The Principles of Statistical Mechanics

40-1 The exponential atmosphere

We have discussed some of the properties of large numbers of intercolliding atoms. The subject is called kinetic theory, a description of matter from the point of view of collisions between the atoms. Fundamentally, we assert that the gross properties of matter should be explainable in terms of the motion of its parts.

We limit ourselves for the present to conditions of thermal equilibrium, that is, to a subclass of all the phenomena of nature. The laws of mechanics which apply just to thermal equilibrium are called *statistical mechanics*, and in this section we want to become acquainted with some of the central theorems of this subject.

We already have one of the theorems of statistical mechanics, namely, the mean value of the kinetic energy for any motion at the absolute temperature T is $\frac{1}{2}kT$ for each independent motion, i.e., for each degree of freedom. That tells us something about the mean square velocities of the atoms. Our objective now is to learn more about the positions of the atoms, to discover how many of them are going to be in different places at thermal equilibrium, and also to go into a little more detail on the distribution of the velocities. Although we have the mean square velocity, we do not know how to answer a question such as how many of them are going three times faster than the root mean square, or how many of them are going one-quarter of the root mean square speed. Or have they all the same speed exactly?

So, these are the two questions that we shall try to answer: How are the molecules distributed in space when there are forces acting on them, and how are they distributed in velocity?

It turns out that the two questions are completely independent, and that the distribution of velocities is always the same. We already received a hint of the latter fact when we found that the average kinetic energy is the same, $\frac{1}{2}kT$ per degree of freedom, no matter what forces are acting on the molecules. The distribution of the velocities of the molecules is independent of the forces, because the collision rates do not depend upon the forces.

Let us begin with an example: the distribution of the molecules in an atmosphere like our own, but without the winds and other kinds of disturbance. Suppose that we have a column of gas extending to a great height, and at thermal equilibrium—unlike our atmosphere, which as we know gets colder as we go up. We could remark that if the temperature differed at different heights, we could demonstrate lack of equilibrium by connecting a rod to some balls at the bottom (Fig. 40-1), where they would pick up $\frac{1}{2}kT$ from the molecules there and would shake, via the rod, the balls at the top and those would shake the molecules at the top. So, ultimately, of course, the temperature becomes the same at all heights in a gravitational field.

If the temperature is the same at all heights, the problem is to discover by what law the atmosphere becomes tenuous as we go up. If N is the total number of molecules in a volume V of gas at pressure P, then we know $PV = NkT$, or $P = nkT$, where $n = N/V$ is the number of molecules per unit volume. In other words, if we know the number of molecules per unit volume, we know the pressure, and vice versa: they are proportional to each other, since the temperature is constant in this problem. But the pressure is not constant, it must increase as the altitude is reduced, because it has to hold, so to speak, the weight of all the gas above it. That is the clue by which we may determine how the pressure changes with height. If we take a unit area at height h, then the vertical force from below,
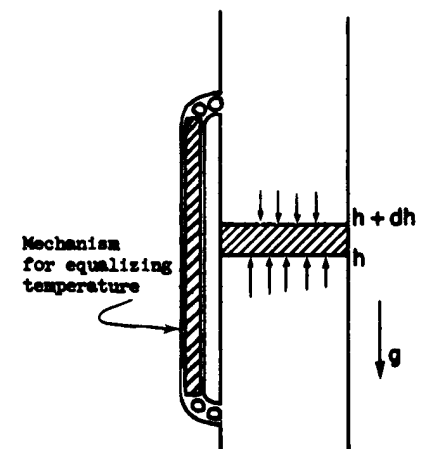
Fig. 40-1. The pressure at height h must exceed that at $h + dh$ by the weight of the intervening gas.

on this unit area, is the pressure P. The vertical force per unit area pushing down at a height $h + dh$ would be the same, in the absence of gravity, but here it is not, because the force from below must exceed the force from above by the weight of gas in the section between h and $h + dh$. Now mg is the force of gravity on each molecule, where g is the acceleration due to gravity, and $n\,dh$ is the total number of molecules in the unit section. So this gives us the differential equation $P_{h+dh} - P_h = dP = -mgn\,dh$. Since $P = nkT$, and T is constant, we can eliminate either P or n, say P, and get

$$\frac{dn}{dh} = -\frac{mg}{kT}\,n$$

for the differential equation, which tells us how the density goes down as we go up in energy.

We thus have an equation for the particle density n, which varies with height, but which has a derivative which is proportional to itself. Now a function which has a derivative proportional to itself is an exponential, and the solution of this differential equation is

$$n = n_0 e^{-mgh/kT}. \tag{40.1}$$

Here the constant of integration, n_0, is obviously the density at $h = 0$ (which can be chosen anywhere), and the density goes down exponentially with height.

