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# STATISTICAL PHYSICS

## 1 Introduction

sec:Intro

We discuss elements of Statistical Physics. This topic will be revisited in the Spring Quarter of your junior year. It is thought that some of its results should not have to wait that long but obviously the material is quite challenging. Physics 4 as opposed to Physics 2 is still a good forum for presenting simple elements of Statistical Physics.

We will start with a derivation of the Boltzmann Factor by example. It is not a proof, that has to wait two years, but the example makes the Boltzmann Factor plausible. This will be followed by an application to the velocities of atoms and molecules in gases. This necessitates a discussion of Probability and how Probability can be used to calculate averages of physical quantities. Concepts of statistics are well worth your time to study as they are applicable to areas of physics and error analysis in experimental physics that go well beyond the material of Physics 4B. We will end with proofs of the Equal Partion of Energy law.

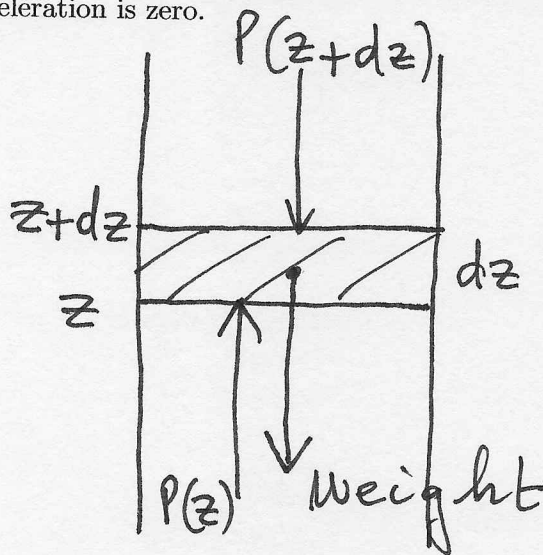
## 2 Barometric Formula

sec:BarFor

Consider a column of gas in a gravitational field. You could think of a column of air of the earth's atmosphere. For simplicity we assume that the air is in equilibrium which requires that the temperature  $T$  is constant independent of height  $z$  above the surface of the earth. The area of the cross section of the column is  $A$ . We shall take the positive  $z$ -direction vertically upward. In the figure we show the column and a narrow horizontal slab of

it with height  $dz$ . We assume that  $dz$  is "small". We will use Newton's Second Law to study what will happen to the slab of gas. Because of the equilibrium conditions the acceleration of the gas in the slab is zero.

We want to sum all forces acting on the slab and set that sum to zero because its acceleration is zero.



The pressure below the slab is  $P(z)$  pointing upward while the pressure above the slab is  $P(z + dz)$  and is pointing downward. Of course pressure at a certain value of  $z$  points equally in all directions but we are interested in the pressure acting on the slab in the  $z$ -direction. The gravitational force acting on the gas in the slab is equal to the force  $mg$  acting on one atom or molecule times the acceleration of gravity  $g$ . If we multiply this force by the number of atoms or molecules in the slab we get the total gravitational force on the slab. If the density of atoms or molecules is  $n(z)$  per unit volume and the volume is  $A dz$  we find that the total gravitational force is  $n(z) A dz m g$ . We expect the density to be dependent upon  $z$  and show that in the equation. Summing all three forces acting on the slab and apply Newton's Second Law we find

$$+AP(z) - AP(z + dz) - n A dz m g = 0 \quad (1)$$

eq:A1

From a Taylor Series expansion of  $P(z + dz)$  around  $z$  we find

$$P(z + dz) = P(z) + dz \frac{dP}{dz} + O(dz)^2 \quad (2)$$

eq:A2

where we truncated the series after two terms because we assume that  $dz$  is “small” so terms with  $(dz)^2$  and higher powers of  $dz$  are even smaller. Substitution of (2) in (1) and simplifying the result gives

$$\frac{dP}{dz} = -n m g \quad (3)$$

eq:A3

We see that the pressure  $P$  decreases with increasing values of  $z$ . The decrease is larger the more mass the atoms or molecules have so if we consider a column of air the density of oxygen drops faster than the density of nitrogen. This is as expected.

