5.5 Example: The Maxwell Distribution

The System

In the previous sections of Chapter 5 we dealt with a system having a finite number of discrete energy levels ε_i having degeneracy g_i. In the current section we shall consider a situation which has an infinite number of energy levels which form a continuum which has no upper limit. However, we shall treat this continuum as if it were a finely grained set of discrete energy levels so we can use the methods developed in Section 5.1. In the end, we shall apply quantum mechanics to show that in fact the energy levels really are discrete.

The system of interest is a box of helium gas near room temperature. Our "particles" then are the individual gas atoms. The gas is treated as an "ideal gas" in that there are no interactions between the atoms so each atom is independent of all the others. The gas is assumed to be made of point particles which have no rotational or vibrational degrees of freedom which can store energy (an H_2 molecule would have both), and the atoms are all in their electronic ground state. So it is a box of featureless point gas atoms of mass m. The atoms have "spin" 0 so they are bosons and therefore any number of them can be placed into any given energy state, as in our previous examples. We say the particles of the gas don't interact, but they do have constant collisions with each other and with the box walls. These *elastic* collisions randomize the direction of an atom's velocity **v** but have no effect on speed v, so we just pretend the collisions are not happening.

The atoms are in a stable state of "thermal equilibrium" at temperature T. The box is sealed and insulated to prevent the transfer of particles or energy in or out. The box contains some total fixed number of atoms M (to be computed later) and has some total energy U = Mu where u is the average energy of a particle.

Connection to Section 5.2

A particle has kinetic energy

$$\varepsilon_i = (1/2)mv^2 \equiv \varepsilon(v) . \qquad (5.5.1)$$

This is the total energy of a particle having speed $v = |\mathbf{v}|$ and mass m. There is no potential energy because the particles don't interact and because we ignore gravity which is only a miniscule effect. In classical mechanics, this energy $\varepsilon(v)$ is continuous because the speed v is a continuous variable. So $\varepsilon(v) = (1/2)mv^2$ represents the "energy levels" for a box of helium.

Let dv be some small but finite speed difference. The amount of energy in the atoms with speed between v and v+dv is $E(v) = (1/2)mv^2dv = \varepsilon(v)dv$. The number of atoms with speed in this range is taken to be N(v)dv, and the degeneracy of the states in this region we shall write as g(v)dv.

To get a number to represent the degeneracy g_i, we hop into velocity space where the axes are v_x,v_y,v_z and we note that the volume in this space corresponding to v in the range (v,v+dv) is $4\pi v^2dv$, since this is

the volume of a shell of radius v and thickness dv. As an artificial (at this point) construct, we shall assume that velocity space is not continuous but is a 3D lattice of allowed values and that the volume of a lattice cube is V. Therefore, we write (at least for now)

$$g_i = [4\pi v^2 dv]/V = g(v)dv \qquad \text{where } g(v) = (4\pi v^2/V) \tag{5.5.2}$$

All the g_i states in this thin shell have energy ε_i. Note that volume V is the assumed cell size in velocity space, it is *not* the volume of our box of gas.

The number N_i of previous sections is now

$$N_i = N(v)dv \tag{5.5.3}$$

and then

$$g_i/N_i = [g(v)\,dv]/[N(v)dv] = g(v)/N(v)\,. \tag{5.5.4}$$

We have the same two constraints as in previous Sections, but here they take the form

$$M = \Sigma_i N_i = \int_0^\infty N(v)dv$$

$$U = \Sigma_i \varepsilon_i N_i = \int_0^\infty \varepsilon(v)\, N(v)dv\,. \tag{5.5.5}$$

Recall from ** that we had this microstate count, assuming $g_i >> N_i$.

$$\Omega(\mathbf{N}) = \frac{g_1^{N_1}}{N_1!}\frac{g_2^{N_2}}{N_2!}\cdots\frac{g_m^{N_m}}{N_m!} = \Pi_{i=1}^{m}\frac{g_i^{N_i}}{N_i!} \tag{***}$$

What happens to this expression for Ω when there are an infinite number of energy states which are spaced closely together? We might write

$$g_i^{N_i} = (g(v)dv)^{N(v)\,dv}$$

$$N_i! = [N(v)dv]! \tag{5.5.6}$$

and then we get a product of an infinite number of terms,

$$\Omega(\mathbf{N}) = \Pi_{n=0}^{\infty}\frac{(g(ndv))^{N(ndv)\,dv}}{(N(ndv)dv)!}\,. \tag{5.5.7}$$