Note that if we have different kinds of molecules with different masses, they go down with different exponentials. The ones which were heavier would decrease with altitude faster than the light ones. Therefore we would expect that because oxygen is heavier than nitrogen, as we go higher and higher in an atmosphere with nitrogen and oxygen the proportion of nitrogen would increase. This does not really happen in our own atmosphere, at least at reasonable heights, because there is so much agitation which mixes the gases back together again. It is not an isothermal atmosphere. Nevertheless, there *is* a tendency for lighter materials, like hydrogen, to dominate at very great heights in the atmosphere, because the lowest masses continue to exist, while the other exponentials have all died out (Fig. 40–2).
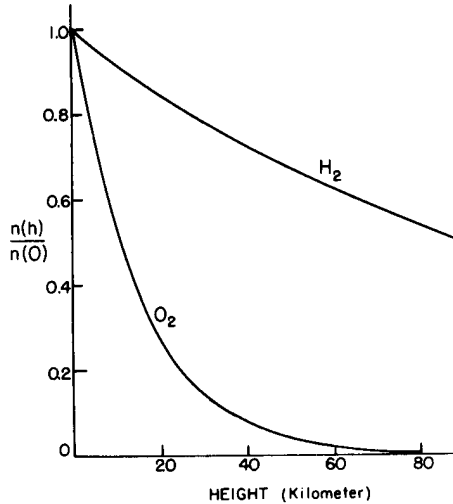

Fig. 40–2. The normalized density as a function of height in the earth's gravitational field for oxygen and for hydrogen, at constant temperature.

40–2 The Boltzmann law

Here we note the interesting fact that the numerator in the exponent of Eq. (40.1) is the *potential energy* of an atom. Therefore we can also state this particular law as: the density at any point is proportional to

$$e^{-(\text{the potential energy of each atom}/kT)}.$$

That may be an accident, i.e., may be true only for this particular case of a uniform gravitational field. However, we can show that it is a more general proposition. Suppose that there were some kind of force other than gravity acting on the molecules in a gas. For example, the molecules may be charged electrically, and may be acted on by an electric field or another charge that attracts them. Or, because of the mutual attractions of the atoms for each other, or for the wall, or for a solid, or something, there is some force of attraction which varies with position and which acts on all the molecules. Now suppose, for simplicity, that the molecules are all the same, and that the force acts on each individual one, so that the total force on a piece of gas would be simply the number of molecules times the force on each one. To avoid unnecessary complication, let us choose a coordinate system with the x-axis in the direction of the force, **F**.

In the same manner as before, if we take two parallel planes in the gas, separated by a distance dx, then the force on each atom, times the n atoms per cm^3 (the generalization of the previous nmg), times dx, must be balanced by the pressure change: $Fn\,dx = dP = kT\,dn$. Or, to put this law in a form which will be useful to us later,

$$F = kT\frac{d}{dx}(\ln n). \tag{40.2}$$

For the present, observe that $-F\,dx$ is the work we would do in taking a molecule from x to $x + dx$, and if F comes from a potential, i.e., if the work done can be represented by a potential energy at all, then this would also be the difference in the potential energy (P.E.). The negative differential of potential energy is the work done, $F\,dx$, and we find that $d(\ln n) = -d(\text{P.E.})/kT$, or, after integrating,

$$n = (\text{constant})e^{-\text{P.E.}/kT}. \tag{40.3}$$

Therefore what we noticed in a special case turns out to be true in general. (What if F does not come from a potential? Then (40.2) has no solution at all. Energy can be generated, or lost by the atoms running around in cyclic paths for which the work done is not zero, and no equilbrium can be maintained at all. Thermal equilibrium cannot exist if the external forces on the atoms are not conservative.) Equation (40.3), known as *Boltzmann's law*, is another of the principles of statistical mechanics: that the probability of finding molecules in a given spatial arrangement varies exponentially with the negative of the potential energy of that arrangement, divided by kT.

This, then, could tell us the distribution of molecules: Suppose that we had a positive ion in a liquid, attracting negative ions around it, how many of them would be at different distances? If the potential energy is known as a function of distance, then the proportion of them at different distances is given by this law, and so on, through many applications.

40-3 Evaporation of a liquid

In more advanced statistical mechanics one tries to solve the following important problem. Consider an assembly of molecules which attract each other, and suppose that the force between any two, say i and j, depends only on their separation r_{ij}, and can be represented as the derivative of a potential function $V(r_{ij})$. Figure 40-3 shows a form such a function might have. For $r > r_0$, the energy decreases as the molecules come together, because they attract, and then the energy increases very sharply as they come still closer together, because they repel strongly, which is characteristic of the way molecules behave, roughly speaking.

