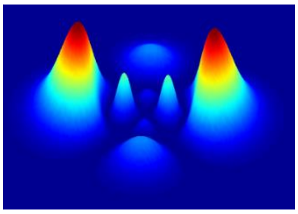

DOING PHYSICS WITH PYTHON

QUANTUM STATISTICS

MAXWELL BOLTZMANN DISTRIBUTIONS

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PYTHON CODES

sm400.py Gaussian random number generator for creating the probability distributions

sm400C.py symbolic integration and differentiation of distribution functions

qmSM04.py In this simulation of the Maxwell distribution of speeds for an ideal gas is modelled. In the input section you specify the number of grid points num, temperature T, mass of the molecules m, the velocity range (vMin = 0, vMax) and the velocity limits (v1, v2) for finding the probability of finding a molecule in the range $v_1 \le v \le v_2$.

```
#%% INPUTS >>>>
# Temperature T [K]
T = 600
# amu [kg] / molecular mass of gas
M = 32
amu = 1.6605e-27
# mass of gas molecule m [kg]  = amu * molecule mass of gas
m = amu*M
# Velocity range  [m/s]
vMin = 0; vMax = 2000
# Velocity limits for probability calculation [m/s]
v1= 000; v2 = 2000
# Grid size
num = 9999
```

The number of grid points `num` and the maximum velocity `vMax` have to be chosen so that the distribution goes to zero as `v` approached `vMax`. The variable, `area` is the area under the distribution curve. Its value has to be very close to 1 as it represents the probability of finding the particle between 0 and `vMax`.

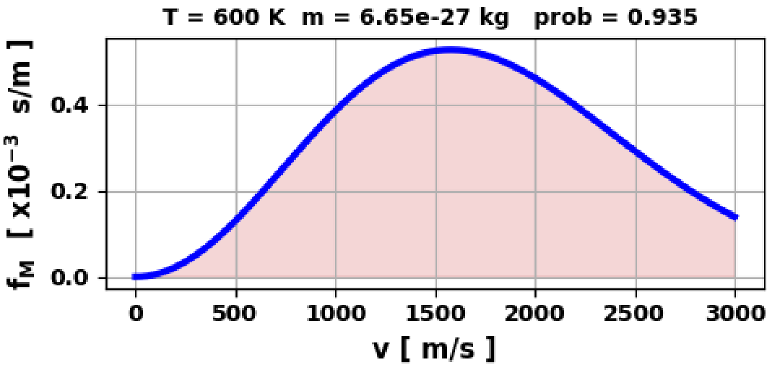

Fig. 1. Maxwell speed distribution. The area under the curve is $0.94 \neq 1$ and the distribution is non-zero at the vMax = 300. It is necessary to increase vMax so that area ~ 1 and the fM ~ 0 at vMax. The results are shown graphically and a summary is displayed in the Console Window. The numerical and the theoretical values are both displayed to make a judgment on the accuracy of the numerical method.

```
Numerical calculations
T = 100 K   M = 32 kg
Normalization area under distribution curve = 1:  area =
1.0000000
Most probable speed: vP = 228 m/s
average speed: vAvg = 257 m/s
RMS speed: vRMS = 279 m/s
Probability of finding particle v1 < v < v2
v1 = 0   v2 = 1000   prob = 1.000

Theoretical calculations
most probable: vP = 228 m/s
average: vAvg = 257 m/s
RMS: vRMS = 279 m/s

Execution time = 0.353 s
```

INTRODUCTION

For an ideal gas, its **temperature** [K] is a measure of **average translational kinetic energy** of the gas molecules.

$$\frac{3}{2}\,k\,T = \frac{1}{2}\,m\,v^2$$

So, different ideal gases at the same temperature will have the same average molecular average translational kinetic energy. However, we would not expect all the molecules in a gas to be travelling at the same speed. The way in which the speed of the molecules vary was first proposed by **James Clerk Maxwell** in 1860. At this time, no experimental evidence was possible because of the nonexistence of proper vacuum equipment. It was not until 1926 that Otto Stern was able to partially confirm Maxwell's predictions.

To start, Maxwell focused on the Cartesian components of velocities of the ideal gas molecules since the velocity components are much more important than the random instantaneous positions as energy depends upon velocity and not position.

We can define a set of velocity distribution functions such that

$$(1) \qquad f(v_x)\,dv_x = \left(\frac{m}{2\pi k_B T}\right)^{1/2} \exp\left(-\frac{m v_x{}^2}{2 k_B T}\right) dv_x$$

where $f(v_x)\,dv_x$ is the probability of finding a particle with the x-component of the velocity between v_x and $v_x + dv_x$. If we integrate over all values of v_x, the result must be one, because every molecule must have a value for its velocity component v_x at every instant of time

$$(2) \qquad \int_{-\infty}^{+\infty} f(v_x)\,dv_x = 1$$

The v_y and v_z velocity components

have a distribution function of the same form as the v_x velocity component.

