4   General Properties of Macroscopic Systems

The statistical equilibrium postulate, introduced in the last chapter, implies that all macroscopic systems share some general properties and can be described by some useful special concepts. These properties and concepts will be discussed in the next few sections and will afterwards be widely applied to more specific situations.

A. Equilibrium and fluctuations

Simplicity of equilibrium situations

A situation where a macroscopic system is in equilibrium is particularly simple for the following reasons:

(1) By its definition, an equilibrium situation is one which does not change with time. (More precisely, the *probability* that a system is found in any of its basic states does not change with time.)

(2) According to the statistical equilibrium postulate (3B-2), a system in equilibrium is equally likely to be found in any one of its possible basic states.

(3) An equilibrium situation is ultimately reached by any isolated macroscopic system after one waits for a sufficiently long time. Furthermore, this equilibrium situation does not depend on the past history of the system.

(4) Probabilities are defined by considering what happens in a statistical assembly of a large number $\mathcal{N}$ of similar systems. But, if a system is in equilibrium so that these probabilities do not change, one can equivalently focus attention on a single system observed at $\mathcal{N}$ different times. (For example, one can imagine taking a movie of the system and then looking at $\mathcal{N}$ frames of this movie. Considering such an assembly of $\mathcal{N}$ frames of a single system at different times is then equivalent to considering an assembly of $\mathcal{N}$ systems at any one time.)

Probabilities in equilibrium

The macroscopic information available about any macroscopic system is very limited. For example, we might know the volume V of such a system and its total internal energy E (which remains constant if the system is isolated). This information might then be sufficient to determine the macroscopic state of the system. However, the system can then still be in any one of an extremely large number of possible basic states (corresponding to the many different possible positions and velocities of the atomic particles in the system).

Probability of being in any basic state. Suppose the total number of possible basic states available to the system is denoted by Ω_{tot} (where Ω is the Greek letter capital *omega*). The statistical postulate (3B-2) then asserts that, if the system is isolated and in equilibrium, it is equally likely to be in any one of these possible states. Hence the probability P_r that the system is in any *one* of these basic states is

$$P_r = \frac{1}{\Omega_{tot}} \qquad \text{(for any basic state r).} \qquad \text{(A-1)}$$

Probability of being in any macrostate. Suppose now that one wants to find the probability P_A that the system is in any particular macroscopically specified situation (or *macrostate*) A. In such an equilibrium situation the system can be, with equal probability, in some number Ω_A of possible basic states (out of the total number Ω_{tot} of basic states available to the system in all possible situations). Hence the probability P_A that the system is in such a macrostate A is

$$P_A = \frac{\Omega_A}{\Omega_{tot}} \qquad \text{(for any macrostate } A \text{).} \qquad \text{(A-2)}$$

In other words, the probability of being in a particular macrostate is simply proportional to the number of possible basic states available in this macrostate. Situations corresponding to a larger number of possible basic states occur thus with greater probability than situations corresponding to a smaller number of possible basic states.

Example: Gas of four molecules in equilibrium

To illustrate the preceding ideas, consider an isolated gas of N molecules in a box. (For example, Fig. A-1 illustrates schematically an extremely simply gas consisting of only four such molecules.) These molecules can move throughout the interior of this box, colliding occasionally with the walls and with each other. We are interested in the probability P_n of encountering a situation where some number n of these molecules are found in the left half of the box (so that the remaining n' = N − n molecules are found in the right half of the box). In particular, we are interested in this probability when the gas has been left sitting for a long enough time that it has reached equilibrium (i.e., so that this probability P_n remains unchanged in time).

Since we are not interested the velocities of these molecules, we shall merely focus attention on their positions. Furthermore, the left and right halves
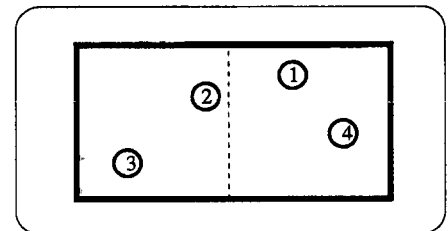
Fig. A-1. A gas of four molecules distributed over the two halves of a box.

of the box have the same size. Hence the number of possible positions available to a molecule in the left half of the box is equal to the number of possible positions available to it in the right half. In the equilibrium situation where any of these possible positions is equally likely, any molecule will thus be found with equal probability in the left half or the right half of the box.