Now suppose we have a whole box full of such molecules, and we would like to know how they arrange themselves on the average. The answer is $e^{-\text{P.E.}/kT}$. The total potential energy in this case would be the sum over all the pairs, supposing that the forces are all in pairs (there may be three-body forces in more complicated things, but in electricity, for example, the potential energy is all in pairs). Then the probability for finding molecules in any particular combination of r_{ij}'s will be proportional to

$$\exp\left[-\sum_{i,j} V(r_{ij})/kT\right].$$

Fig. 40-3. A potential-energy function for two molecules, which depends only on their separation.

Now, if the temperature is very high, so that $kT \gg |V(r_0)|$, the exponent is relatively small almost everywhere, and the probability of finding a molecule is almost independent of position. Let us take the case of just two molecules: the $e^{-\text{P.E.}/kT}$ would be the probability of finding them at various mutual distances r. Clearly, where the potential goes most negative, the probability is largest, and where the potential goes toward infinity, the probability is almost zero, which occurs for very small distances. That means that for such atoms in a gas, there is no chance that they are on top of each other, since they repel so strongly. But there is a greater chance of finding them *per unit volume* at the point r_0 than at any other point. How much greater, depends on the temperature. If the temperature is very large compared with the difference in energy between $r = r_0$ and $r = \infty$, the exponential is always nearly unity. In this case, where the mean kinetic energy (about kT) greatly exceeds the potential energy, the forces do not make much difference. But as the temperature falls, the probability of finding the molecules at the preferred distance r_0 gradually increases relative to the probability of finding them elsewhere and, in fact, if kT is much less than $|V(r_0)|$, we have a relatively
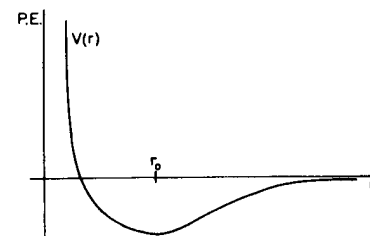
large positive exponent in that neighborhood. In other words, in a given volume they are *much more* likely to be at the distance of minimum energy than far apart. As the temperature falls, the atoms fall together, clump in lumps, and reduce to liquids, and solids, and molecules, and as you heat them up they evaporate.

The requirements for the determination of exactly how things evaporate, exactly how things should happen in a given circumstance, involve the following. First, to discover the correct molecular-force law $V(r)$, which must come from something else, quantum mechanics, say, or experiment. But, given the law of force between the molecules, to discover what a billion molecules are going to do merely consists of studying the function $e^{-\Sigma V_{ij}/kT}$. Surprisingly enough, since it is such a simple function and such an easy idea, given the potential, the labor is *enormously complicated;* the difficulty is the tremendous number of variables.

In spite of such difficulties, the subject is quite exciting and interesting. It is often called an example of a "many-body problem," and it really has been a very interesting thing. In that single formula must be contained all the details, for example, about the solidification of gas, or the forms of the crystals that the solid can take, and people have been trying to squeeze it out, but the mathematical difficulties are very great, not in writing the law, but in dealing with so enormous a number of variables.

That then, is the distribution of particles in space. That is the end of classical statistical mechanics, practically speaking, because if we know the forces, we can, in principle, find the distribution in space, and the distribution of velocities is something that we can work out once and for all, and is not something that is different for the different cases. The great problems are in getting particular information out of our formal solution, and that is the main subject of classical statistical mechanics.

40–4 The distribution of molecular speeds

Now we go on to discuss the distribution of velocities, because sometimes it is interesting or useful to know how many of them are moving at different speeds. In order to do that, we may make use of the facts which we discovered with regard to the gas in the atmosphere. We take it to be a perfect gas, as we have already assumed in writing the potential energy, disregarding the energy of mutual attraction of the atoms. The only potential energy that we included in our first example was gravity. We would, of course, have something more complicated if there were forces between the atoms. Thus we assume that there are no forces between the atoms and, for a moment, disregard collisions also, returning later to the justification of this. Now we saw that there are fewer molecules at the height h than there are at the height 0; according to formula (40.1), they decrease exponentially with height. How can there be fewer at greater heights? After all, do not all the molecules which are moving up at height 0 arrive at h? No!, because some of those which are moving up at 0 are going too slowly, and cannot climb the potential hill to h. With that clue, we can calculate how many must be moving at various speeds, because from (40.1) we know *how many* are moving with less than enough speed to climb a given distance h. Those are just the ones that account for the fact that the density at h is lower than at 0.

