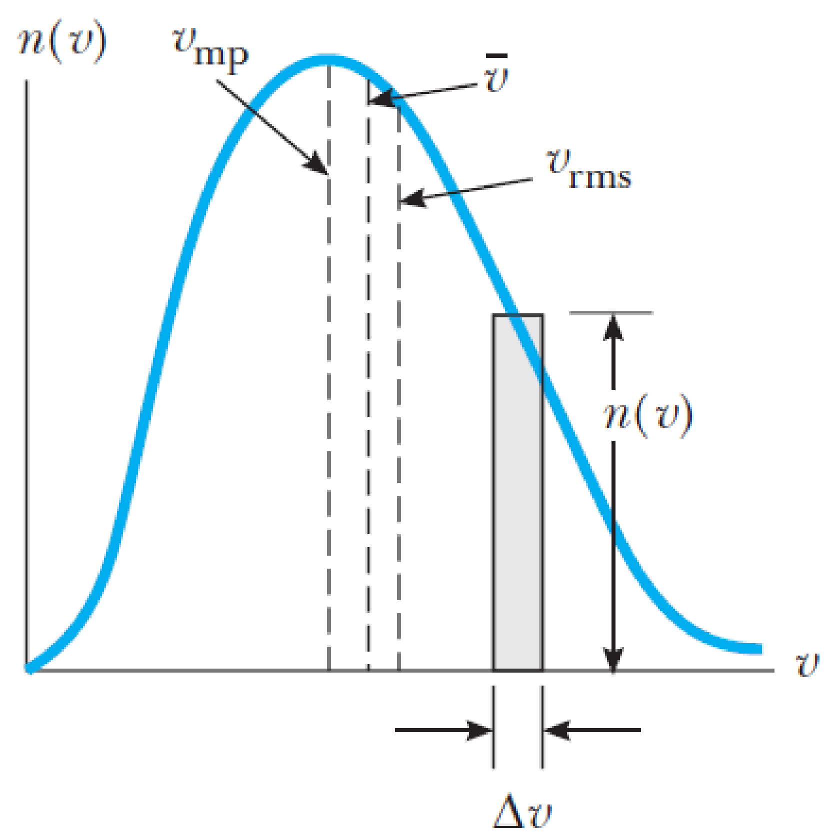
Application of M-B Distribution

Maxwell-Boltzmann Distribution

Maxwell speed distribution function for gas molecules at thermal equilibrium at temperature T

$$n(v)\ dv = \frac{4\pi N}{V}\left(\frac{m}{2\pi k_B T}\right)^{\frac{3}{2}} v^2 e^{-\frac{mv^2}{2k_B T}}\ dv$$

Here, $n(v)\ dv$ is the number of (ideal) gas molecules (of mass *m*) ***per unit volume*** with speed between v and $v + dv$.