We can calculate the mean velocity components and the mean kinetic energy of the molecules by performing the necessary integrations in Python using symbolic commands.

Mean velocity $\langle v_x \rangle$

$$(3) \qquad \langle v_x \rangle = \int_{-\infty}^{+\infty} v_x \; f(v_x)\,dv_x = 0$$

$\langle v_x \rangle = 0$ makes sense physically, because in a random distribution of velocities one would expect the velocities to be evenly distributed evenly around the peak at $v_x = 0$.

Mean velocity squared $\langle {v_x}^2 \rangle$

$$(4)\qquad \left\langle {v_x}^2 \right\rangle = \int_{-\infty}^{+\infty} {v_x}^2 \, f(v_x)\, dv_x = \frac{k_B\, T}{m}$$

Mean kinetic energy $\left\langle K \right\rangle$

$$(5)\qquad \left\langle K \right\rangle = \tfrac{1}{2} m \left(\left\langle {v_x}^2 \right\rangle + \left\langle {v_y}^2 \right\rangle + \left\langle {v_z}^2 \right\rangle \right) = \tfrac{3}{2} k_B\, T$$

Let $b = k_B\, T$ and $a = b\, m / 2$. So, using equation 1 and 3

$$f(v_x) = \left(\frac{a}{\pi} \right)^{1/2} \exp\left(-a\, x^2 \right)$$

We can now use the Code **sm400C.py** for calculating the integrals symbolically.

```
from sympy import *
import sympy as sy
# Normalization
def f1(x):
   g1 = (a/pi)**0.5*exp(-a*x**2)
   return g1

def f2(x):
   g2 = x*(a/pi)**0.5*exp(-a*x**2)
   return g2

def f3(x):
   g3 = x**2*(a/pi)**0.5*exp(-a*x**2)
   return g3
```

```
# Define symbolic variables
x = sy.Symbol("x")
a = sy.Symbol("a")

# Probability
prob = sy.integrate(f1(x), (x, -oo, oo))
print(prob)   → 1
print(' ')

# Mean value x
xAvg = sy.integrate(f2(x), (x, -oo, oo))
print(xAvg)  → 0
print(' ')

# mean value x**2
x2Avg = sy.integrate(f3(x), (x, -oo, oo))
print(x2Avg)  → (1/(2*a)
print(' ')
```

The result shown in equation 5 illustrates the **equipartition theorem**. For a monatomic gas there are three degrees of freedom (translational motion in the x, y and z directions). The average kinetic energy of the molecules for each degree of freedom is

Mean kinetic energy / degree of freedom = $\frac{1}{2}k_B T$

and the mean kinetic energy is independent of the mass of the gas molecules, it only depends upon the temperature T of the gas.

The standard deviation σ_x for the distribution of v_x is

$$(6) \qquad \sigma_x = \sqrt{\left\langle {v_x}^2 \right\rangle - \left\langle v_x \right\rangle^2} = \sqrt{\frac{k_B T}{m}}$$

From equation 1 we can write the Maxwell factor as

$$(7) \qquad f(v_x) = \left(\frac{1}{2\pi {\sigma_x}^2} \right)^{1/2} \sigma_x \exp\left(-\frac{{v_x}^2}{2{\sigma_x}^2} \right)$$

The Maxwell speed distribution

$$(8) \qquad f(v)\; dv = 4\pi \left(\frac{m}{2\pi k_B T} \right)^{3/2} v^2 \exp\left(-\frac{m v^2}{2 k_B T} \right) dv$$

$f(v)\; dv$ is the probability of finding a molecule with speed v to $v+dv$.

The Maxwell energy distribution (total energy E = kinetic energy K)

$$(9) \qquad f(E)\; dE = \frac{8\pi}{\sqrt{2}} \left(\frac{1}{k_B T} \right)^{3/2} \sqrt{E} \exp\left(-\frac{E}{k_B T} \right) dE$$

$f(E)\; dE$ is the probability of finding a molecule with energy (kinetic energy) E to $E + dE$.