Now let us put that idea a little more precisely: let us count how many molecules are passing from below to above the plane $h = 0$ (by calling it height = 0, we do not mean that there is a floor there; it is just a convenient label, and there is gas at negative h). These gas molecules are moving around in every direction, but some of them are moving through the plane, and at any moment a certain number per second of them are passing through the plane from below to above with different velocities. Now we note the following: if we call u the velocity which is just needed to get up to the height h (kinetic energy $mu^2/2 = mgh$), then the number of molecules per second which are passing upward through the lower plane in a vertical direction with velocity component greater than u is exactly the same as the number which pass through the upper plane with *any* upward velocity. Those molecules whose vertical velocity does not exceed u cannot get through the upper
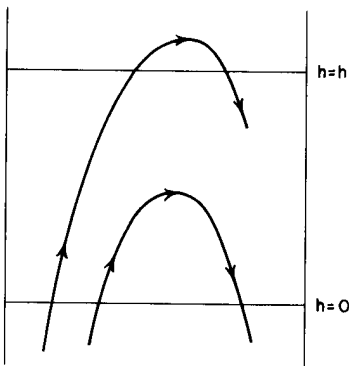

Fig. 40–4. Only those molecules moving up at $h = 0$ with sufficient velocity can arrive at height h.

40–4

plane. So therefore we see that

Number passing $h = 0$ with $v_z > u$ = number passing $h = h$ with $v_z > 0$.

But the number which pass through h with any velocity greater than 0 is less than the number which pass through the lower height with any velocity greater than 0, because the number of atoms is greater; that is all we need. We know already that the distribution of velocities is the same, after the argument we made earlier about the temperature being constant all the way through the atmosphere. So, since the velocity distributions are the same, and it is just that there are *more atoms* lower down, clearly the number $n_{>0}(h)$, passing with positive velocity at height h, and the number $n_{>0}(0)$, passing with positive velocity at height 0, are in the same ratio as the densities at the two heights, which is $e^{-mgh/kT}$. But $n_{>0}(h) = n_{>u}(0)$, and therefore we find that

$$\frac{n_{>u}(0)}{n_{>0}(0)} = e^{-mgh/kT} = e^{-mu^2/2kT},$$

since $\frac{1}{2}mu^2 = mgh$. Thus, in words, the number of molecules per unit area per second passing the height 0 with a z-component of velocity greater than u is $e^{-mu^2/2kT}$ times the total number that are passing through the plane with velocity greater than zero.

Now this is not only true at the arbitrarily chosen height 0, but of course it is true at any other height, and thus the distributions of velocities *are* all the same! (The final statement does not involve the height h, which appeared only in the intermediate argument.) The result is a general proposition that gives us the distribution of velocities. It tells us that if we drill a little hole in the side of a gas pipe, a very tiny hole, so that the collisions are few and far between, i.e., are farther apart than the diameter of the hole, then the particles which are coming out will have different velocities, but the fraction of particles which come out at a velocity greater than u is $e^{-mu^2/2kT}$.

Now we return to the question about the neglect of collisions: Why does it not make any difference? We could have pursued the same argument, not with a finite height h, but with an infinitesimal height h, which is so small that there would be no room for collisions between 0 and h. But that was not necessary: the argument is evidently based on an analysis of the energies involved, the conservation of energy, and in the collisions that occur there is an exchange of energies among the molecules. However, we do not really care whether we follow the same molecule if energy is merely exchanged with another molecule. So it turns out that even if the problem is analyzed more carefully (and it is more difficult, naturally, to do a rigorous job), it still makes no difference in the result.

It is interesting that the velocity distribution we have found is just

$$n_{>u} \propto e^{-\text{kinetic energy}/kT}. \tag{40.4}$$

This way of describing the distribution of velocities, by giving the number of molecules that pass a given area with a certain minimum z-component, is not the most convenient way of giving the velocity distribution. For instance, inside the gas, one more often wants to know how many molecules are moving with a z-component of velocity between two given values, and that, of course, is not directly given by Eq. (40.4). We would like to state our result in the more conventional form, even though what we already have written is quite general. *Note that it is not possible to say that any molecule has exactly some stated velocity;* none of them has a velocity *exactly* equal to 1.7962899173 meters per second. So in order to make a meaningful statement, we have to ask how many are to be found in some *range* of velocities. We have to say how many have velocities between 1.796 and 1.797, and so on. On mathematical terms, let $f(u)\,du$ be the fraction of all the molecules which have velocities between u and $u + du$ or, what is the same thing (if du is infinitesimal), all that have a velocity u with a range du. Figure 40–5 shows a possible form for the function $f(u)$, and the shaded part, of width du and mean height $f(u)$, represents this fraction $f(u)\,du$. That is, the ratio of the shaded
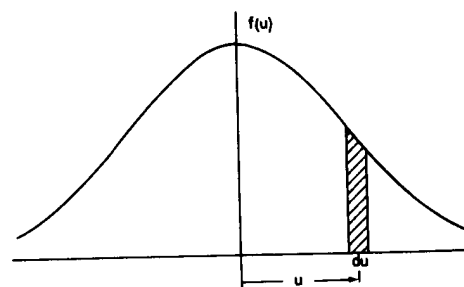