We use the ideal gas law to obtain a relation between pressure  $P$  and density  $n$ . For 1 kmol of gas the ideal gas law reads  $P V = R T$ . If we have  $N(z)$  (not  $n(z)$ ) total number atoms or molecules in the slab and thus  $N(z)/N_A$  kmols of gas in the slab the ideal gas law applied to the slab of gas becomes

$$P V = N(z) k T \quad (4)$$

eq:A4

with  $k$  Boltzmann’s constant and  $V$  the volume under consideration, here the slab of gas. We use that  $n(z) = N(z)/V$  in (4) to get

$$P = n(z) k T \quad (5)$$

eq:A5

We differentiate this equation with respect to  $z$  and because we assume that  $T$  is constant independent of  $z$  (this assumption is manifestly incorrect but we make it anyway) we get

$$\frac{dP}{dz} = \frac{dn}{dz} k T \quad (6)$$

eq:A6

We eliminate  $dP/dz$  between (6) and (3) to get

$$\frac{dn}{dz} = -\frac{m g}{k T} n(z) \quad (7)$$

eq:A7

This is a homogeneous and linear differential equation of first order with



constant coefficients. These are among the simplest to solve. To solve it we rewrite (7) as

$$\frac{dn}{n} = -\frac{mg}{kT} dz \quad (8)$$

eq:A8

and integrate both sides. We get

$$\ln n(z) = -\frac{mg}{kT} z + C \quad (9)$$

eq:A9

where  $C$  is a constant yet to be determined. It appears because we do an indefinite integration. We solve for  $n$  in (9) by exponentiation

$$n(z) = e^{-mgz/(kT)+C} = C' e^{-mgz/(kT)} \quad (10)$$

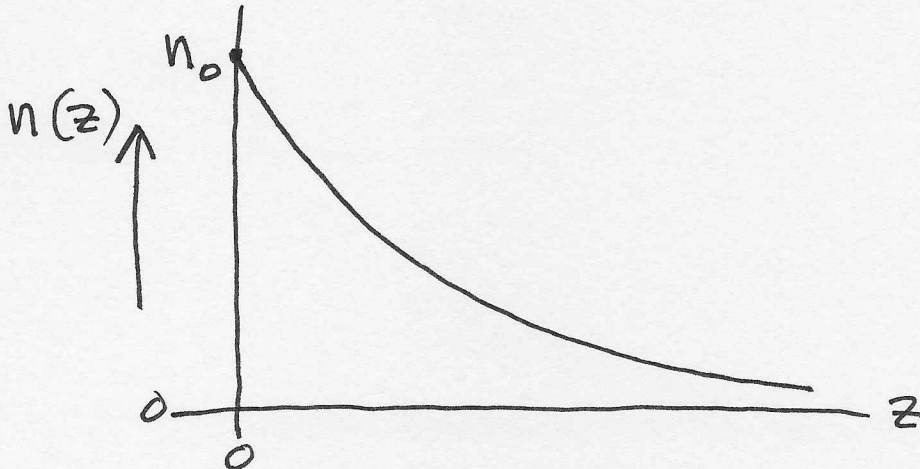
eq:A10

The constant  $C'$  is determined when we define the density of the number of atoms or molecules at  $z = 0$  as  $n_0$ . So finally the solution of (7) is

$$n(z) = n_0 e^{-mgz/(kT)} \quad (11)$$

eq:A11

The solution is plotted in the Figure. It is seen that the density  $n(z)$  drops exponentially to zero as  $z$  increases and that the drop is faster for atoms or molecules with larger masses.



The form of (11) is valid in general rather than only in this example.

