V25.0651 - Physical Chemistry I

The Maxwell Velocity Distribution

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The material below is taken from Sidney Golden's *Elements of the Theory of Gases*, Addison-Wesley, 1964, pages 101 and beyond.

We are interested in the distribution of velocities of molecules in an ideal gas at equilibrium. The distribution will be denoted by:

$$f(v_x, v_y, v_z)dv_x dv_y dv_z \tag{1}$$

which stands for the fraction of molecules moving with velocities simultaneously between v_x and $v_x + dv_x$, v_y and $v_y + dv_y$, and v_z and $v_z + dv_z$.

We will make a number of assumptions. The first is that the gas is ideal. That is that these are mass points of mass m per molecule and that the gas is *isotropic*. Isotropy means that the behavior of the gas is the same in all directions. Thus what is true of the x direction will also be true of the y direction and the z direction.

Curiously, this requirement demands that the distribution of velocities depend on the *speed* of the molecules. Otherwise the likelihood of finding a molecule of the specified speed will differ depending on the direction in which the molecule is moving. You can see this for example by interchanging the x and y velocities. We do not expect the distribution function to change at all. So the distribution cannot depend on the velocities separately. Thus if s, the speed of a molecule is given by:

$$s^2 = v_x^2 + v_y^2 + v_z^2 \tag{2}$$

we have that:

$$f(v_x, v_y, v_z) = f(v_x^2 + v_y^2 + v_z^2) \tag{3}$$

In other words, whatever function f is of the three velocities, it is the *same* function of the speed.

There is yet more. If the properties of the gas depend only on the motion of the molecules in, say, the x-direction, independently of what goes on in the y or z directions, then if we change the conditions to involve only the y direction, the distribution must not change.[1] In other words, the distribution of velocities is to be independent of direction. This implies that:

$$f(v_x^2 + v_y^2 + v_z^2) = f(v_x^2)\,f(v_y^2)\,f(v_z^2) \tag{4}$$

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[1] Think of a barometer that reads only molecular impacts from the x-direction. Then move the barometer so that it now reads only impacts from the y-direction. We expect no changes in reading or in the distribution.

where again, the f's on the right are the same functions of their arguments as the f on the left.[2]

One last thing: We want the distributions to be *normalized*. We want their integrals to be 1. This is because we want to interpret our distribution as a probability.

Now we can begin: The first result comes from Equation (4). To see how it works I'll take a simpler example. Let a function g obey:

$$g(x+y) \;=\; f(x)f(y) \tag{5}$$

Now I'm going first to differentiate Equation (5) with respect to x, holding y constant and then with respect to y holding x constant. I can make this more simple by defining

$$z \;=\; x+y \tag{6}$$

so that we have

$$g(z) \;=\; g(x)g(y) \tag{7}$$

Now

$$\left[\frac{\partial g(z)}{\partial x}\right] = \left[\frac{\partial g(z)}{\partial z}\right]\left[\frac{\partial z}{\partial x}\right] = \left[\frac{\partial g(z)}{\partial z}\right] \tag{8}$$

since the other derivative is 1. Similarly we find that

$$\left[\frac{\partial g(z)}{\partial y}\right] = \left[\frac{\partial g(z)}{\partial z}\right]\left[\frac{\partial z}{\partial y}\right] = \left[\frac{\partial g(z)}{\partial z}\right] \tag{9}$$

just as before. So, looking back at Equation (7) we have:

$$\left[\frac{\partial g(z)}{\partial z}\right] = \left[\frac{\partial g(x)}{\partial x}\right]g(y) \tag{10}$$

and

$$\left[\frac{\partial g(z)}{\partial z}\right] = \left[\frac{\partial g(y)}{\partial y}\right]g(x) \tag{11}$$

The left-hand side of Equations (10) and (11) are identical, so the right hand sides must be equal.

$$\left[\frac{\partial g(x)}{\partial x}\right]g(y) \;=\; \left[\frac{\partial f(y)}{\partial y}\right]g(x) \tag{12}$$

and rearranging:

$$\left[\frac{g'(x)}{g(x)}\right] = \left[\frac{g'(y)}{g(y)}\right] \tag{13}$$

where the primes indicate differentiation.