The basic state of the gas can then be specified with adequate precision by specifying whether each molecule is in the left half or the right half of the box.

Total number of basic states. What is the total number Ω_{tot} of such basic states when we are dealing with a gas of N molecules? Consider the simple case of Fig. A-1 where we are dealing with only 4 such molecules (labeled by 1, 2, 3, and 4). The first of these molecules can be in two possible basic states, i.e., in can be either in the left half or the right half of the box. Corresponding to each of these two possibilities, there are two possibilities for the second molecule (i.e., it too can be either in the left half or the right half). Hence there are $2 \times 2 = 2^2 = 4$ possibilities for these two molecules. For each of these possibilities, there are 2 possibilities for the third molecule. Hence there are $2^2 \times 2 = 2^3 = 8$ possibilities for these three molecules. Continuing in this way, we see that the total number Ω_{tot} of possibilities for four molecules is equal to

$$\Omega_{tot} = 2^4 = 16. \tag{A-3}$$

Enumeration of possible basic states. These 16 possible basic states are explicitly listed in Fig. A-2. Each state is indicated by specifying which of the four molecules (labeled 1, 2, 3, and 4) are in the left half of the box and which of the remaining molecules are in the right half of the box.

Calculation of probabilities. Out of these 16 equally likely basic states, how many states are there in which n molecules are located in the left half of the box? Fig. A-2 shows that there is only one state in which all the four molecules are located in the left half of the box. Hence the probability P_4 that all the 4 molecules are located in the left half is

$$P_4 = \frac{1}{16} = 0.0625. \tag{A-4}$$

Similarly, there is only one state in which all the molecules are located in the right half of the box (i.e., which no molecules are located in the left half). Hence the probability P_0 that zero molecules are in the left half of the box is similarly

$$P_o = \frac{1}{16} = 0.0625 \tag{A-4}$$

Out of the 16 basic states listed in Fig. A-2, there are 4 states in which 3 molecules are in the left half (and the remaining one molecule is in the right half) Similarly, there are 4 basic states in which 1 molecule is in the left half (and the remaining 3 molecules are in the right half). The probability P_3 that 3 molecules are in the left half, or the probability P_1 that 1 molecule is in the left half are thus each equal to

$$P_3 = P_1 = \f(4/16) = 0.25. \tag{A-5}$$

n	n'	Left	Right
4	0	1 2 3 4	
3	1	1 2 3	4
		1 2 4	3
		1 3 4	2
		2 3 4	1
2	2	1 2	3 4
		1 3	2 4
		1 4	2 3
		2 3	1 4
		2 4	1 3
		3 4	1 2
1	3	1	2 3 4
		2	1 3 4
		3	1 2 4
		4	1 2 3
0	4		1 2 3 4

Fig. A-2. Possible position states for 4 molecules each of which can be either in the left or right half of a box. Here n denotes the number of molecules in the left half and n' the number in the right half. The molecules are labeled 1, 2, 3, and 4.

Finally, out of the 16 basic states listed in Fig. A-2, there are 6 states in which 2 molecules are in the left half and the remaining 2 molecules are in the right half. Hence the probability P_2 that this happens is

$$P_2 = \frac{6}{16} = 0.375. \tag{A-4}$$

The preceding calculated probabilities are summarized in the bar graph of Fig. A-3.