The general form of the function can be written as

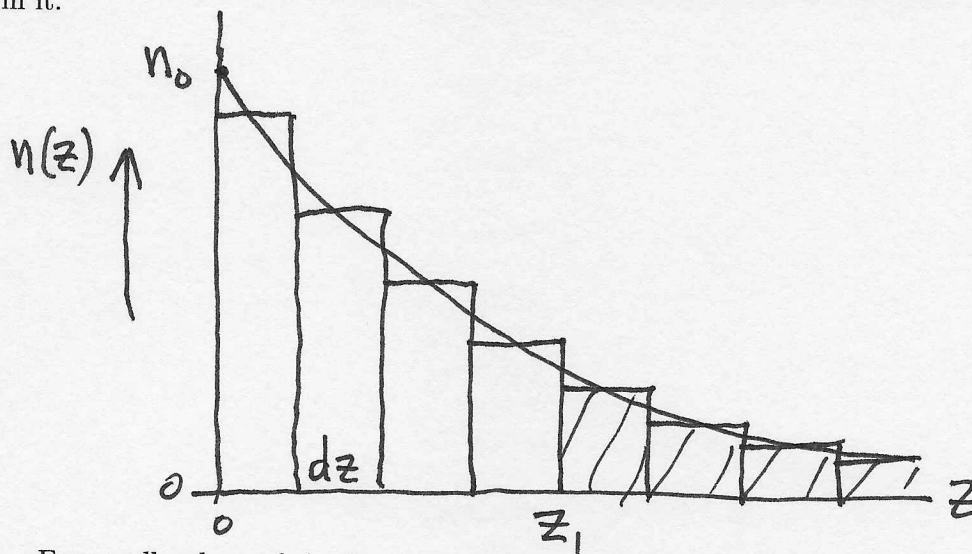
$$e^{-E/(kT)} \quad (12)$$

eq:A12

where  $E$  is either the potential energy or the kinetic energy of an atom or molecule or their sum. The expression in (12) is called the Boltzmann factor. As mentioned earlier, its proper derivation has to wait.

### 3 Statistics

We are now in a position to answer some questions about the distribution of the position of the density of atoms or molecules within the column. For example we can ask how many atoms or molecules are found at a height greater than  $z_1$ . To answer this question we "bin" the density of atoms or molecules by dividing the abscissa in many "bins". The binning is shown in the figure. Each bin is labeled by the value of  $z$  at its center. We take the "bin width" to be  $dz$  where we assume that  $dz$  is "small". Binning means that we ask which densities of atoms or molecules fall into each bin. A bin with  $z$  in the interval  $[z, z + dz]$  has  $n(z) dz$  density of atoms or molecules in it.



For small values of  $dz$  the density of atoms or molecules in the bin is seen to be proportional to  $dz$  as desired. To find the density of atoms or molecules with their  $z \geq z_1$  we need to sum the density of atoms or molecules

in each bin that is to the right of the bin labeled by  $z_1$ . It does not matter whether the value of  $z$  we assign to the bin is its left boundary, center, or right boundary because we will take the limit  $dz \rightarrow 0$ . The sum is evidently the cross-hatched area in the figure and is given by

$$\int_{z_1}^{\infty} n_0 e^{-mgz/(kT)} dz = n_0 \frac{kT}{mg} e^{-mgz_1/(kT)} \quad (13)$$

eq:B1

When  $z_1 = 0$  this should be equal to the total density of atoms or molecules in the column and we find that that equals  $n_0 kT/(mg)$ . When  $z_1 = \infty$  we see that the density of atoms or molecules exceeding the height  $z_1$  is zero, as expected.

We can now ask about the probability that the density of atoms or molecules has a height  $z$  exceeding  $z_1$ . This probability is the density of atoms or molecules with  $z > z_1$  divided by the total density of atoms or molecules. Using (13) this probability  $P$  is given by

$$P = \frac{n_0 \frac{kT}{mg} e^{-mgz_1/(kT)}}{n_0 \frac{kT}{mg}} = e^{-mgz_1/(kT)} \quad (14)$$

eq:B2

When  $z_1 = 0$  we find that  $P = 1$ . Of course all atoms and molecules have a  $z \geq 0$  so the probability to find any density at  $z \geq 0$  is 1. Similarly when  $z_1 = \infty$  we find that  $P = 0$  as expected.

We can ask about the average height of an atom or molecule. Each bin with density  $n(z) dz$  of atoms or molecules in it has a value of  $z$  assigned to it. To get the average  $\langle z \rangle$  of  $z$  we must evaluate

$$\langle z \rangle = \frac{\int_0^{\infty} z n_0 e^{-mgz/(kT)} dz}{\int_0^{\infty} n_0 e^{-mgz/(kT)} dz} \quad (15)$$

eq:B3

The numerator is a sum over bins with density  $n(z) dz$  of atoms or molecules in each bin that has its specific value of  $z$ . There two quantities are multiplied together because one indicates the density of atoms or molecules with a value of  $z$  between  $z$  and  $z + dz$  and the second indicates the value of  $z$  that belongs to that density. The denominator is the total density of atoms or molecules as above. You see that  $n_0$  cancels, this is true for any multiplicative constant.