Now look at Equation (13) closely. Let us imagine that we make a change in the value of x. The left hand

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[2] In particular this means that if the function on the right is an exponential involving the velocities, then the functions on the left are exponentials involving *their* velocities.

side will certainly change. But the right hand side will certainly *not* change. How can this be? They are equal to each other?

This is an ancient mathematical trick. The only way Equation (13) can be correct is if each side is constant. Then changing x (or y) will *not* change the value of either side.

So we have for the left-hand side:

$$\left[\frac{g'(x)}{g(x)}\right] = -b \tag{14}$$

This equation has the solution:

$$g(x) = ae^{-bx} \tag{15}$$

where both a and b are constants.[3] This is exactly the situation we have in Equation (4).[4] So we now know what the solution is for $f(v_x^2)$:

$$f(v^{x^2}) = ae^{-bv_x^2} \tag{16}$$

Let's normalize this function.

$$\int_{-\infty}^{\infty} ae^{-bv_x^2} dv_x = 1 \tag{17}$$

This integral has to be looked up in tables. It turns out that its value is $\sqrt{(}b/\pi)$. So to make the integral equal to 1 we must have:

$$a = \left[\frac{b}{\pi}\right] \tag{18}$$

with the result that:

$$f(v^{x^2}) = (b/\pi)^{1/2} e^{-bv_x^2} \tag{19}$$

Now we have to evaluate b. One way to do this is to make use of a previous result. It has been shown that

$$< v_x^2 > = RT/M \tag{20}$$

where M is the molecular weight of the gas. Now we can calculate $< v_x^2 >$ from Equation (19):

$$< v_x^2 > = \int_{-\infty}^{\infty} v_x^2 \times (b/\pi)^{1/2} e^{-bv_x^2} = \frac{1}{2b} \tag{21}$$

where I've had to look up the integral. From Equations (20) and (21) we have

$$b = \frac{M}{2RT} \tag{22}$$

and

$$f(v_x^2) = \left(\frac{M}{2\pi RT}\right)^{1/2} e^{-\frac{Mv_x^2}{2RT}} \tag{23}$$

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[3] Check it out. Plug Equation (15) back into Equation (14) and see if it doesn't work!

[4] Go ahead and look at Equation (4). I'll wait.

We are now almost done. We know that $f(v_y^2)$ and $f(v_z^2)$ are identical to $f(v_x^2)$ if we just substitute v_y (or v_z) for v_x. Putting the pieces together gives:

$$f(v_x^2 + v_y^2 + v_z^2) \;=\; \left(\frac{M}{2\pi RT}\right)^{3/2} \exp\left[-\frac{M(v_x^2 + v_y^2 + v_z^2)}{2RT}\right] \tag{24}$$

This is the distribution of velocities. It is symmetric about zero and tails off quickly as the velocities increase.

Of interest is the distribution of *speeds*. That is slightly different than Equation (24) although we can get it from that equation. The difference is this: the velocity distribution depends on the three components of velocity. There are three variables. For the speed, there is only one.

To get the speed distribution we have to integrate Equation (24) over all directions. That involves changing the variables from *x*-, *y*-, and *z*- components to *s*, the speed, and two angles. Similarly $dv_x dv_y dv_z$ must also be transformed. Then one integrates over the two angles. The result is:[5]

$$g(s)ds \;=\; 4\pi\left(\frac{M}{2\pi RT}\right)^{3/2} s^2 e^{-\frac{Ms^2}{2RT}}\, ds \tag{25}$$

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[5] I've not only spared *you* the pain of doing this (doing it adds nothing to your physical understanding), I also spare myself the pain of typing it out...