Fig. 40–5. A velocity distribution function. The shaded area is $f(u)\,du$, the fraction of particles having velocities within a range du about u.

area to the total area of the curve is the relative proportion of molecules with velocity u within du. If we define $f(u)$ so that the fraction having a velocity in this range is given directly by the shaded area, then the total area must be 100 percent of them, that is,

$$\int_{-\infty}^{\infty} f(u)\, du = 1. \tag{40.5}$$

Now we have only to get this distribution by comparing it with the theorem we derived before. First we ask, what is the number of molecules passing through an area per second with a velocity greater than u, expressed in terms of $f(u)$? At first we might think it is merely the integral of $\int_{u}^{\infty} f(u)\, du$, but it is not, because we want the number that are passing the area *per second*. The faster ones pass more often, so to speak, than the slower ones, and in order to express how many pass, you have to multiply by the velocity. (We discussed that in the previous chapter when we talked about the number of collisions.) In a given time t the total number which pass through the surface is all of those which have been able to arrive at the surface, and the number which arrive come from a distance ut. So the number of molecules which arrive is not simply the number which are there, but the number that are there per unit volume, multiplied by the distance that they sweep through in racing for the area through which they are supposed to go, and that distance is proportional to u. Thus we need the integral of u *times* $f(u)\, du$, an infinite integral with a lower limit u, and this must be the same as we found before, namely $e^{-mu^2/2kT}$, with a proportionality constant which we will get later:

$$\int_{u}^{\infty} u f(u)\, du = \text{const} \cdot e^{-mu^2/2kT}. \tag{40.6}$$

Now if we differentiate the integral with respect to u, we get the thing that is inside the integral, i.e., the integrand (with a minus sign, since u is the lower limit), and if we differentiate the other side, we get u times the same exponential (and some constants). The u's cancel and we find

$$f(u)\, du = C e^{-mu^2/2kT}\, du. \tag{40.7}$$

We retain the du on both sides as a reminder that it is a *distribution*, and it tells what the proportion is for velocity between u and $u + du$.

The constant C must be so determined that the integral is unity, according to Eq. (40.5). Now we can prove* that

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

Using this fact, it is easy to find that $C = \sqrt{m/2\pi kT}$.

Since velocity and momentum are proportional, we may say that the distribution of momenta is also proportional to $e^{-\text{K.E.}/kT}$ per unit momentum range. It turns out that this theorem is true in relativity too, if it is in terms of momentum, while if it is in velocity it is not, so it is best to learn it in momentum instead of in velocity:

$$f(p)\, dp = C e^{-\text{K.E.}/kT}\, dp. \tag{40.8}$$

So we find that the probabilities of different conditions of energy, kinetic and potential, are both given by $e^{-\text{energy}/kT}$, a very easy thing to remember and a rather beautiful proposition.

---

* To get the value of the integral, let

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

Then

$$I^2 = \int_{-\infty}^{\infty} e^{-x^2}\, dx \cdot \int_{-\infty}^{\infty} e^{-y^2}\, dy = \int_{-\infty}^{\infty}\int_{-\infty}^{\infty} e^{-(x^2+y^2)}\, dy\, dx,$$

which is a double integral over the whole xy-plane. But this can also be written in polar coordinates as

$$I^2 = \int_{0}^{\infty} e^{-r^2} \cdot 2\pi r\, dr = \pi \int_{0}^{\infty} e^{-t}\, dt = \pi.$$

So far we have, of course, only the distribution of the velocities "vertically." We might want to ask, what is the probability that a molecule is moving in another direction? Of course these distributions are connected, and one can obtain the complete distribution from the one we have, because the complete distribution depends only on the square of the magnitude of the velocity, not upon the z-component. It must be something that is independent of direction, and there is only one function involved, the probability of different magnitudes. We have the distribution of the z-component, and therefore we can get the distribution of the other components from it. The result is that the probability is still proportional to $e^{-\text{K.E.}/kT}$, but now the kinetic energy involves three parts, $mv_x^2/2$, $mv_y^2/2$, and $mv_z^2/2$, summed in the exponent. Or we can write it as a product:

$$f(v_x, v_y, v_z)\, dv_x\, dv_y\, dv_z$$
$$\propto e^{-mv_x^2/2kT} \cdot e^{-mv_y^2/2kT} \cdot e^{-mv_z^2/2kT}\, dv_x\, dv_y\, dv_z. \qquad (40.9)$$

You can see that this formula must be right because, first, it is a function only of v^2, as required, and second, the probabilities of various values of v_z obtained by integrating over all v_x and v_y is just (40.7). But this one function (40.9) can do both those things!