If you have trouble understanding (15) consider the simple example of calculating the average of 10 numbers: 3, 1, 2, 1, 2, 3, 1, 2, 2, 1. Their average is  $18 / 10 = 1.8$ . One could also bin the numbers in 3 bins: 0.5 - 1.5 (4 entries), 1.5 - 2.5 (4 entries), and 2.5 - 3.5 (2 entries). A calculation of the average is now:  $(4 \times 1 + 4 \times 2 + 2 \times 3) / (4 + 4 + 2) = 1.8$ . We multiply the number of entries in a bin (the “weight”) by the center of the bin and sum over all bins (3 here). We then sum the entries in each bin to get the total number (10) and divide by it. The latter average is called a weighted average. A plot of the binned numbers is called a histogram. If someone gives you such a histogram of numbers without the numbers themselves you can still figure out their total number and their mean from the histogram alone. When the numbers are real numbers instead of integers the average and the weighted average may differ depending upon the binsize. Do you understand why?

To evaluate the integrals in (15) we use a trick. This trick will be used later as well and is useful in other fields of science. Consider

$$\int_0^{\infty} e^{-\alpha x} dz = \frac{1}{\alpha} \quad (16)$$

eq:B4

Here  $\alpha = mg/(kT)$ . The left-hand side and the righthand side are functions of  $\alpha$ . So we can differentiate each side with respect to  $\alpha$  to get

$$\int_0^{\infty} z e^{-\alpha x} dz = \frac{1}{\alpha^2} \quad (17)$$

eq:B5

This result could also have been obtained by partial integration. We shall use this trick later when partial integration will not work. Using these results in (15) we find that

$$\langle z \rangle = \frac{\int_0^{\infty} z n_0 e^{-mgz/(kT)} dz}{\int_0^{\infty} n_0 e^{-mgz/(kT)} dz} = \frac{1/\alpha^2}{1/\alpha} = \frac{1}{\alpha} = \frac{kT}{mg} \quad (18)$$

eq:B6

We see that the average height increases with temperature and decreases with mass. This makes sense because atoms' and molecules' velocity increases with temperature so they reach higher altitudes but the affect of gravity works the other way. Equation (11) shows that the density of atoms or molecules has dropped by a factor  $1/e$  from its value at  $z = 0$ . When

in (14)  $z_1 = \langle z \rangle$  we see that the probability for an atom or molecule to exceed their average height is  $1/e$ .

The differential probability  $dP(z)$  to find a density  $n(z)$  of atoms or molecules at height between  $z$  and  $z + dz$  is

$$dP(z) = \frac{n(z) dz}{\int_0^\infty n(z) dz} = \frac{mg}{kT} e^{-mgz/(kT)} dz \quad (19)$$

eq:B7

where (11) was used for  $n(z)$  and the common factor  $n_0$  has been canceled between numerator and denominator. The probability  $dP(z)$  is differential because the rest of the equation is differential in  $dz$ . This differential probability is obviously bounded by 0 and 1 as it should be. Using (19) and the discussion below (13) one sees that the differential probability  $dP$  integrates to 1 so it is normalized to 1 as a proper probability should be. This means that is the total probability of any density  $n(z)$  is 1 as it should be. In the simple example above this corresponds to saying that the probability to find a number in bin 1 equals entries in bin1 / total =  $4/10 = 0.4$ , for bin2 also the probability is 0.4, and for bin 3 the probability is  $2/10 = 0.2$ . Note that the three probabilities add up to 1.0. Sometimes people do not want to divide by denominators when doing calculations and use  $P(z)$  instead of  $n(z)$ . For example, using  $dP(z)$  from (19) in (15) instead of  $n(z)$  we get

$$\langle z \rangle = \int_0^\infty z dP(z) \quad (20)$$

eq:B8

It's the same amount of work but the last equation looks more elegant. Note that the probability is  $dP(z)$ , not  $P(z)$ , to find  $z$  in the range between  $z$  and  $z + dz$ .