Just as an infinite sum $\Sigma_n a_n$ can converge only if $a_n \to 0$, an infinite product $\Pi_n a_n$ can only converge if $a_n \to 1$. There is a developed theory of such infinite products, but we leave this topic to the interested reader. Here are a few examples of infinite products taken from GR7,

$$\frac{c}{c-z} = \prod_{n=1}^{\infty} e^{\frac{1}{n}\left(\frac{z}{c}\right)^n}$$

$$\operatorname{sinc}(\pi z) = \prod_{n=1}^{\infty}\left(1 - \frac{z^2}{n^2}\right)$$

$$\frac{1}{\Gamma(z)} = z e^{\gamma z}\prod_{n=1}^{\infty}\left(1 + \frac{z}{n}\right)e^{-\frac{z}{n}} \qquad (5.5.8)$$

and can see that in fact $a_n \to 1$ in these three cases.

The object $f = \ln(\Omega)$ is a little more tractable since it is merely an infinite sum,

$$f = \Sigma_i N_i [1 + \ln(g_i/N_i)]$$

$$= \Sigma_{n=0}^{\infty} N(ndv)dv [\ 1 + \ln\{g(ndv)/N(ndv)\}] \ . \qquad (5.5.9)$$

Conveniently, we shall avoid dealing directly with Ω and $f = \ln(\Omega)$ and instead just make use of results derived in previous sections for a finite number of energy levels.

<u>The Maxwell-Boltzmann speed distribution and a few averages</u>

Our main result of interest is *** which says that the components N_i of the vector **N** which cause Ω to have a maximum are these,

$$N_i = A\ g_i\ e^{-\beta\epsilon_i} \qquad (****)$$

where $A \equiv e^{\lambda_1}$ and $\beta \equiv -\lambda_2$ are the derived Lagrange multipliers. Using (5.5.1,2,3) for ε_i, g_i and N_i we write the above as

$$\{N(v)dv\} = A\ \{[4\pi v^2 dv]/V\}\ \ \{\exp(-\beta m v^2/2)\ \}$$

or

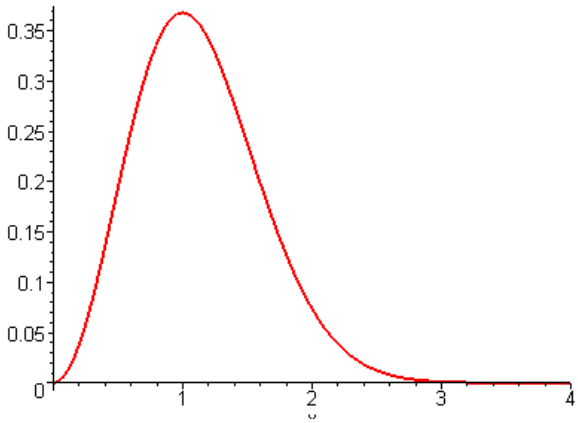
$$N(v) = 4\pi(A/V)\ \ v^2 \exp(-\beta m v^2/2) \qquad (5.5.10)$$

By cribbing results from our earlier sections, we have arrived with very little work at the very famous Maxwell-Boltzmann speed distribution, where for now we ignore the constant $4\pi(A/V)$ which will get a slight repair below. The general shape of this distribution is as follows :

```
N := v^2*exp(-v^2);
```

$$N := v^2 e^{(-v^2)}$$

```
plot(N,v=0..4,thickness = 2);
```



The quadratic left end of the plot arises from the fact that $g_i = (4\pi v^2/V)$, and the right end comes from the decaying exponential which here is just $\exp(-v^2)$.

The first item of interest is the **average energy** of a particle in the gas. Maple does the calculation,

$$\langle \varepsilon \rangle = u = \frac{\int_0^\infty (1/2)mv^2\, N(v)dv}{\int_0^\infty N(v)dv} \qquad (5.5.16)$$

```
N :=v^2*exp(-beta*m*v^2/2);
```

$$N := v^2 e^{\left(-\frac{1}{2}\beta m v^2\right)}$$

```
assume(beta>0,m>0);
top := int((1/2)*m*v^2*N,v=0..infinity);
```

$$top := \frac{3}{4}\frac{m\sqrt{2}\sqrt{\pi}}{\left(\frac{5}{2}\right)(\beta m)}$$

```
bot := int(N,v=0..infinity);
```

$$bot := \frac{1}{2}\frac{\sqrt{2}\sqrt{\pi}}{\left(\frac{3}{2}\right)(\beta m)}$$

```
simplify(top/bot);
```

$$\frac{3}{2}\frac{1}{\beta}$$

and therefore, using $\beta = 1/(kT)$,

$$\langle\varepsilon\rangle = u = \frac{3}{2}kT \qquad (5.5.17)$$

This is the "equipartition theorem" at work (we are not proving this here) : each quadratic term in the energy expression ends up with (1/2)kT of energy in equilibrium, and we have $\varepsilon(v) = (1/2)m(v_x^2+v_y^2+v_z^2)$.