Predictions about this gas. Consider a statistical assembly of a very large number of gases in equilibrium, each gas similar to the one in Fig. A-3. Then the preceding probabilities predict in what fraction Pn of these gases one will observe n molecules in the left half of the box. Since the gas is in equilibrium so that the probabilities don't change with time, one could equivalently take a movie of the gas and consider a very large number of successive movie frames (similar to those illustrated in Fig. A-4.) Then the preceding probabilities predict in what fraction Pn of these frames one will observe n molecules in the left half of the box. For example, one would predict that 1/16 (or about 6%) of these frames would show all molecules in the left half of the box and that 6/16 (or about 37%) of these frames would show equal numbers of molecules in both halves of the box.

The following features are worthy of note:

(1) An extreme situation where all molecules are in one half of the box can be realized in only one possible way. Hence it is relatively unlikely (probability of 1/16) that such a situation occurs.

(2) A situation where equal numbers of molecules are in both halves of the box can be realized in the largest possible numbers of ways. Hence it is most likely (probability 6/16) that this situation occurs.

(3) Although the *probabilities* do not change in the equilibrium situation, the number of molecules in any half of the box fluctuates in the course of time (as is apparent in Fig. A-§). In other words, this number molecules, observed at different times, is most likely to be equal to 2. But this number of molecules can also be different from 2, although values that deviate appreciably from 2 are increasingly less likely to be observed.
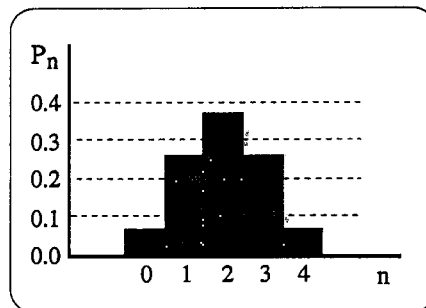

Fig. A-3. Probability P_n that n molecules, out of the 4 molecules of the gas in Fig. A-1, are located in the left half of the box (when this gas is in equilibrium).

Problems

[A-1] *Gas of six molecules in equilibrium*

Consider a very simple gas consisting of 6 molecules in equilibrium inside a box. Each of these molecules is then equally likely to be found in the left half or the right half of the box.

(a) What is the total number of ways that these molecules can be distributed over the two halves of this box?

(b) In how many ways can these molecules be distributed so that all of them are in the left half of the box?

(c) List (in a manner similar to that in Fig. A-2) all the ways that these molecules can be distributed so that half of them (i.e., 3 molecules) are in the left half of the box. How many such ways are there? *<h-3>*

(d) What is the probability P_6 that all 6 of the molecules are found in the left half of the box? What is the probability that 3 of these molecules are found in the left half of the box?