## 4 Application to Monoatomic Gases

sec:Gases

We will now apply the concepts of Section 2 to gases, first to calculate the average of the square of the velocity of atoms or molecules along the  $x$ -axis. We expect that the average of the velocity along any axis is zero because such projections are equally likely to be positive or negative. Consider an atom or molecule between two collisions. Its motion is specified by six variables:  $x, y, z, v_x, v_y, v_z$ . Because between collisions the particle is free its



acceleration is zero and is therefore not listed. When we bin the particle's variables we see that we are dealing with binning in more than one variable. In the most general case we must bin in all six variables and ask for the probability that an atom or molecule has its  $x$  position in the interval  $[x, x + dx]$ , its  $y$  position in the interval  $[y, y + dy]$ , its  $z$  position in the interval  $[z, z + dz]$ , its  $v_x$  velocity component in the interval  $[v_x, v_x + dv_x]$ , its  $v_y$  velocity component in the interval  $[v_y, v_y + dv_y]$ , and its  $v_z$  velocity component in the interval  $[v_z, v_z + dv_z]$ . The size of this six-dimensional bin is  $dx dy dz dv_x dv_y dv_z$ . This looks worse than it usually is because we often only care about either one or three of these six variables. We use the Boltzmann Factor  $\exp(-E/(kT))$  from (12) discussed in Section 2 where the energy  $E$  can be either kinetic or potential energy. We are now ready to write down the expression for  $\langle v_x^2 \rangle$ . In analogy with (15) we get

$$\langle v_x^2 \rangle = \frac{\int_{-\infty}^{\infty} v_x^2 e^{-\frac{1}{2}mv_x^2/(kT)} dv_x}{\int_{-\infty}^{\infty} e^{-\frac{1}{2}mv_x^2/(kT)} dv_x} \quad (21)$$

eq:C1

The variable  $z$  in (15) is  $v_x$  here and the energy  $E$  is  $\frac{1}{2}mv_x^2$  instead of  $mgz$ . This integral can be done by using a trick. For the denominator we must evaluate an integral of the form

$$\int_{-\infty}^{+\infty} e^{-\alpha x^2} dx \quad (22)$$

eq:C2

where  $\alpha = \frac{1}{2}m/(kT)$ , see (21) and we have temporarily changed the integration limits. Instead we will evaluate its square

$$\left[ \int_{-\infty}^{+\infty} e^{-\alpha x^2} dx \right] \left[ \int_{-\infty}^{+\infty} e^{-\alpha y^2} dy \right] = \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} e^{-\alpha(x^2+y^2)} dx dy \quad (23)$$

eq:C3

This integral look more complicated but we can actually do it. We go from rectangular  $(x, y)$  coordinates to  $(r, \phi)$  polar coordinates. The change of variables replaces  $dx dy$  by  $r dr d\phi$  where the factor  $r$  is the Jacobian of the transformation. The integration limits change to 0 and  $\infty$  for  $r$  and 0 and  $2\pi$  for  $\phi$ . Thus (23) becomes

$$\int_0^{\infty} \int_0^{2\pi} e^{-\alpha r^2} r dr d\phi \quad (24)$$

eq:C4

The integrand does not contain the variable  $\phi$  so we can do the integral over  $\phi$  to get  $2\pi$ . The integral over  $r$  can be done because  $r dr = \frac{1}{2} d(r^2)$  and  $r^2$  appears also in the exponent so the integration variable is really  $r^2$ .

