PHY101

Lecture 37

- You'll remember that we started out our analysis of pressure and temperature in the kinetic theory by looking at a single particle velocity v.

- We then generalised this result to a large number of particles by taking either the mean velocity $\langle v \rangle$ or more commonly the root-mean-square velocity $\langle v^2 \rangle^{1/2}$, which prevents the direction (either + vs – for v_x or the direction in 3D space for a true vector v) from making our result zero.

- The use of this average masks the actual behaviour of the particles in the gas, and it's easy to think that they all travel at the average velocity, but this is absolutely not the case! The particles in the gas have a wide range of velocities from near zero to several times the average.

  So a good logical question is:

  Suppose I pick a particle at random in my gas, what is its velocity likely to be?

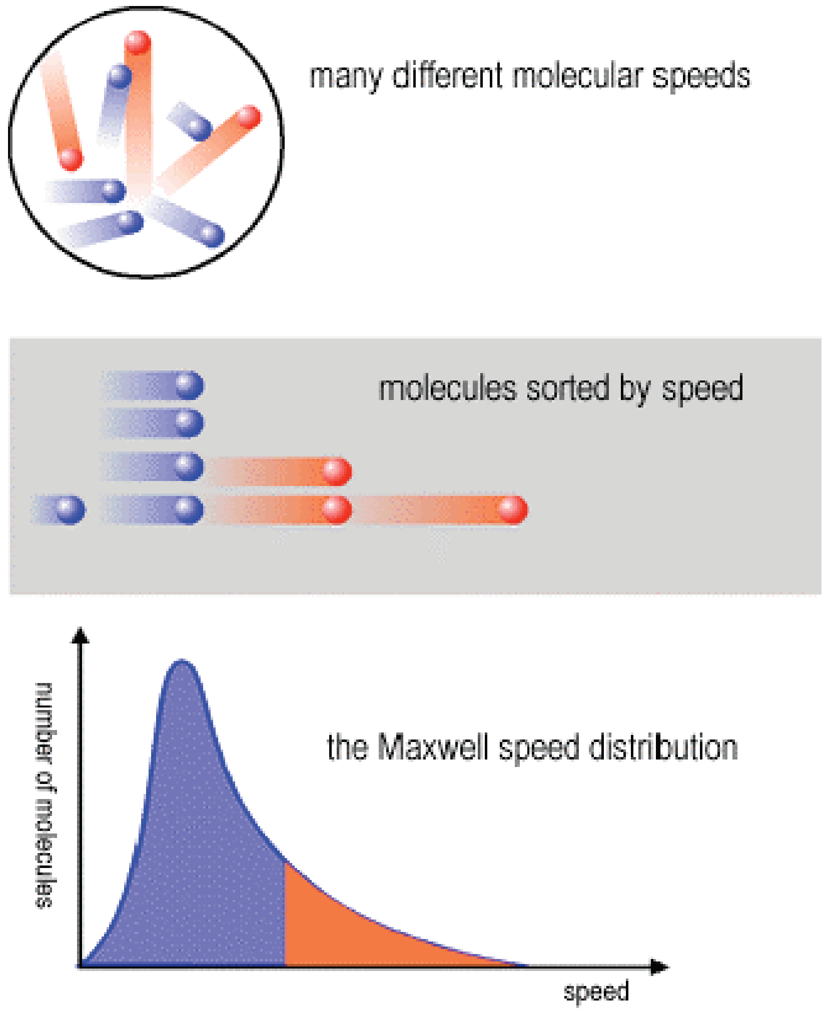
- This is a question that Maxwell looked at in 1866. He derived what is known as the Maxwell velocity distribution. It is sometimes also known as the Maxwell-Boltzmann distribution, because Boltzmann added some contributions to Maxwell's earlier work when he developed much of statistical mechanics.

What does the Maxwell distribution look like?

The Maxwell velocity distribution (see below) is a plot of the probability density *D*(*v*) on the *y*-axis as a function of the particle speed *v* on the *x*-axis, for a particular gas at a particular temperature.

The probability that a particle has a precisely given speed is *zero*. Since there are so many particles, their speed can vary continuously over infinitely many values, each particular speed has infinitesimal probability (i.e., zero).