Next we calculate the **mean speed** v of a particle,

$$v_{mean} = \langle v\rangle = \frac{\int_0^\infty v\, N(v)dv}{\int_0^\infty N(v)dv} \qquad (5.5.11)$$

```
N :=v^2*exp(-beta*m*v^2/2);
```

$$N := v^2\, e^{\left(-\frac{1}{2}\beta m v^2\right)}$$

```
assume(beta>0,m>0);
top := int(v*N,v=0..infinity);
```

$$top := 2\frac{1}{\beta^2 m^2}$$

```
bot := int(N,v=0..infinity);
```

$$bot := \frac{1}{2}\frac{\sqrt{2}\sqrt{\pi}}{(\beta m)^{\left(\frac{3}{2}\right)}}$$

```
top/bot;
```

$$2\frac{\sqrt{2}\,(\beta m)^{\left(\frac{3}{2}\right)}}{\beta^2 m^2\sqrt{\pi}}$$

Thus the mean speed of the Maxwell distribution is,

$$v_{mean} = \langle v\rangle = (2\sqrt{2}/\sqrt{\pi m\beta}) = \sqrt{\frac{8kT}{\pi m}}\ . \qquad (5.5.12)$$

The root **mean square speed** is given by

$$v_{rms} \equiv \sqrt{\langle v^2\rangle} = \sqrt{\frac{\langle(1/2)mv^2\rangle}{(1/2)m}} = \sqrt{\frac{2}{m}}\sqrt{\langle\varepsilon\rangle} = \sqrt{\frac{2}{m}}\sqrt{\frac{3}{2}kT} = \sqrt{\frac{3kT}{m}} \qquad (5.5.13)$$

Finally, the **peak speed** (most likely speed) occurs where the distribution slope is zero :

```
N :=v^2*exp(-beta*m*v^2/2);
```

$$N := v^2 e^{\left(-\frac{1}{2}\beta m v^2\right)}$$

```
diff(N,v);
```

$$2 v e^{\left(-\frac{1}{2}\beta m v^2\right)} - v^3 \beta m e^{\left(-\frac{1}{2}\beta m v^2\right)}$$

```
solve(diff(N,v)=0,v);
```

$$0, \frac{\sqrt{2}\sqrt{\beta m}}{\beta m}, -\frac{\sqrt{2}\sqrt{\beta m}}{\beta m}$$

and the meaningful root is the second item, so

$$v_{peak} = \sqrt{\frac{2kT}{m}} \tag{5.5.14}$$

The three values are not too far apart,

$$v_{peak} = \sqrt{\frac{2kT}{m}} = 1.41 \sqrt{\frac{kT}{m}} = 1.00\, v_{peak}$$

$$v_{mean} = \sqrt{\frac{8kT}{\pi m}} = 1.60 \sqrt{\frac{kT}{m}} = 1.13\, v_{peak}$$

$$v_{rms} = \sqrt{\frac{3kT}{m}} = 1.73 \sqrt{\frac{kT}{m}} = 1.23\, v_{peak} \tag{5.5.15}$$

Putting in some numbers, we compute the mean speed of Helium at room temperature.

```
mP := 1.6726219e-27 * kg;     # proton mass
```

$$mP := .16726219\, 10^{-26}\, kg$$

```
mHe := 4*mP; # He atom mass (approx)
```

$$mHe := .66904876\, 10^{-26}\, kg$$

```
T := 294*K; # 21C = 70F
```

$$T := 294\, K$$

```
k := 1.38064852e-23*J/K; #Boltzmann constant
```

$$k := .138064852\, 10^{-22}\, \frac{J}{K}$$

```
v := evalf(sqrt(8*k*T/(Pi*mHe)));
```

$$v := 1242.957855 \sqrt{\frac{J}{kg}}$$

```
simplify(subs(J/kg = m^2/s^2,v));
```

$$1242.957855\, \frac{m}{s}$$

so the mean speed of a Helium atom at room temperature is about 1243 m/sec = 772 mph. Of course the atoms don't go very far between elastic collisions.

So what happens next??