$$\int_0^\infty e^{-\alpha r^2} \frac{1}{2} d(r^2) = \frac{1}{2} \left[ \frac{e^{-\alpha r^2}}{-\alpha} \right]_0^\infty = \frac{1}{2\alpha} \quad (25)$$

eq:C5

Putting it all together we get that (24) becomes

$$\int_0^{+\infty} \int_0^{2\pi} e^{-\alpha r^2} r dr d\phi = \frac{\pi}{\alpha} \quad (26)$$

eq:C6

We now take the square-root and find that (22) becomes

$$\int_{-\infty}^{+\infty} e^{-\alpha x^2} dx = \sqrt{\frac{\pi}{\alpha}} \quad (27)$$

eq:C7

We will need this integral with its integrand multiplied by  $x^2$  and  $x^4$ . We can get these integrals by using the same trick we used in the previous Section near (16) and (17): Differentiate (27) with respect to  $\alpha$ . We find

$$\int_{-\infty}^{+\infty} x^2 e^{-\alpha x^2} dx = \frac{1}{2} \sqrt{\frac{\pi}{\alpha^3}} \quad (28)$$

eq:C8

Differentiate this equation with respect to  $\alpha$  and get

$$\int_{-\infty}^{+\infty} x^4 e^{-\alpha x^2} dx = \frac{3}{4} \sqrt{\frac{\pi}{\alpha^5}} \quad (29)$$

eq:C9

The integrands in (28) and (29) are even in the integration variable  $x$  so changing the lower integration limit from  $-\infty$  to 0 gives a factor  $\frac{1}{2}$  in the result.

Returning to (21) with  $\alpha = \frac{1}{2}m/(kT)$  and use (28) in the numerator and (27) in the denominator to get

$$\langle v_x^2 \rangle = \frac{\frac{1}{2} \sqrt{\pi/\alpha^3}}{\sqrt{\pi/\alpha}} = \frac{1}{2\alpha} = \frac{kT}{m} \quad (30)$$

eq:C10

We see that the average of the  $x$ -component squared of the velocity goes to zero as the temperature approaches absolute zero and that heavier atoms or molecules move slower. We can now calculate the average kinetic energy due to the  $x$ -component of the velocity and get

$$\langle \frac{1}{2}mv_x^2 \rangle = \frac{1}{2}m \langle v_x^2 \rangle = \frac{1}{2}kT \quad (31)$$

eq:C11

The average kinetic energy due to the  $x$ -component of the velocity of an atom or molecule is  $\frac{1}{2}kT$  independent of their mass so it is the same for any type of gas. For example, two different gases in the same volume in equilibrium at a given temperature will share the available energy equally on average between their atoms or molecules irrespective of difference in the mass of their atoms or molecules. Of course the  $x$ -direction is not special so the above results also apply to  $v_y$  and  $v_z$  and all three components of the velocity carry on average the same amount of energy. This is called Equipartition of Energy. We shall see that the equipartition extends beyond independence of type of gas.

At this point one can verify that indeed  $\langle v_x \rangle = 0$  because in analogy with (21) it is given by

$$\langle v_x \rangle = \frac{\int_{-\infty}^{+\infty} v_x e^{-\frac{1}{2}mv_x^2/(kT)} dv_x}{\int_{-\infty}^{+\infty} e^{-\frac{1}{2}mv_x^2/(kT)} dv_x} \quad (32)$$

eq:C12

It is seen that the integrand of the integral in the numerator is an odd function of  $v_x$  and we integrate from  $-\infty$  to  $+\infty$ , symmetrically around  $v_x = 0$  so that integral is zero. The denominator is not zero because the integrand is positive for all  $v_x$ .

We next calculate  $\langle v^2 \rangle$ . Because  $E = \frac{1}{2}mv^2 = \frac{1}{2}m(v_x^2 + v_y^2 + v_z^2)$  we now must deal with three variables instead of one as above. Our binning is now done in three dimensions  $v_x, v_y, v_z$  instead of one dimension. In analogy with (21) we must calculate

$$\langle v^2 \rangle = \frac{\int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} v^2 e^{-\frac{1}{2}m(v_x^2 + v_y^2 + v_z^2)/(kT)} dv_x dv_y dv_z}{\int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} e^{-\frac{1}{2}m(v_x^2 + v_y^2 + v_z^2)/(kT)} dv_x dv_y dv_z} \quad (33)$$

eq:C13

To evaluate the integral we transform the rectangular coordinates  $(x, y, z)$



of freedom, see (21), and translational motion has 3 degrees of freedom ( $v_x, v_y, v_z$ ) so the energy per degree of freedom gets multiplied by 3. Two different gases in the same volume in equilibrium at a given temperature will share the available energy on average equally between their atoms or molecules irrespective of the mass and thus independent of the type of gas. This is another example of the Equipartition of Energy. We shall see that the equipartition extends beyond independence of type of gas.