(e) What is the ratio P_6/P_3? (This ratio compares the probability P_6 of the extreme situation, where all molecules are in the left half of the box, with the probability P_3 that half of the molecules are in each half of the box.)
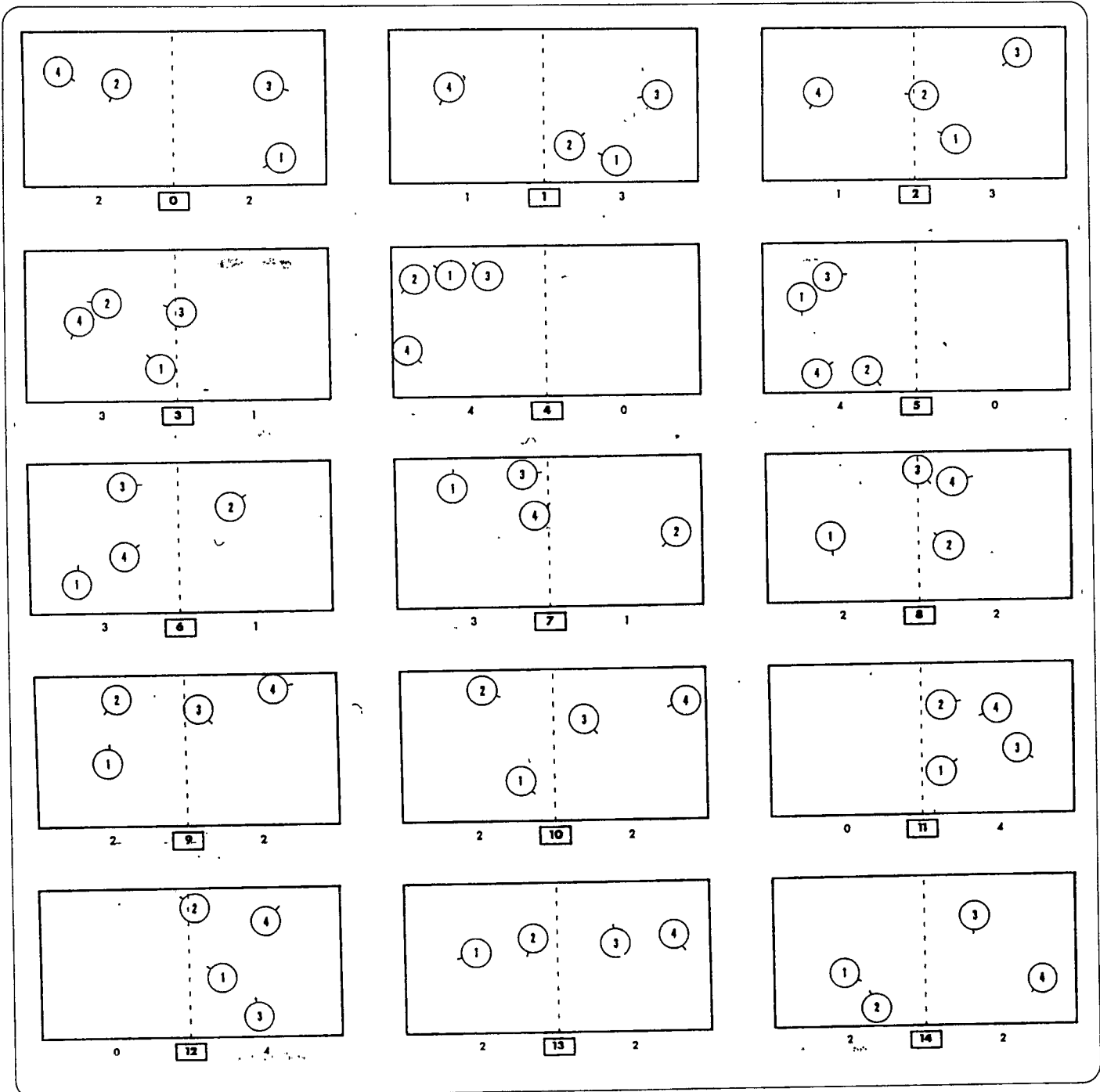   <a-8>

Fig. A-4. Successive movie frames of a gas of 4 molecules in equilibrium inside a box. [The figure was produced by a computer-generated simulation of a gas of 4 molecules colliding with each other and with the walls of the box.]

B. Fluctuations in equilibrium

The preceding examples of very simple gases indicate that, even when a system is in equilibrium, observable macroscopic quantities (like the number n of molecules in one half of a box) don't remain constant but fluctuate in the course of time. How large are such fluctuations?

The size of fluctuations depends on the number N of particles in the system. For example, let us compare the probability P_N of the extreme situation where all N molecules are in one half of the box with the probability $P_{N/2}$ of the most likely situation where half of the molecules are in each half of the box. In the case of a gas of 4 molecules, the probability of the extreme situation is 6 times smaller than that of the most likely situation. But in the case of the gas of 6 molecules, the probability of the extreme situation is 20 times smaller than that of the most likely situation.

Example: Gas of forty molecules in equilibrium

To examine how fluctuations are affected by the number N of particles, consider a gas of forty molecules in equilibrium inside a box. (Fig. B-2 shows a computer simulation of movie frames taken of such molecules at successive times.) Since each of the 40 molecules can be in either of the two halves of the box, there are $2^{40} = 1.1 \times 10^{12}$ possible ways that these molecules can be distributed over the two halves. Out of this total number of ways, there is only *one* way in which all the molecules can be in one half of the box. The probability that this happens is thus only $1/2^{40} \approx 10^{-12}$. This extreme situation would thus practically never be observed. By contrast, there are very many ways in which the molecules can be distributed so that equal numbers of molecules are in both halves of the box. (Indeed, calculation show that there are more than 10^{11} such ways.) Hence it is very likely (indeed, most probable) that the molecules are equally distributed over both halves of the box.