M-B Distribution

We know $n(E)\ dE = g(E)\ f(E)\ dE$

In the present case: $f_{\mathrm{MB}}(E) = A\ e^{-\frac{E}{k_B T}}$

Also, we know $E = \frac{1}{2}mv^2$

So, every *v* corresponds to unique *E*

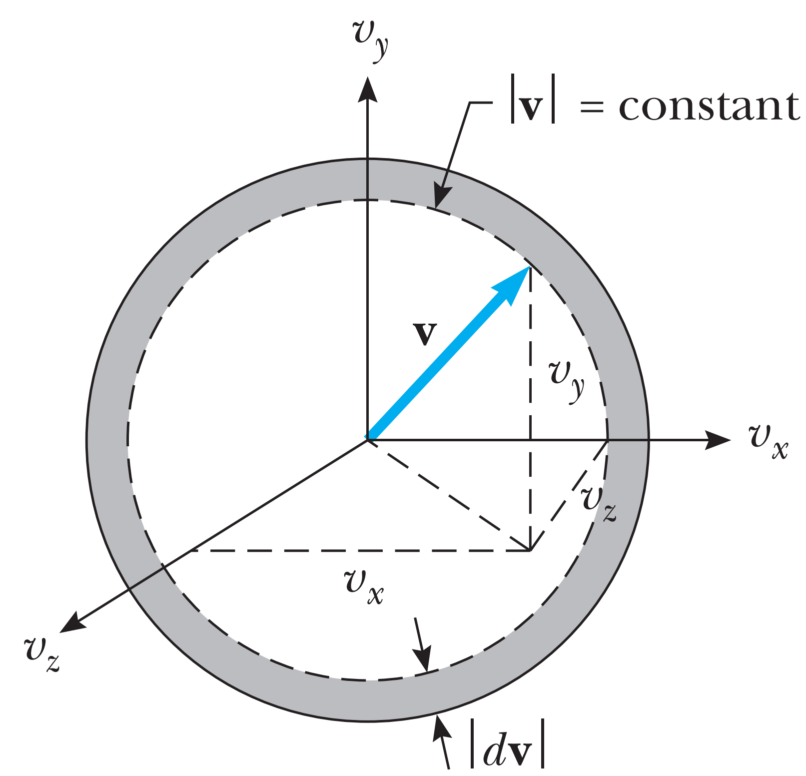
and therefore, $g(E)\ dE = g(v)\ dv$

Density of states in the energy interval *E* and E+*dE*

Density of states in the velocity interval *v* and *v*+*dv*

So, let us estimate number of states with velocity between *v* and *v*+*dv*

M-B Distribution



$g(v)\ dv \propto$ Volume of the spherical shell between *v* and *v*+*dv*

$$g(v)\ dv = \underbrace{C}_{\text{constant}}4\pi v^2\ dv$$

$$n(E)\ dE = n(v)\ dv = g(v)\ Ae^{-\frac{mv^2}{2k_BT}}\ dv$$

$$= A'4\pi v^2\ e^{-\frac{mv^2}{2k_BT}}\ dv$$

$$A' = AC$$

Total number of particles per unit volume = $\dfrac{N}{V}$

M-B Distribution

Total number of particles per unit volume = $\dfrac{N}{V}$

$$\frac{N}{V} = \int_0^{\infty} n(v)\ dv = 4\pi A' \int_0^{\infty} v^2\ e^{-\frac{mv^2}{2k_B T}}\ dv$$

$$\boxed{\int_0^{\infty} v^2\ e^{-\frac{mv^2}{2k_B T}}\ dv = \frac{\sqrt{\pi}}{4}\left(\frac{m}{2k_B T}\right)^{-3/2}}$$

$$A' = \left(\frac{N}{V}\right)\left(\frac{m}{2\pi k_B T}\right)^{3/2}$$

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

Maxwell Boltzmann speed distribution for gas molecules in thermal equilibrium at temperature *T*.

M-B Distribution

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

No. of gas molecules per unit volume having velocity in *v* and *v*+*dv*

Total number of molecules per unit volume

$$\frac{n(v)}{N/V} = 4\pi \left(\frac{m}{2\pi k_B T}\right)^{3/2} \ v^2\ e^{-\frac{mv^2}{2k_B T}} = f_{\mathrm{MB}}(v)$$

Maxwell-Boltzmann speed distribution

Fraction of molecules having velocity in *v* and *v*+*dv*

M-B Distribution

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

Average speed

$$\bar{v} = \frac{\int_0^\infty v\ n(v)\ dv}{\int_0^\infty n(v)\ dv} = \frac{\int_0^\infty v\ n(v)\ dv}{N/V} = 4\pi \left(\frac{m}{2\pi k_B T}\right)^{3/2} \int_0^\infty v^3\ e^{-\frac{mv^2}{2k_BT}} dv$$

$$\boxed{\int_0^\infty v^3\ e^{-\frac{mv^2}{2k_BT}} dv = \frac{1}{2}\left(\frac{m}{2k_B T}\right)^{-2}}$$

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

M-B Distribution

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

Mean square speed

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

$$\boxed{\int_0^\infty v^4\ e^{-\frac{mv^2}{2k_BT}} dv = \frac{3\sqrt{\pi}}{8} \left(\frac{m}{2k_BT}\right)^{-5/2}}$$

Root mean square speed

$$v_{\mathrm{rms}} = \sqrt{\langle v^2 \rangle} = \sqrt{\frac{3k_BT}{m}}$$

M-B Distribution

Most probable speed

We know

$$f_{\mathrm{MB}}(v) = 4\pi \left(\frac{m}{2\pi k_B T} \right)^{3/2} \; v^2 \; e^{-\frac{mv^2}{2k_B T}}$$