40-5 The specific heats of gases

Now we shall look at some ways to test the theory, and to see how successful is the classical theory of gases. We saw earlier that if U is the internal energy of N molecules, then $PV = NkT = (\gamma - 1)U$ holds, sometimes, for some gases, maybe. If it is a monatomic gas, we know this is also equal to $\frac{2}{3}$ of the kinetic energy of the center-of-mass motion of the atoms. If it is a monatomic gas, then the kinetic energy is equal to the internal energy, and therefore $\gamma - 1 = \frac{2}{3}$. But suppose it is, say, a more complicated molecule, that can spin and vibrate, and let us suppose (it turns out to be true according to classical mechanics) that the energies of the internal motions are also proportional to kT. Then at a given temperature, in addition to kinetic energy kT, it has internal vibrational or rotational energy. So the total U includes not just the internal kinetic energy, but also the rotational energy, and we get a different value of γ. Technically, the best way to measure γ is by measuring the specific heat, which is the change in energy with temperature. We will return to that approach later. For our present purposes, we may suppose γ is found experimentally from the PV^γ curve for adiabatic compression.

Let us make a calculation of γ for some cases. First, for a monatomic gas U is the total energy, the same as the kinetic energy, and we know already that γ should be $\frac{5}{3}$. For a diatomic gas, we may take, as an example, oxygen, hydrogen iodide, hydrogen, etc., and suppose that the diatomic gas can be represented as two atoms held together by some kind of force like the one of Fig. 40-3. We may also suppose, and it turns out to be quite true, that at the temperatures that are of interest for the diatomic gas, the pairs of atoms tend strongly to be separated by r_0, the distance of potential minimum. If this were not true, if the probability were not strongly varying enough to make the great majority sit near the bottom, we would have to remember that oxygen gas is a mixture of O_2 and single oxygen atoms in a nontrivial ratio. We know that there are, in fact, very few single oxygen atoms, which means that the potential energy minimum is very much greater in magnitude than kT, as we have seen. Since they are clustered strongly around r_0, the only part of the curve that is needed is the part near the minimum, which may be approximated by a parabola. A parabolic potential implies a harmonic oscillator, and in fact, to an excellent approximation, the oxygen molecule can be represented as two atoms connected by a spring.

Now what is the total energy of this molecule at temperature T? We know that for each of the two atoms, each of the kinetic energies should be $\frac{3}{2}kT$, so the kinetic energy of both of them is $\frac{3}{2}kT + \frac{3}{2}kT$. We can also put this in a different way: the same $\frac{3}{2}$ plus $\frac{3}{2}$ can also be looked at as kinetic energy of the center of mass

Table 40–1

Values of the specific heat ratio, γ,
for various gases

Gas	T (°C)	γ
He	—180	1.660
Kr	19	1.68
Ar	15	1.668
H_2	100	1.404
O_2	100	1.399
HI	100	1.40
Br_2	300	1.32
I_2	185	1.30
NH_3	15	1.310
C_2H_6	15	1.22

Fig. 40–6. Experimental values of γ as a function of temperature for hydrogen and oxygen. Classical theory predicts $\gamma = 1.286$, independent of temperature.

($\tfrac{3}{2}$), kinetic energy of rotation ($\tfrac{2}{2}$), and kinetic energy of vibration ($\tfrac{1}{2}$). We know that the kinetic energy of vibration is $\tfrac{1}{2}$, since there is just one dimension involved and each degree of freedom has $\tfrac{1}{2}kT$. Regarding the rotation, it can turn about either of two axes, so there are two independent motions. We assume that the atoms are some kind of points, and cannot spin about the line joining them; this is something to bear in mind, because if we get a disagreement, maybe that is where the trouble is. But we have one more thing, which is the *potential* energy of vibration; how much is that? In a harmonic oscillator the average kinetic energy and average potential energy are equal, and therefore the potential energy of vibration is $\tfrac{1}{2}kT$, also. The grand total of energy is $U = \tfrac{7}{2}kT$, or kT is $\tfrac{2}{7}U$ per atom. That means, then, that γ is $\tfrac{9}{7}$ instead of $\tfrac{5}{3}$, i.e., $\gamma = 1.286$.

We may compare these numbers with the relevant measured values shown in Table 40–1. Looking first at helium, which is a monatomic gas, we find very nearly $\tfrac{5}{3}$, and the error is probably experimental, although at such a low temperature there may be some forces between the atoms. Krypton and argon, both monatomic, agree also within the accuracy of the experiment.