Probabilities of various situations. Fig. B-1 shows the calculated probabilities that n out of the 40 molecules are located in the left half of the box. As already mentioned, the most probable situation is that where the molecules are equally distributed over both halves of the box (i.e., where 20 molecules are in each half). But fluctuations deviating from this situation can occur with varying probabilities.

Deviations from the most probable situation. The magnitude of a fluctuation may be described by the magnitude of the difference $\Delta n = n - N/2$ between the number n of molecules in the left half of the box and the most probable number $N/2 = 20$. As is apparent from Fig. B-2, situations corresponding to deviations of small magnitude $|\Delta n|$ are somewhat less likely to occur than the most probable situation. But situations where the magnitude of this deviation is as large 10 (i.e., where n is less than 10 or larger than 30) are quite rare. Indeed, a situation where the number of molecules in any half of the box is less then 10 occurs only with a probability less than 1% as large as the probability of the most probable situation. And a situation where the magnitude of this deviation is as large as 15 (i.e., where the number of molecules in any

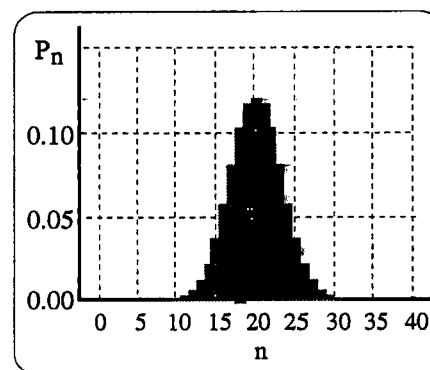Problem G-3 indicates how these probabilities can be calculated.

Fig. B-1. Probability P_n that n molecules, out of a gas of 40 molecules in equilibrium, are found in the left half of the containing box.