From the Maxwell speed distribution, we can find the most probable speed v_{peak}, the mean speed $\langle v \rangle$ and the root mean speed v_{rms} using the Python's symbolic commands.

$$(8) \qquad f(v)\,dv = 4\pi\left(\frac{m}{2\pi k_B T}\right)^{3/2} v^2 \exp\left(-\frac{m v^2}{2 k_B T}\right) dv$$

Most probable speed $df(v)/dv = 0$ →

$$v_{peak} = \sqrt{\frac{2k_B T}{m}}$$

Mean speed $\langle v \rangle = \int_0^\infty v\, f(v)\, dv = \frac{4}{\sqrt{2\pi}}\sqrt{\frac{k_B T}{m}}$

Root mean speed $v_{rms} = \sqrt{\int_0^\infty v^2\, f(v)\, dv} = \sqrt{\frac{3k_B T}{m}}$

sm400C.py

```
#%% Speed v
# Normalization
def f1(x):
    g1 = 4*pi*(a/pi)**1.5 * x**2 * exp(-a*x**2)
    return g1

def f2(x):
    g2 = 4*pi*(a/pi)**1.5 * x**3 * exp(-a*x**2)
    return g2

def f3(x):
    g3 = 4*pi*(a/pi)**1.5 * x**4 * exp(-a*x**2)
    return g3
```

```
# Define symbolic variables
x = sy.Symbol("x")
a = sy.Symbol("a")

# Probability
prob = sy.integrate(f1(x), (x, 0, oo))
print(prob)  → 1
print(' ')

# Mean value x
xAvg = sy.integrate(f2(x), (x, 0, oo))
```

`print(xAvg)` → 2/(pi**0.5*a**0.5) → $\langle v \rangle = \frac{4}{\sqrt{2\pi}}\sqrt{\frac{k_B T}{m}}$

```
print(' ')

# mean value x**2
x2Avg = sy.integrate(f3(x), (x, 0, oo))
```

`print(x2Avg)` → 3/(2*a) → $v_{rms} = \sqrt{\frac{3k_B T}{m}}$

```
print(' ')

# Find peak velocity
def D(x):
   return 4*pi*(a/pi)**1.5 * x**2 * exp(-a*x**2)
```

`peak = sy.diff(D(x),x)` → 8*a**1.5*x*exp(-a*x**2)/pi**0.5 - 8*a**2.5*x**3*exp(-a*x**2)/pi**0.5

peak = 0 → $a\,v^2 = 1$ → $v_{peak} = \sqrt{\frac{2k_B T}{m}}$

Equation 7 is a Gaussian function with mean zero and standard deviation σ_x. We can use the Python random number generator to give a Gaussian (normal) distribution.

```
import random
random(mean,std)
```

The Python Code **sm400.py** generates the probability distributions for the velocity components and plots the results as a histogram. From the velocity component data, the Maxwell speed and energy distributions can also be plotted as histograms. For the simulations, one million molecules are used and the temperature of the gas be specified for different simulations. The theoretical distributions are also calculated and plotted as a red curve superimposed on the histograms. The histograms show the number of molecules within each bin, the total number of molecules being one million.

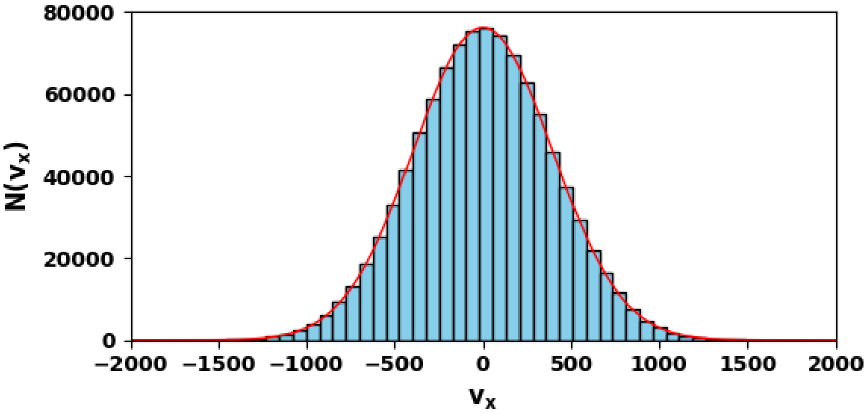

Fig. 1. The number distribution for the velocity component v_x and the Gaussian distribution given by equation 1 for the gas at a temperature T = 300 K.

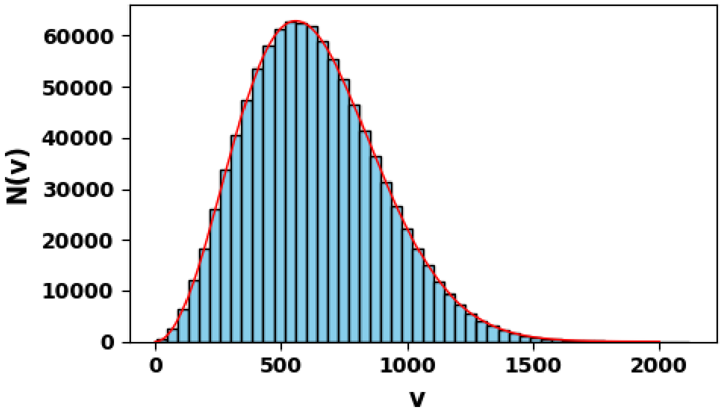

Fig. 2. The Maxwell distribution of molecular speeds $v = \sqrt{{v_x}^2 + {v_y}^2 + {v_z}^2}$ at $T = 300$ K.