We turn to the diatomic gases and find hydrogen with 1.404, which does not agree with the theory, 1.286. Oxygen, 1.399, is very similar, but again not in agreement. Hydrogen iodide again is similar at 1.40. It begins to look as though the right answer is 1.40, but it is not, because if we look further at bromine we see 1.32, and at iodine we see 1.30. Since 1.30 is reasonably close to 1.286, iodine may be said to agree rather well, but oxygen is far off. So here we have a dilemma. We have it right for one molecule, we do not have it right for another molecule, and we may need to be pretty ingenious in order to explain both.

Let us look further at a still more complicated molecule with large numbers of parts, for example, C_2H_6, which is ethane. It has eight different atoms, and they are all vibrating and rotating in various combinations, so the total amount of internal energy must be an enormous number of kT's, at least $12kT$ for kinetic energy alone, and $\gamma - 1$ must be very close to zero, or γ almost exactly 1. In fact, it *is* lower, but 1.22 is not so much lower, and is higher than the $1\tfrac{1}{12}$ calculated from the kinetic energy alone, and it is just not understandable!

Furthermore, the whole mystery is deep, because the diatomic molecule cannot be made rigid by a limit. Even if we made the couplings stiffer indefinitely, although it might not vibrate much, it would nevertheless keep vibrating. The vibrational energy inside is still kT, since it does not depend on the strength of the coupling. But if we could imagine *absolute* rigidity, stopping all vibration to eliminate a variable, then we would get $U = \tfrac{5}{2}kT$ and $\gamma = 1.40$ for the diatomic case. This looks good for H_2 or O_2. On the other hand, we would still have problems, because γ for either hydrogen or oxygen varies with temperature! From the measured values shown in Fig. 40–6, we see that for H_2, γ varies from about 1.6 at -185°C to 1.3 at 2000°C. The variation is more substantial in the case of hydrogen than for oxygen, but nevertheless, even in oxygen, γ tends definitely to go up as we go down in temperature.

40–6 The failure of classical physics

So, all in all, we might say that we have some difficulty. We might try some force law other than a spring, but it turns out that anything else will only make γ higher. If we include more forms of energy, γ approaches unity more closely, contradicting the facts. All the classical theoretical things that one can think of will only make it worse. The fact is that there are electrons in each atom, and we know from their spectra that there are internal motions; each of the electrons should have at least $\tfrac{1}{2}kT$ of kinetic energy, and something for the potential energy, so when these are added in, γ gets still smaller. It is ridiculous. It is wrong.

The first great paper on the dynamical theory of gases was by Maxwell in 1859. On the basis of ideas we have been discussing, he was able accurately to explain a great many known relations, such as Boyle's law, the diffusion theory, the viscosity of gases, and things we shall talk about in the next chapter. He listed all these great successes in a final summary, and at the end he said, "Finally, by
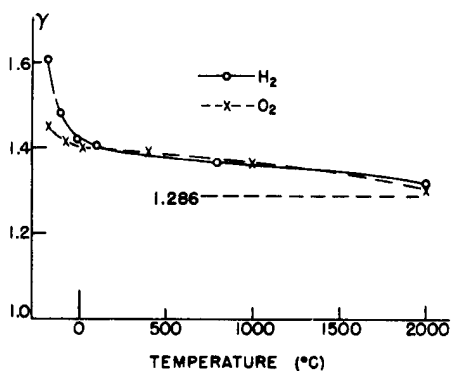
establishing a necessary relation between the motions of translation and rotation (he is talking about the $\frac{1}{2}kT$ theorem) of all particles not spherical, we proved that a system of such particles could not possibly satisfy the known relation between the two specific heats." He is referring to γ (which we shall see later is related to two ways of measuring specific heat), and he says we know we cannot get the right answer.

Ten years later, in a lecture, he said, "I have now put before you what I consider to be the greatest difficulty yet encountered by the molecular theory." These words represent the first discovery that the laws of classical physics were wrong. This was the first indication that there was something fundamentally impossible, because a rigorously proved theorem did not agree with experiment. About 1890, Jeans was to talk about this puzzle again. One often hears it said that physicists at the latter part of the nineteenth century thought they knew all the significant physical laws and that all they had to do was to calculate more decimal places. Someone may have said that once, and others copied it. But a thorough reading of the literature of the time shows they were all worrying about something. Jeans said about this puzzle that it is a very mysterious phenomenon, and it seems as though as the temperature falls, certain kinds of motions "freeze out."