half of the box is less than 5) occurs only with a probability less than 0.001% as large as the probability of the most probable situation. Such a situation is thus almost never observed.
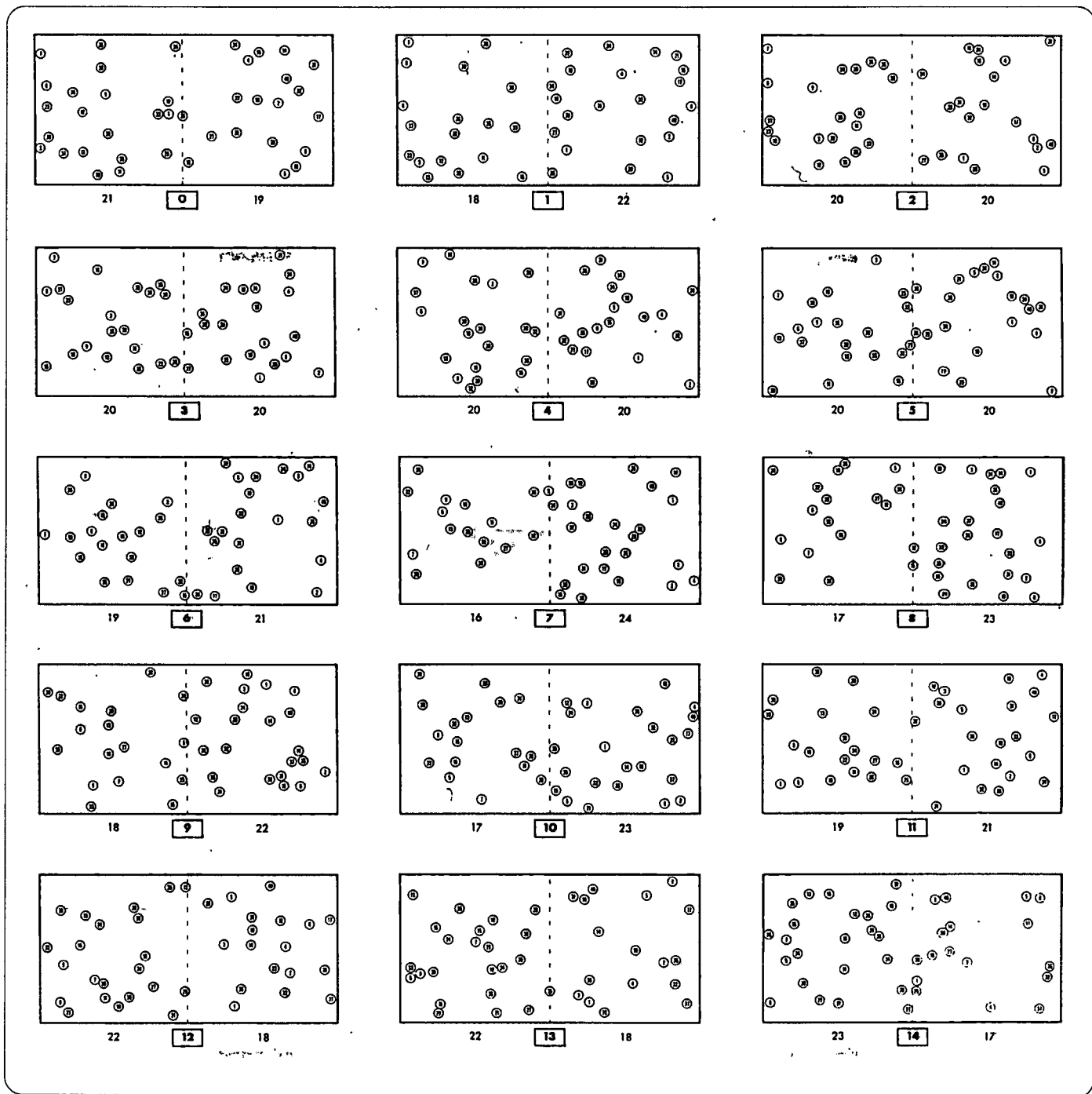

Fig. B-2. Successive movie frames of a gas of 40 molecules in equilibrium inside a box. [The figure was produced by a computer-generated simulation of a gas of 40 molecules colliding with each other and with the walls of the box.]

Summary. If a gas of N molecules is in equilibrium inside a box, the number of molecules in any half of the box is most likely equal to its most probable value of N/2 (corresponding to equal distribution of the molecules throughout the box). Fluctuations about this value do occur. (For example, Fig. B-3 indicates the fluctuations observed in the case of the gas of 4 molecules illustrated in Fig. A-4 and the gas of 40 molecules illustrated in Fig. B-2.) But if the number of molecules is large, these fluctuations are relatively small (i.e., very large deviations from the most probable situation are highly unlikely to occur).

Fluctuations in a real gas

The preceding very simple examples illustrate that fluctuations become relatively smaller when one deals with a gas consisting of a larger number of molecules. Let us then consider an actual gas consisting of a realistically large number N of molecules in equilibrium, e.g., at a gas consisting of some 10^{24} molecules.

In such a situation, the most probable situation is again that were the molecules are equally distributed throughout the box (i.e., the situation where $N/2 = 5 \times 10^{23}$ molecules are in each half of the box). Fluctuations about this number again occur. (See Fig. B-4.) Indeed, in a gas of 10^{24} molecules, one is quite likely to encounter situations where there are 10^{12} more molecules in one half of the box than in the other half. On the other hand, one is very unlikely to encounter situations where the number of molecules in both halves differs by much more than 10^{12}.

Fluctuations differing from the most probable number by as many as 10^{12} molecules may seem large. But, compared to the most probable number of 5×10^{23} molecules they are exceedingly small (i.e., they are about 10^{12} times smaller than this most probable number). Indeed, for most practical purposes, they are utterly negligible. Observations of the gas will then almost always show that half of the molecules are in either half of the box.