Hence, the actual value of a distribution function *D*(*v*) at a particular *v* isn't very meaningful by itself – it doesn't even have sensible units for a probability (i.e., none), its units are 1/*v* or s/m. The distribution function exists to be integrated – to turn it into a probability you need to integrate it over some range of velocities or interval *dv*.



Extracting the probability

So, it's more correct to ask, what is the probability that a particle has a velocity between v_1 and v_2, and this probability is then given by:

$$P(v_1...v_2) = \int_{v_1}^{v_2} D(v)dv \qquad (7.1)$$

This is equivalent to an area under the distribution curve as shown below. Note that you can make v_1 and v_2 arbitrarily close and for example integrate between v and $v + dv$, but in the limit where dv goes to zero (i.e., you ask for a precise velocity), you get back a zero (or infinitesimal) probability.

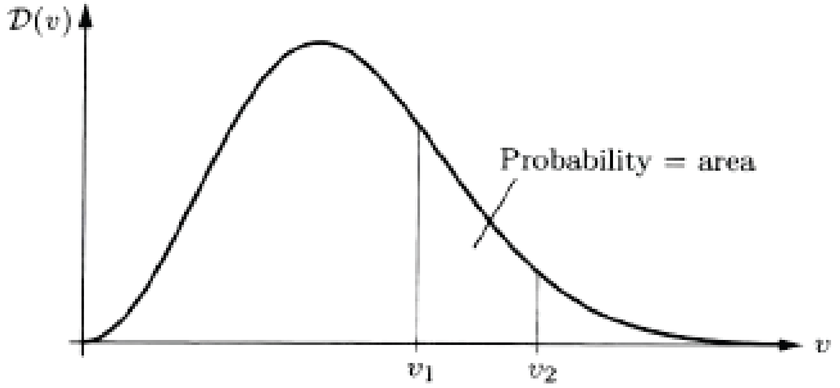


Figure 6.11. A graph of the relative probabilities for a gas molecule to have various speeds. More precisely, the vertical scale is defined so that the area under the graph within any interval equals the probability of the molecule having a speed in that interval.

So what is $D(v)$?

- The distribution function $D(v)$ is given by:

$$D(v) = \left(\frac{m}{2\pi k_B T}\right)^{3/2} 4\pi v^2 \exp\left(-\frac{mv^2}{2k_B T}\right) \qquad \textbf{(7.2)}$$

- Derivation is rather complicated & will be shown in next class.
- One thing to note is that the factor at the front is a normalisation factor to ensure that the total area under the curve (i.e., the probability of the particle having *any velocity) is equal to 1. In other words:*

$$P(0 \ldots \infty) = \int_0^\infty D(v)\,dv = 1 \qquad \textbf{(7.3)}$$

D(v) function, **whose purpose in life to be integrated !!!**

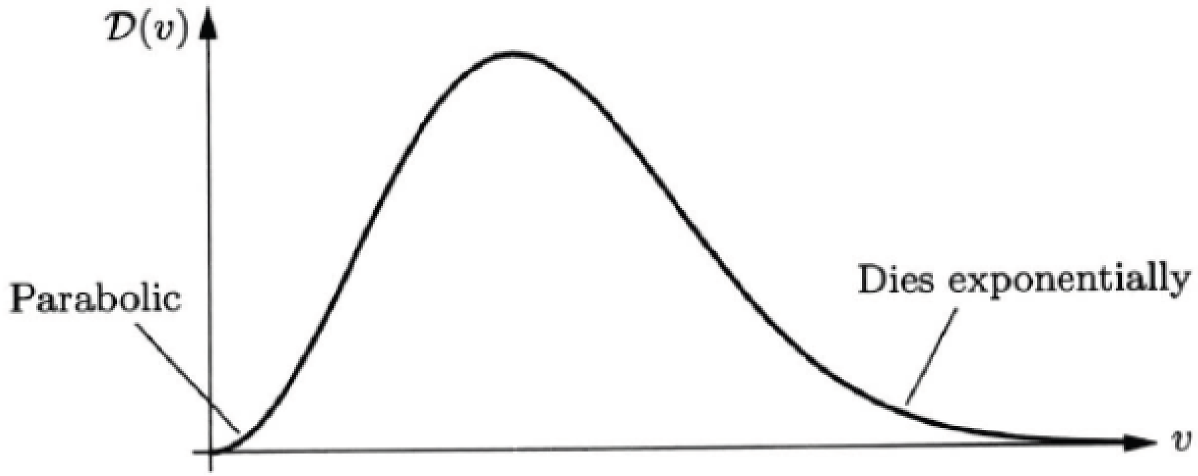
- The distribution function has two parts. The first is the probability of an atom having speed, *v*. That's given by the Boltzmann probability distribution. The second factor is a multiplicity factor—how many velocity <u>vectors</u> have the same <u>magnitude</u>, *v*.