The above results confirm the relation between temperature and kinetic energy that was used when we discussed the derivation of the Ideal Gas Law using Newton's Second Law when studying collisions between atoms and molecules and the wall of the vessel in which they are contained.

Question: Have we derived the relation between kinetic energy and temperature that was postulated when deriving the Ideal Gas Law? (Think about where the factor  $k$  in the Boltzmann Factor came from!)

## 5 Application to Diatomic Gases

Consider a gas consisting of diatomic molecules where each molecule consists of two atoms. These atoms can be identical or different. The two atoms are bound together by a chemical bond. A physicist's model of such a molecule consists of two point particles connected together by a spring with spring constant  $K$  (we use capital  $K$  to avoid confusion with Boltzmann's constant  $k$ ). The atoms can vibrate around their equilibrium position causing the spring to be stretched or compressed. The potential energy associated with the spring's change in length is  $U = \frac{1}{2}Kx^2$  where  $x$  is the change in length of the spring relative to its equilibrium length. The value of  $x$  can be positive (for a stretched spring) or negative (for a compressed spring). The average potential energy of a vibrating diatomic molecule is in analogy with (21) given by

$$\langle U \rangle = \frac{\int_{-\infty}^{+\infty} (\frac{1}{2}Kx^2) e^{-\frac{1}{2}Kx^2/(kT)} dx}{\int_{-\infty}^{+\infty} e^{-\frac{1}{2}Kx^2/(kT)} dx} \quad (38)$$

We set  $\alpha = \frac{1}{2}K/(kT)$  and find that

$$\langle U \rangle = \frac{(\frac{1}{2}K) \int_{-\infty}^{+\infty} x^2 e^{-\alpha x^2/(kT)} dx}{\int_{-\infty}^{+\infty} e^{-\alpha x^2/(kT)} dx} \quad (39)$$

The numerator and denominator's integrals can be taken from (28) and (27) respectively giving

$$\langle U \rangle = \frac{K \frac{1}{2} \sqrt{\pi} \alpha^{-3/2}}{2 \sqrt{\pi} \alpha^{-1/2}} = \frac{K}{4\alpha} \quad (40)$$

When we substitute  $\alpha = \frac{1}{2}K/(kT)$  we get

$$\langle U \rangle = \frac{K}{4} \frac{kT}{\frac{1}{2}K} = \frac{1}{2}kT \quad (41)$$

We know from our study of the Harmonic Oscillator that it has equal amounts of average potential and average kinetic energy so using (41) we may set

$$\langle K \rangle = \langle U \rangle = \frac{1}{2}kT \quad (42)$$

so the total average energy is given by  $\langle E \rangle = \langle U \rangle + \langle K \rangle = kT$ . This corresponds to two degrees-of-freedom, one from average potential energy and one from average kinetic energy. This result does not contain the masses of the atoms in the diatomic molecule so the result is valid for any diatomic molecule. The result also does not depend upon the spring constant  $K$  so weak and strong chemical bonds lead to the same  $\frac{1}{2}kT$ . If  $K$  is large the vibration must have a smaller amplitude and vice versa. This is another example of the Equipartition of Energy because the energy is the same as the energy related to kinetic energy of translation along one coordinate axis and is the same for all diatomic gases. This is a really remarkable result but contains a contradiction. Assume that we let the spring constant  $K$  go to zero. The average potential energy does not change according to (41). When  $K$  is infinitely close to zero that average potential energy is still  $\frac{1}{2}kT$ . That can not be and indeed Quantum Physics will modify this result in a significant and deep manner. This is the first (?) indication you have in Physics 4 that something might be wrong with Classical Physics That is ultimately governed by Newton's Laws. So that must mean that Newton's Laws need modification. A shocking conclusion!