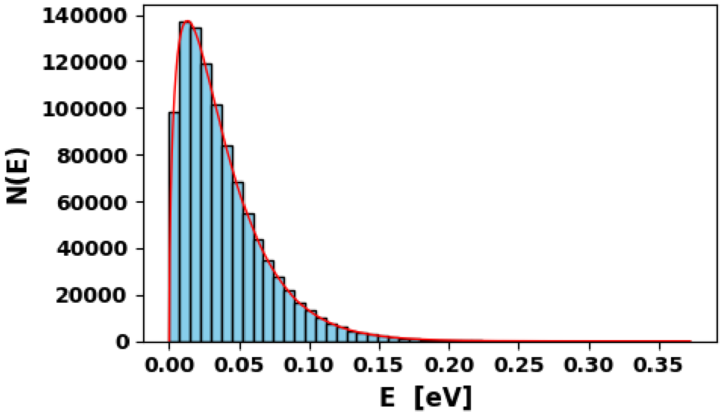

Fig. 3. The Maxwell distribution of molecular energy (translational kinetic energy) $K = \frac{1}{2} m v^2$ at $T = 300$ K.

If the temperature T is increased, the standard deviation is greater $\left(\sigma_x \propto \sqrt{T}\right)$ and the distributions have a lower peaks and are broader. If the temperature is decreased, the distributions have a higher peak and are narrower.