If we could assume that the vibrational motion, say, did not exist at low temperature and did exist at high temperature, then we could imagine that a gas might exist at a temperature sufficiently low that vibrational motion does not occur, so $\gamma = 1.40$, or a higher temperature at which it begins to come in, so γ falls. The same might be argued for the rotation. If we can eliminate the rotation, say it "freezes out" at sufficiently low temperature, then we can understand the fact that the γ of hydrogen approaches 1.66 as we go down in temperature. How can we understand such a phenomenon? Of course that these motions "freeze out" cannot be understood by classical mechanics. It was only understood when quantum mechanics was discovered.

Without proof, we may state the results for statistical mechanics of the quantum-mechanical theory. We recall that according to quantum mechanics, a system which is bound by a potential, for the vibrations, for example, will have a discrete set of energy levels, i.e., states of different energy. Now the question is: how is statistical mechanics to be modified according to quantum-mechanical theory? It turns out, interestingly enough, that although most problems are more difficult in quantum mechanics than in classical mechanics, problems in statistical mechanics are much easier in quantum theory! The simple result we have in classical mechanics, that $n = n_0 e^{-\text{energy}/kT}$, becomes the following very important theorem: If the energies of the set of molecular states are called, say, E_0, E_1, E_2, $\ldots$, E_i, $\ldots$, then in thermal equilibrium the probability of finding a molecule in the particular state of having energy E_i is proportional to $e^{-E_i/kT}$. That gives the probability of being in various states. In other words, the relative chance, the probability, of being in state E_1 relative to the chance of being in state E_0, is

$$\frac{P_1}{P_0} = \frac{e^{-E_1/kT}}{e^{-E_0/kT}}, \tag{40.10}$$

which, of course, is the same as

$$n_1 = n_0 e^{-(E_1-E_0)/kT}, \tag{40.11}$$

since $P_1 = n_1/N$ and $P_0 = n_0/N$. So it is less likely to be in a higher energy state than in a lower one. The ratio of the number of atoms in the upper state to the number in the lower state is e raised to the power (minus the energy difference, over kT)—a very simple proposition.

Now it turns out that for a harmonic oscillator the energy levels are evenly spaced. Calling the lowest energy $E_0 = 0$ (it actually is not zero, it is a little different, but it does not matter if we shift all energies by a constant), the first one is then $E_1 = \hbar\omega$, and the second one is $2\hbar\omega$, and the third one is $3\hbar\omega$, and so on.

Now let us see what happens. We suppose we are studying the vibrations of a diatomic molecule, which we approximate as a harmonic oscillator. Let us ask

what is the relative chance of finding a molecule in state E_1 instead of in state E_0. The answer is that the chance of finding it in state E_1, relative to that of finding it in state E_0, goes down as $e^{-\hbar\omega/kT}$. Now suppose that kT is much less than $\hbar\omega$, and we have a low-temperature circumstance. Then the probability of its being in state E_1 is extremely small. Practically all the atoms are in state E_0. If we change the temperature but still keep it very small, then the chance of its being in state $E_1 = \hbar\omega$ remains infinitesimal—the energy of the oscillator remains nearly zero; it does not change with temperature so long as the temperature is much less than $\hbar\omega$. All oscillators are in the bottom state, and their motion is effectively "frozen"; *there is no contribution of it to the specific heat.* We can judge, then, from Table 40-1, that at 100°C, which is 373 degrees absolute, kT is much less than the vibrational energy in the oxygen or hydrogen molecules, but not so in the iodine molecule. The reason for the difference is that an iodine atom is very heavy, compared with hydrogen, and although the forces may be comparable in iodine and hydrogen, the iodine molecule is so heavy that the natural frequency of vibration is very low compared with the natural frequency of hydrogen. With $\hbar\omega$ higher than kT at room temperature for hydrogen, but lower for iodine, only the latter, iodine, exhibits the classical vibrational energy. As we increase the temperature of a gas, starting from a very low value of T, with the molecules almost all in their lowest state, they gradually begin to have an appreciable probability to be in the second state, and then in the next state, and so on. When the probability is appreciable for many states, the behavior of the gas approaches that given by classical physics, because the quantized states become nearly indistinguishable from a continuum of energies, and the system can have almost any energy. Thus, as the temperature rises, we should again get the results of classical physics, as indeed seems to be the case in Fig. 40-6. It is possible to show in the same way that the rotational states of atoms are also quantized, but the states are so much closer together that in ordinary circumstances kT is bigger than the spacing. Then many levels are excited, and the rotational kinetic energy in the system participates in the classical way. The one example where this is not quite true at room temperature is for hydrogen.

This is the first time that we have really deduced, by comparison with experiment, that there was something wrong with classical physics, and we have looked for a resolution of the difficulty in quantum mechanics in much the same way as it was done originally. It took 30 or 40 years before the next difficulty was discovered, and that had to do again with statistical mechanics, but this time the mechanics of a photon gas. That problem was solved by Planck, in the early years of this century.