Diatomic molecules also can rotate. There are three possible mutually perpendicular rotation axes. One is along the line connecting the two atoms, call this the  $y$ -axis and the other two are perpendicular to this line and perpendicular to each other. The axes pass through the center-of-mass of the molecule. If the two atoms are identical the center-of-mass is in the

middle between the two atoms. If the atoms are different the location of the center-of-mass must be calculated. There are three inertial moments:  $I_x, I_y, I_z$ . Review the Physics 4A material about their definitions. Because we assume that the atoms are point particles  $I_y = 0$ .  $I_x$  and  $I_z$  are equal to  $(m_1 + m_2) \ell^2 / 4$ . The kinetic energy of the rotating molecule is  $E = \frac{1}{2} I \omega^2$  where  $I$  equal  $I_x$  when the rotation axis is along the  $x$ -axis and  $I_z$  if the rotation axis is along the  $z$ -axis. We will consider the latter case. The average kinetic energy of the rotating molecule is given by

$$\langle E \rangle = \frac{\int_{-\infty}^{+\infty} (\frac{1}{2} I_z \omega^2) e^{-\frac{1}{2} I_z \omega^2 / (kT)} d\omega}{\int_{-\infty}^{+\infty} e^{-\frac{1}{2} I_z \omega^2 / (kT)} d\omega} \quad (43)$$

Here angular velocity  $\omega$  is the variable that needs to be binned in bins with bin width  $d\omega$  because it is the variable in the problem. The integration goes from  $-\infty$  to  $+\infty$  because  $\omega$  can be positive and negative. As before we introduce  $\alpha = \frac{1}{2} I_z / (kT)$  and write (42) as

$$\langle E \rangle = \frac{(\frac{1}{2} I_z) \int_{-\infty}^{+\infty} \omega^2 e^{-\alpha \omega^2 / (kT)} d\omega}{\int_{-\infty}^{+\infty} e^{-\alpha \omega^2 / (kT)} d\omega} \quad (44)$$

The numerator and denominator's integrals can be taken from (28) and (27) respectively giving

$$\langle E \rangle = \frac{I_z \frac{1}{2} \sqrt{\pi} \alpha^{-3/2}}{2 \sqrt{\pi} \alpha^{-1/2}} = \frac{I_z}{4 \alpha} \quad (45)$$

When we substitute  $\alpha = \frac{1}{2} I_z / (kT)$  we get

$$\langle E \rangle = \frac{I_z \frac{1}{2} \sqrt{\pi} \alpha^{-3/2}}{2 \sqrt{\pi} \alpha^{-1/2}} = \frac{I_z}{4 \alpha} = \frac{1}{2} kT \quad (46)$$

Are you are getting used to the calculations? You begin to see where the Equipartition of Energy originates. Again, this result does not contain the masses of the atoms in the diatomic molecule so the result is valid for any diatomic molecule. The result also does not depend upon the inertial moment  $I_z$  so large and small inertial moments lead to the same  $\frac{1}{2} kT$ . If  $I_z$  is large the angular velocity must be smaller and vice versa. The calculation holds when we replace  $I_z$  by  $I_x$  so the average kinetic energy of a molecule that rotates around the  $x$ -axis is also  $\frac{1}{2} kT$ .



This is yet another example of the Equipartition of Energy because the energy is the same as the energy related to kinetic energy of translation along one coordinate axis and the vibrational energy, the same for all diatomic gases. The number of degrees of freedom for rotations is 2, not 3 because rotations around one of the three axes do not carry kinetic energy.

## 6 Summary

A monoatomic molecule has 3 degrees of freedom corresponding to  $(v_x, v_y, v_z)$  while a diatomic molecule has 7 degrees of freedom corresponding to the same three degrees of freedom  $(v_x, v_y, v_z)$  (3), vibration (2), and rotation (2). Each of these degrees of freedom carries  $\frac{1}{2} k T$  irrespective of mass, spring constant, inertial moment, or type of gas.

Note that the total energy per molecule is different for an monoatomic gas than for a diatomic gas and that this fact does not violate the Equipartition of Energy. Temperature is still proportional to the kinetic energy of the center-of-mass with the same proportionality constant for all gases as per Equipartition of Energy. There is no energy flow from diatomic molecules to monoatomic molecules if they are in the same container even though they have different energy. Compare two containers of water, both at the same temperature, but one much larger than the other. Even though the larger container contains more energy than the smaller container there is no flow of heat (energy) from the larger container to the smaller container.