$$D(v) = (\text{probability of molecules having velocity } v) \times (\text{number of velocity vectors with } v)$$

$$D(v) = \left(\frac{m}{2\pi k_B T} \right)^{3/2} 4\pi v^2 \exp\left(-\frac{mv^2}{2k_B T} \right)$$

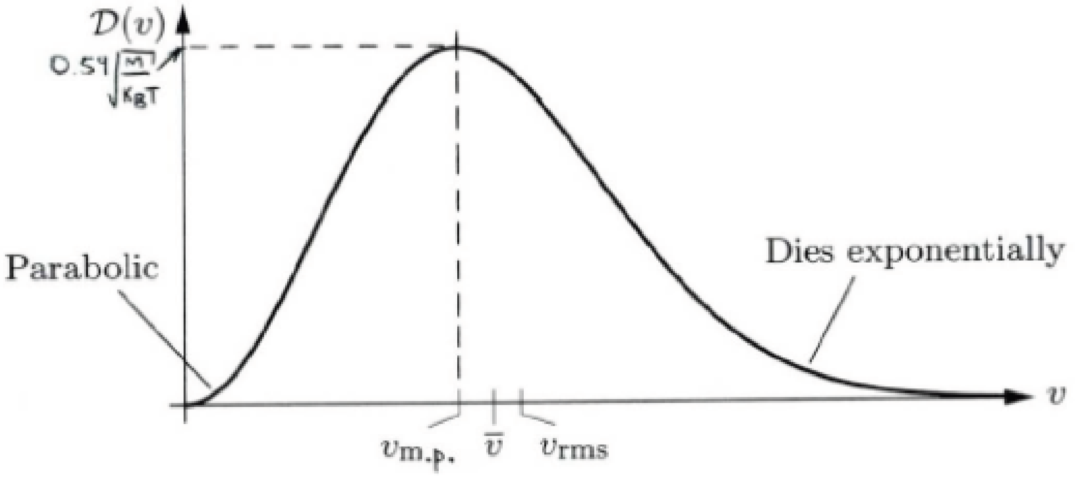
Maxwell distribution in the limits of v

Firstly, let's look the limits $v \to 0$ and $v \to \infty$. In both cases D(v) drops to zero. In the $v \to 0$ limit, $\exp(-v^2) \ll v^2$ so the v^2 term dominates and the fall-off is roughly parabolic. In contrast, in the $v \to \infty$ limit, $\exp(-v^2) \gg v^2$ so the $\exp(-v^2)$ term dominates and the fall-off is roughly exponential.



Three characteristic velocities

We can also place three speeds on our distribution function.