Let us differentiate this wrt *v*

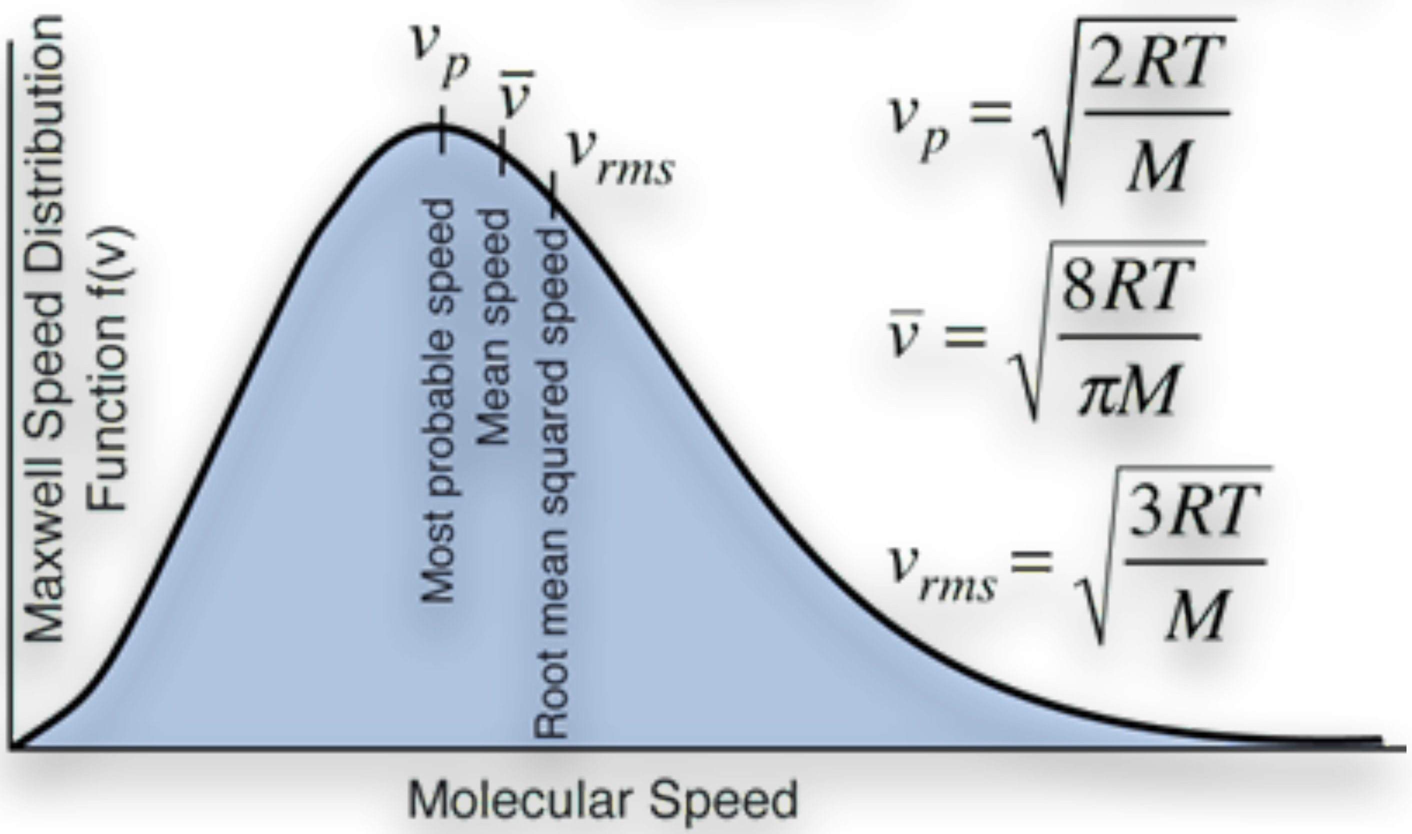
$$\frac{f_{\mathrm{MB}}(v)}{dv} = 4\pi \left(\frac{m}{2\pi k_B T} \right)^{3/2} \; \left(2v - 2v^3 \frac{m}{2k_B T} \right) \; e^{-\frac{mv^2}{2k_B T}} \quad = 0$$

$$v^2 = \frac{2k_B T}{m} \qquad v_{\mathrm{mp}} = \sqrt{\frac{2k_B T}{m}}$$

$$v_{\mathrm{rms}} > \bar{v} > v_{\mathrm{mp}} \Longrightarrow \sqrt{3} > \sqrt{8/\pi} > \sqrt{2}$$