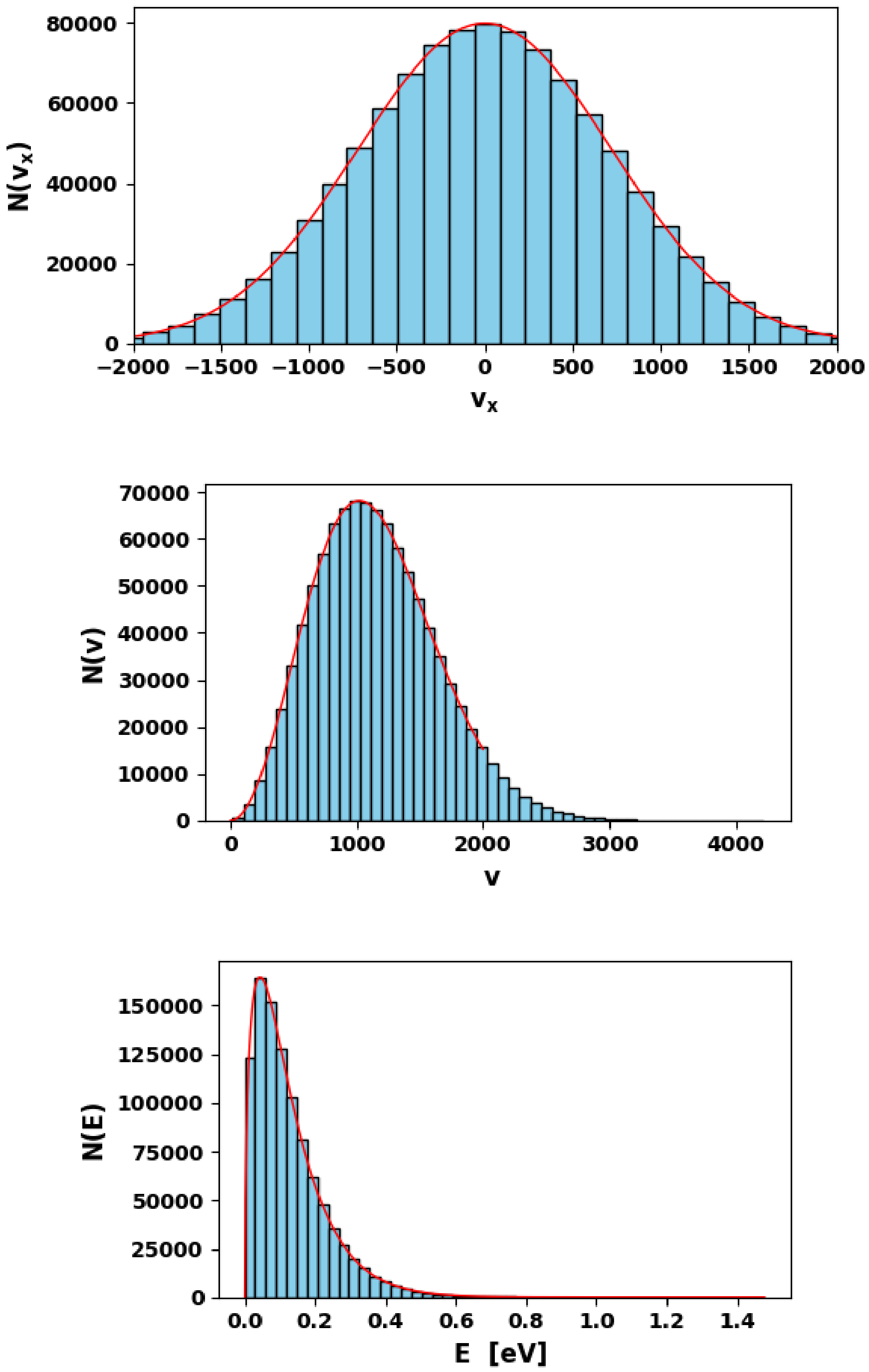

Fig. 4. The distribution at temperature T = 1000 K.

The energy distribution given by equation 9 has two energy terms $\sqrt{E}$ and $\exp\left(-E/k_B T\right)$. The exponential term is fundamentally more important and Boltzmann showed that it is a characteristic of any classical system, regardless of how other than molecular speeds may affect the energy of a given state. Thus, we can define the Maxwell-**Boltzmann distribution factor** f_{MB} for a classical system as

$$f_{MB} = A\exp\left(-\frac{E}{k_B T}\right) \tag{10}$$

where A is a normalization constant. Therefore, the energy distribution for a classical system will have the form

$$n(E)\,dE = g(E)\,F_{MB}\,dE \tag{11}$$

where $n(E)\,dE$ is the number of particles with energies between E and $E + dE$. The function $g(E)$ is the **density of states** and it gives the number of available states per unit energy range.

Maxwell distribution of molecular speeds

The Maxwell distribution of molecular speeds gives the most probable distribution of speeds in a gas where the gas molecules are assumed to move randomly with varying speeds. The Maxwell distribution function can be expressed by

$$f_M(v) = 4\pi \left(\frac{M}{2\pi RT} \right)^{3/2} v^2 \exp\left(-\frac{M v^2}{2RT} \right)$$

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

where

$f_M(v)$ = Maxwell distribution function

v = speed of a gas molecule

T = temperature [K]

$k_B = 1.381 \text{x} 10^{-23}$ J.K^{-1} Boltzmann constant

$R = 8.3145$ J.K^{-1}.mol^{-1} Universal gas constant

M = molecular mass of the gas [kg.mol^{-1}]

m = mass of a gas molecule [kg]

The Maxwell speed distribution $f_M(v)$ is a **probability density function** where

$$\int_0^\infty f_M(v)\, dv = 1$$

and the probability of the gas molecules of having a speed *v* in the range $\left(v_1 \le v \le v_2\right)$ is

$$\text{probability}\left(v_1 \le v \le v_2\right) = \int_{v_1}^{v_2} f_M(v)\, dv$$

From the Maxwell speed distribution, after lots of algebra we can calculate the following velocities;

Most probable velocity $v_P = \sqrt{\dfrac{2\,k_B\,T}{m}}$

The most probable speed can be numerically estimated from the velocity at the peak of the distribution

```
# Most probable speed
target_value = max(fM)
index1 = np.argmin(np.abs(fM - target_value))
vP = v[index1]
```

Average speed $<v>=\sqrt{\dfrac{8\,k_B\,T}{\pi\, m}}$

The average speed can be estimated numerically from

$$<v>=\int_0^{vMax} v\, f_M(v)\, dv$$

```
# Average speed
fn = v*fM
vAvg = simps(fn,v)
```

The root mean square speed $v_{RMS} = \sqrt{\dfrac{3k_B\,T}{m}}$

The rms speed can be estimated numerically from

$$v_{RMS} = \sqrt{\int_0^{vMax} v^2 \; f_M(v)\, dv}$$

```
# RMS speed
fn = v**2 * fM
vRMS =sqrt(simps(fn,v))
```

SIMULATIONS qmSM04.py

Figures 2, 3 and 4 shows the Maxwell speed distribution for oxygen gas (M = 32) at gas temperatures 100, 300 and 900 K. In each figure, the **red** vertical line is the speed v_P of molecules at the peak of the Maxwell distribution f_M, the **back** vertical line is the average speed <v> and the **magenta** line is for the rms speed $v_{RM}S$.