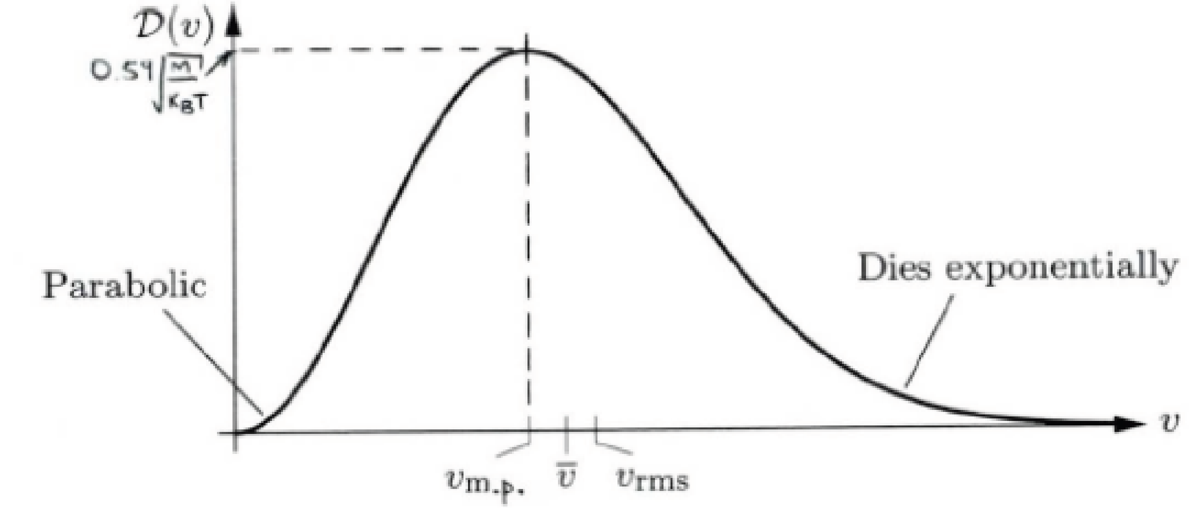
The first is the most probable speed $v_{m.p.} = (2k_BT/m)^{1/2}$, which you can obtain by setting the derivative of $D(v)$ equal to zero and solving for v. The most probable speed $v_{m.p.}$ coincides with the peak in the Maxwell distribution, which lies at $D(v) = 0.59(m/k_BT)^{1/2}$.

The second is the average speed v_{av}, which is the weighted average velocity:

$$\overline{v} = v_{av} = \int_0^\infty vD(v)dv = \sqrt{\frac{8k_BT}{\pi m}} \qquad \textbf{(7.4)}$$

Three characteristic velocities

We can also place three speeds on our distribution function.



The third is the root-mean-squared velocity v_{rms}, which we can obtain as the square-weighted average:

$$v_{rms} = \int_0^\infty v^2 D(v)dv = \sqrt{\frac{3k_B T}{m}} \qquad \textbf{(7.5)}$$

Note that this is the same result we got from the equipartition of energy, which is reassuring, and is the average velocity of the particles in our gas. We find that v_{av} is 13% larger than $v_{m.p.}$, and v_{rms} is 22% larger than $v_{m.p.}$.

$$V_{mp} = \sqrt{\frac{2KT}{m}}$$

$$V_{avg} = \sqrt{\frac{8KT}{m\pi}}$$

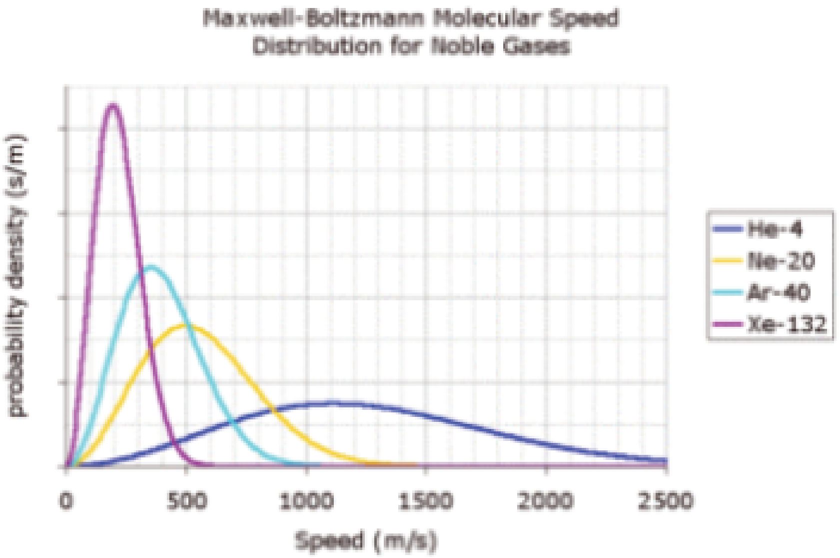
$$V_{rms} = \sqrt{\frac{3KT}{m}}$$

As can be observed,

$$\boxed{V_{mp} < V_{avg} < V_{rms}.}$$

Maxwell distribution vs mass and temperature

There is one final thing to consider, and that is how *D*(*v*) varies with the two parameters that we can control *m* and *T*.