From Kinetic Theory of Gases

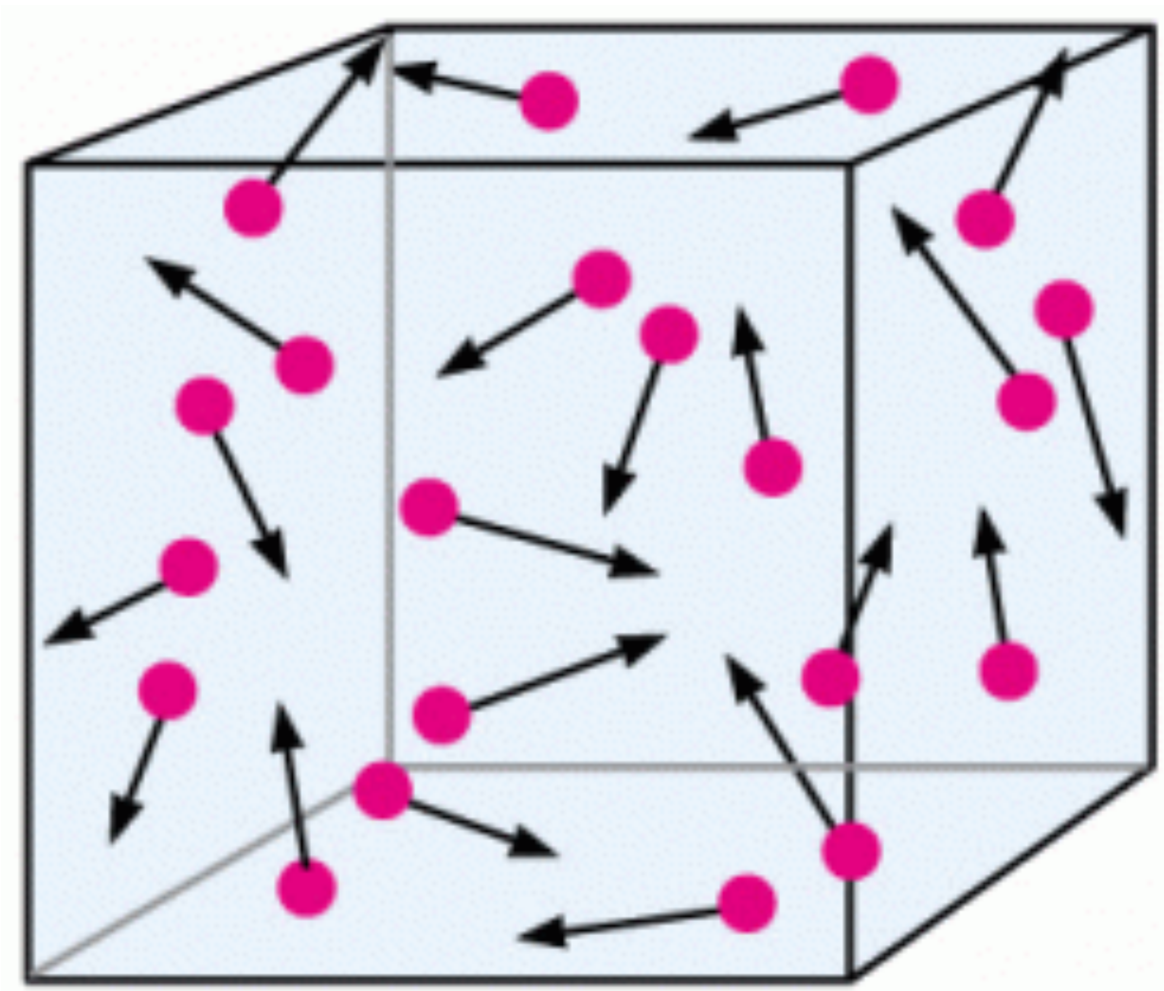
$$f(v) = 4\pi \left[\frac{M}{2\pi RT}\right]^{\frac{3}{2}} v^2 \exp\left[\frac{-Mv^2}{2RT}\right]$$



$$v_p = \sqrt{\frac{2RT}{M}}$$

$$\bar{v} = \sqrt{\frac{8RT}{\pi M}}$$

$$v_{rms} = \sqrt{\frac{3RT}{M}}$$



M-B Distribution

Average Kinetic Energy

Kinetic Energy = $\frac{1}{2}mv^2$

Average Kinetic Energy = $\langle K \rangle = \frac{1}{2}m\langle v^2 \rangle$

Mean square speed

$$\bar{v}^2 = \langle v^2 \rangle = \frac{3k_B T}{m}$$

$$\langle K \rangle = \frac{3}{2}k_B T$$

This is the statement of equipartition theorem

A classical molecule in thermal equilibrium at temperature T has an average energy of $k_B T/2$ for each degree of freedom.

Show that standard deviation of the molecular speeds is given by

$$\sigma_v = \sqrt{3 - \frac{8}{\pi}} \cdot \sqrt{\frac{k_\mathrm{B} T}{m}}$$

Recommended Readings

Statistical Physics, Chapter 10