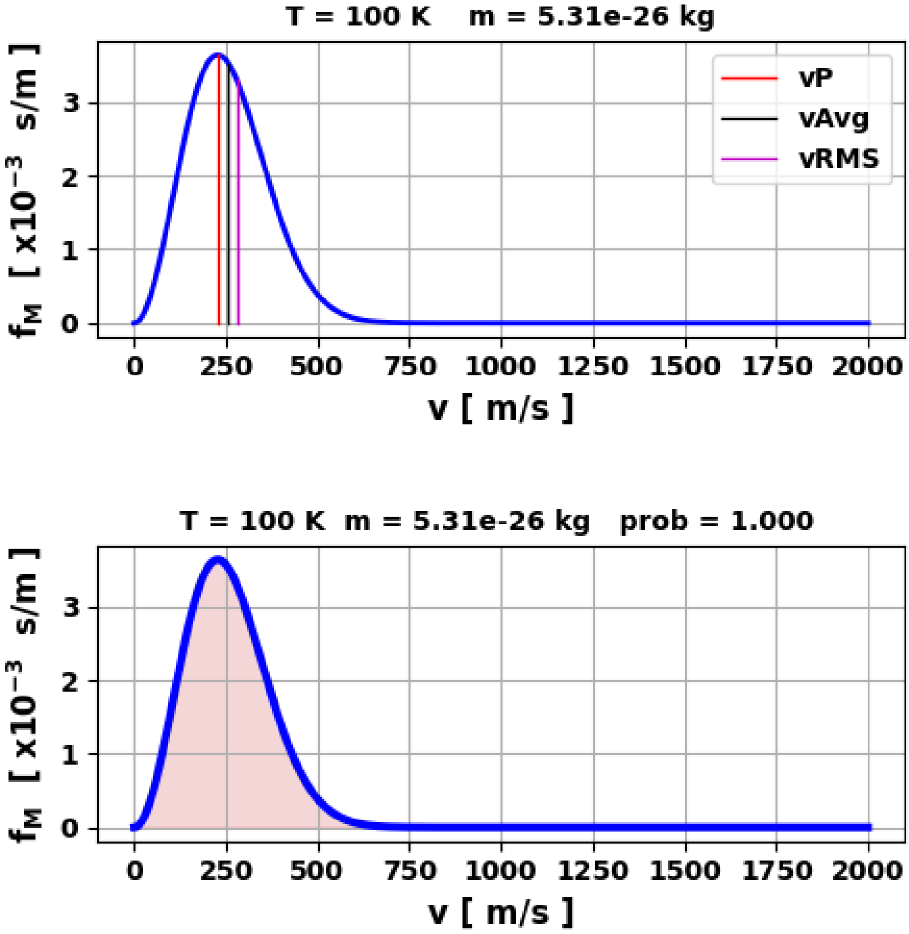

Fig. 2. Oxygen gas: M = 32, T = 100 K

```
Numerical calculations

T = 100 K   M = 32 kg

Normalization area under distribution curve = 1:  area =

1.0000000

Most probable speed: vP = 228 m/s

average speed: vAvg = 257 m/s

RMS speed: vRMS = 279 m/s

Probability of finding particle v1 < v < v2

v1 = 0   v2 = 1000   prob = 1.000
```