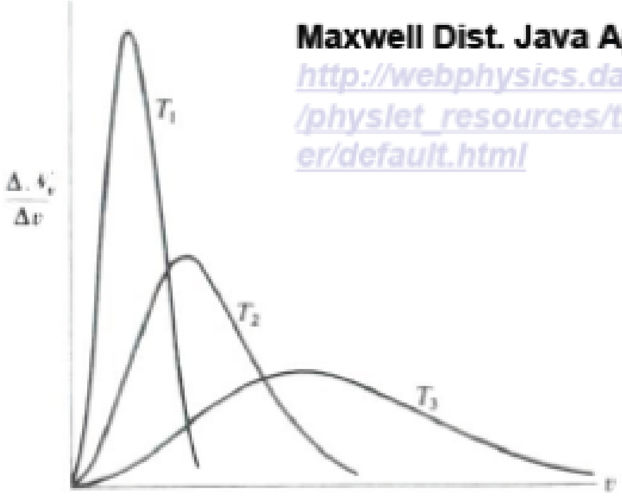


Fig. 12–5 Graph of M-B *speed* distribution function at three different temperatures, $T_3 > T_2 > T_1$.

Maxwell Dist. Java Applet - http://webphysics.davidson.edu/physlet_resources/thermo_paper/default.html

The behaviour of *D*(*v*) with *m* at constant *T* is shown above left – we find that increasing *m* squashes the distribution to the left, raising the peak and lowering the most probable, average and rms speeds.

The behaviour of *D*(*v*) with *T* at constant *m* is shown above right - reducing *T* pushes the distribution to the left, raising the peak and lowering the most probable, average and rms speeds.

STUDENTS HOME WORKS

- Derivation of Distribution Function
- Derivation of Average, RMS and Most Probable Speeds

Derivation of Distribution Function

- Note that the quantity $\int_u^\infty f(u)du$ will give the fraction of molecules which have velocities greater than u.
- However, $n_{>u}$ gives the fractions of molecules crossing some area per unit time. If we want to calculate this quantity using $f(u)$ we need $\int_u^\infty u\, f(u)du$.

[$f(u)$ decides the number of molecules between u and $u + du$. The molecules within distance ut from the chosen surface will be able to cross it. Thus per unit time the number will be decided by $u\, f(u)$].

Thus we obtain the relation

$$\int_u^\infty u\, f(u)du = A\, e^{-mu^2/2kT}$$

where A is a constant yet to be determined.

$$\int_{u}^{\infty} u\, f(u)du = A\, e^{-mu^2/2kT}$$

Differentiate both sides with respect to u, we obtain

$$-u\, f(u) = -\frac{mA}{kT} u\;\; e^{-mu^2/2kT}$$

which yielding finally,

$$f(u) = C\, e^{-mu^2/2kT}$$

where $C = \frac{mA}{kT}$ is another constant.

The constant C can be found using the normalization condition

$$\int_{-\infty}^{\infty} f(u)du = 1$$

We have the standard Gaussian integral result

$$\int_{-\infty}^{\infty} e^{-x^2}\,dx = \sqrt{\pi}\,.$$

Taking $x = \sqrt{m/2kT}\,u$, so that $dx = \sqrt{m/2kT}\,du$. Thus,

$$\sqrt{m/2kT}\int_{-\infty}^{\infty} e^{-mu^2/2kT}\,du = \sqrt{\pi}$$

$$\Rightarrow \sqrt{\frac{m}{2\pi kT}}\int_{-\infty}^{\infty} e^{-mu^2/2kT}\,du = 1.$$

Comparing with $\int_{-\infty}^{\infty} f(u)du = C\int_{-\infty}^{\infty} e^{-mu^2/2kT}\,du = 1$ we find $C = \sqrt{m/2\pi kT}$. Hence

$$f(u) = \sqrt{\frac{m}{2\pi kT}}\,e^{-mu^2/2kT}$$

Derivation of Most Probable Speed

MOST PROBABLE SPEED

- It is the speed most likely to be possessed by any molecule (of the same mass *m*) in the system. It is the value at which the maxima of the distribution curve occurs, i.e.,

$$\frac{\partial f(v)}{\partial v} = 0$$

$$\Rightarrow \frac{\partial}{\partial v}\left(4\pi\left(\frac{m}{2\pi kT}\right)^{3/2} \boldsymbol{v^2 e^{-mv^2/2kT}}\right) = 0$$

$$\Rightarrow \left(2v - v^2\left(\frac{mv}{kt}\right)\right) e^{-mv^2/2kT} = 0$$

$$\Rightarrow v = 0, v = \sqrt{\frac{2kT}{m}}.$$

- The first value corresponds to the minimum, while the second value gives the maximum. Thus, the most probably speed is