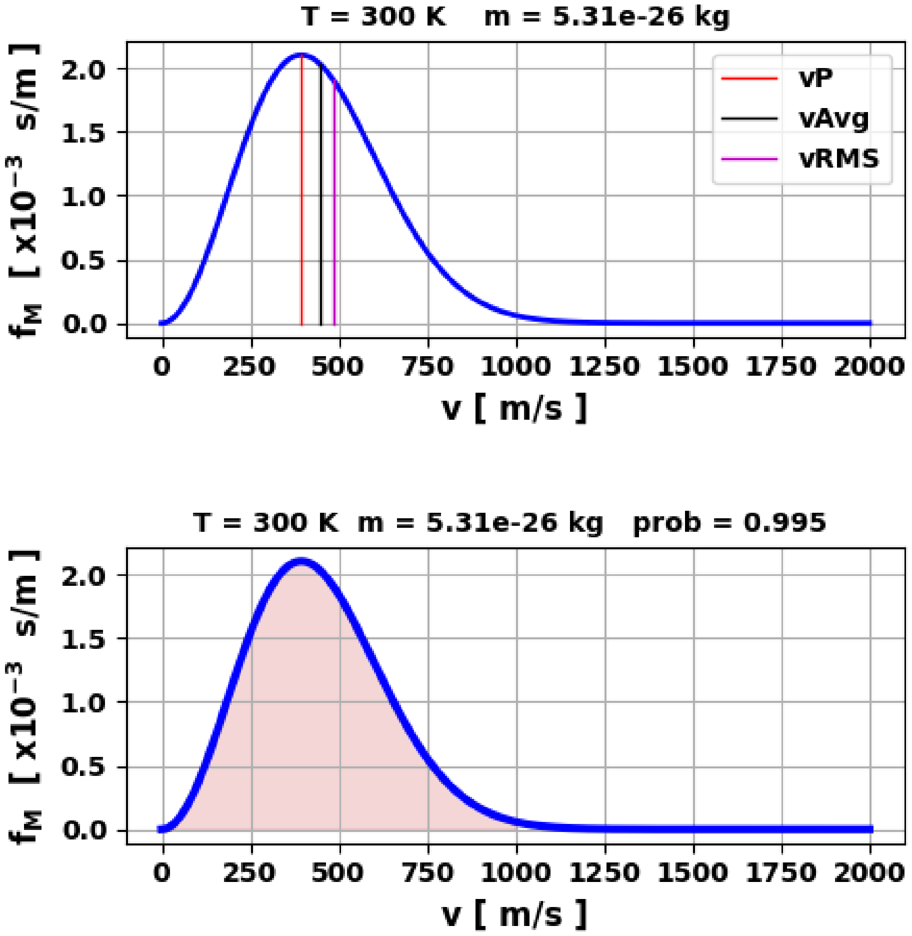

Fig. 3.   Oxygen gas: *M* = 32, *T* = 300 K

Numerical calculations

T = 300 K   M = 32 kg

Normalization area under distribution curve = 1:

area = 1.0000000

Most probable speed: vP = 395 m/s

average speed: vAvg = 445 m/s

RMS speed: vRMS = 483 m/s

Probability of finding particle v1 < v < v2

v1 = 0   v2 = 1000   prob = 0.995

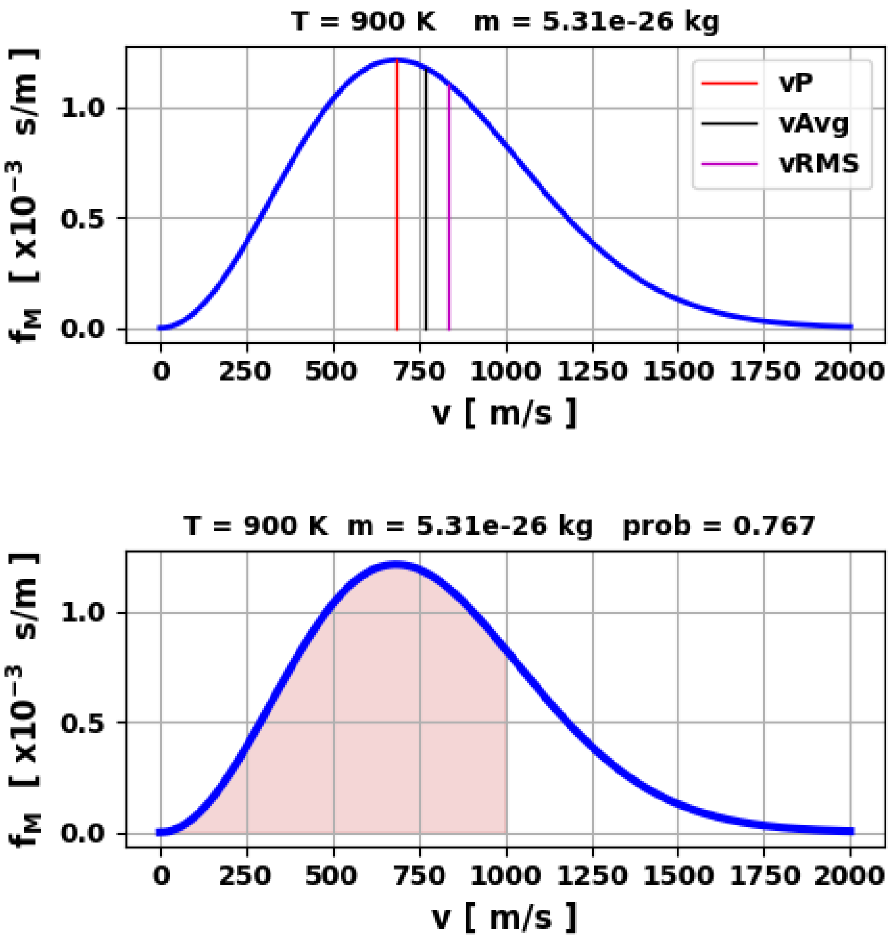

Fig. 4.   Oxygen gas: *M* = 32, *T* = 900 K

```
Numerical calculations

T = 900 K   M = 32 kg

Normalization area under distribution curve = 1:

area = 0.9993301

Most probable speed: vP = 684 m/s

average speed: vAvg = 770 m/s

RMS speed: vRMS = 836 m/s

Probability of finding particle v1 < v < v2

v1 = 0   v2 = 1000   prob = 0.767
```