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

MOST PROBABLE SPEED

- If M is the molar mass, i.e., mass of one mole of the molecules, then
- $M = N_0 m$, where N_0 is the Avogadro number.
- Thus,

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

$$\Rightarrow v_P = \sqrt{\frac{2N_0 kT}{M}}$$

$$\Rightarrow v_P = \sqrt{\frac{2RT}{M}}$$

Here R is the universal gas constant.

Derivation of MEAN SPEED

MEAN SPEED

Mean speed can be obtained using

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

Note that it is the continuous analog of

$$\langle v\rangle = \frac{1}{N}\sum_{i=1}^{r} n_i v_i = \sum_{i=1}^{r} \frac{n_i}{N} v_i.$$

with $N = \sum_{i=1}^{r} n_i$.

Thus,

$$\langle v\rangle = \int_0^\infty v \left(4\pi\left(\frac{m}{2\pi kT}\right)^{3/2} v^2 e^{-mv^2/2kT}\right) dv$$

The substitution $\frac{mv^2}{2kT} = s$ leads to

$$\langle v\rangle = \sqrt{\frac{8kT}{\pi m}} \int_0^\infty s e^{-s} ds = \sqrt{\frac{8kT}{\pi m}}.$$

$$n! = \int_0^\infty x^n e^{-x}\, dx.$$

MEAN SPEED

We can also express this in terms of the molar mass and universal gas constant. We have

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

$$\Rightarrow \langle v \rangle = \sqrt{\frac{8N_0kT}{\pi M}}$$

$$\Rightarrow \langle v \rangle = \sqrt{\frac{8RT}{\pi M}}$$

Derivation of RMS SPEED

ROOT MEAN SQUARE (RMS) SPEED

RMS speed can be obtained using

$$v_{RMS}^2 = \langle v^2 \rangle = \int_0^\infty v^2 f(v)dv.$$

Note that $\langle v^2 \rangle$ above is the continuous analog of

$$\langle v^2 \rangle = \frac{1}{N}\sum_{i=1}^r n_i v_i^2 = \sum_{i=1}^r \frac{n_i}{N} v_i^2.$$

with $N = \sum_{i=1}^r n_i$.

Thus,

$$\langle v^2 \rangle = \int_0^\infty v^2 \left(4\pi \left(\frac{m}{2\pi kT}\right)^{3/2} v^2 e^{-mv^2/2kT}\right) dv$$

The integral can be performed either using Gamma function result or Gaussian integral result. We have,

$$\int_0^\infty s^4 e^{-as^2} ds = \frac{3}{8}\frac{\pi^{1/2}}{a^{5/2}}; \qquad a > 0.$$

$$\int_0^\infty x^2 e^{-ax^2} dx = \frac{1}{4}\sqrt{\frac{\pi}{a^3}}.$$

$$\int_0^\infty x^n e^{-ax} dx = (n!)a^{-(n+1)}.$$

$$n! = \int_0^\infty x^n e^{-x} dx.$$

3.2 $\int_0^\infty x^2 e^{-ax^2} dx = \frac{1}{4}\sqrt{\frac{\pi}{a^3}}$

$\frac{d}{da} \to$

$-\int_0^\infty x^4 e^{-ax^2} dx = \frac{1}{4}\sqrt{\pi}\,\frac{d}{da}\left(a^{-3/2}\right) = \frac{\sqrt{\pi}}{4}\left(-\frac{3}{2}\right)a^{-5/2}$

$\to \int_0^\infty x^4 e^{-ax^2} dx = \frac{3\sqrt{\pi}}{8\,a^{5/2}}$

ROOT MEAN SQUARE (RMS) SPEED

Therefore, we obtain

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

This is in agreement with $\left\langle \frac{1}{2} m v^2 \right\rangle = \frac{3kT}{2}$.

Finally,

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

$$\Rightarrow v_{RMS} = \sqrt{\frac{3N_0 kT}{M}}$$

$$\Rightarrow v_{RMS} = \sqrt{\frac{3RT}{M}}$$