T [m]	100	300	900
v_P [m/s]	228	395	684
$< v >$ [m/s]	257	445	770
v_{RMS} [m/s]	279	483	836
prob $v \leq 1000$	1.000	0.995	0.767
prob $v > 1000$	0.000	0.005	0.233

As the temperature increases, more and more of the gas molecules acquire greater speeds and greater translational kinetic energy.

The Code **qmSM04.py** can be executed to see the variation in the in the Maxwell speed distribution due to changes in mass. Two examples are shown in figure 5 (oxygen M = 32) and figure 6 (hydrogen M = 2).

The hydrogen molecules on average are moving much more rapidly than the oxygen molecules because of their much smaller particle mass. The area under each curve is one. The oxygen distribution has a much higher peak, therefore the distribution for the hydrogen must be much broader.

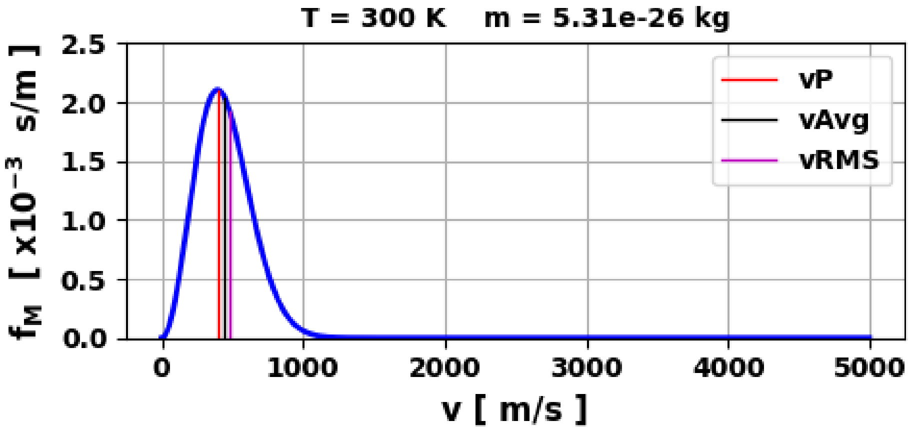

Fig. 5. Oxygen gas: $M = 32$, $T = 300$, $v_{RMS} = 486$ m/s.

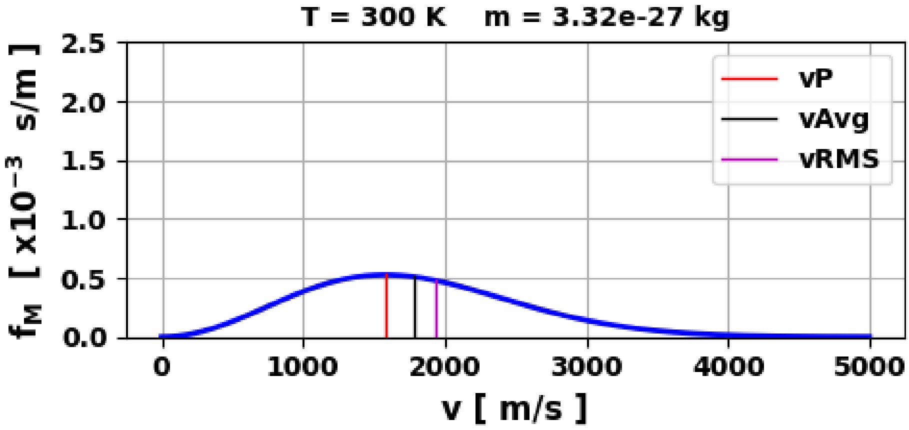

Fig. 6. Hydrogen gas: $M = 2$, $T = 300$ K, $v_{RMS} = 1933$ m/s.

The ratio of the speeds are

$$\frac{v_{RMS}(\text{hydrogen})}{v_{RMS}(\text{oxygen})} = \frac{1933}{486} = 3.977$$

This is agreement with the theoretical prediction

$$\frac{3}{2}k_B T = \tfrac{1}{2}m\left\langle v^2 \right\rangle \Rightarrow \frac{v_{RMS}(\text{hydrogen})}{v_{RMS}(\text{oxygen})} = \sqrt{\frac{M(\text{oxygen})}{M(\text{hydrogen})}} = \sqrt{\frac{32}{2}} = 4$$