General conclusion

The insights derived from the preceding examples of gases are more generally applicable to any macroscopic system. When such a system is in equilibrium, any of its macroscopically measurable quantities remains always very close to its most probable value which does not change with time. But fluctuations about this value *do* occur. The relative size of these fluctuations is, however, so very small that they are ordinarily of negligible importance, especially in the case of a macroscopic system consisting of very many atomic particles.

These fluctuations may become significant in certain cases, especially if the system is small or if highly precise measurements need to be made. Indeed, the existence of these fluctuations often determines the maximum possible precision with which various quantities can be measured.
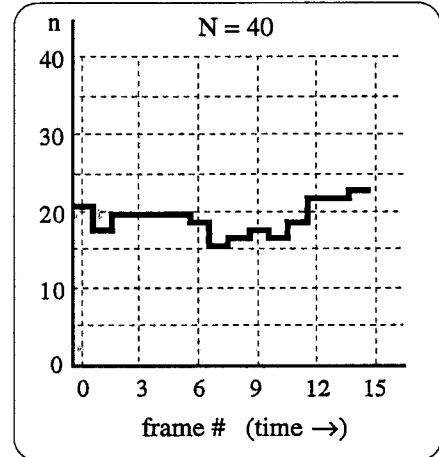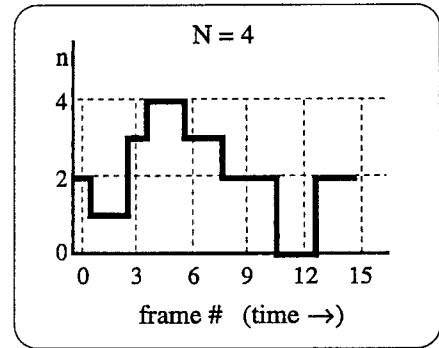

Fig. B-3. Number n of molecules found in the left half of a box. (a) In successive frames of the gas of 4 molecules in Fig. A-4. (b) In successive frames of the gas of 40 molecules in Fig. B-2.

In general, one can show that fluctuations much larger than $\sqrt{N}$ are very unlikely.
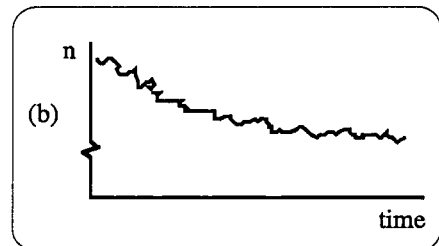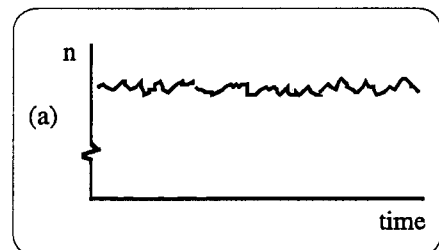

Fig. B-4. Fluctuations (shown much exaggerated) in a the number n of molecules in one half of a box of gas. (a) When the gas is in equilibrium. (b) When the gas is approaching an equilibrium situation.

Problems

[B-1] *Energies of systems in thermal equilibrium*

A spoon is immersed in a cup of tea. The entire system (consisting of the spoon and cup of tea) is thermally insulated from its surroundings.

(a) Can the internal energy of the spoon change? Can the internal energy of the cup of tea change? Can the internal energy of the entire system (consisting of the spoon and the cup of tea) change?

(b) In equilibrium, does the internal energy of the spoon tend to change in the course of time? If not, does it fluctuate about some most probable value?

(c) In equilibrium, does the internal energy of the cup of tea tend to change in the course of time? If not, does it fluctuate about some most probable value?

(d) If fluctuations in energy occur, how large are these compared to the internal energy of the spoon or the cup of tea?

(d) Suppose that the internal energy of the spoon increases momentarily as a result of a small fluctuation. What then happens to the internal energy of the cup of tea? <a-2>

[B-2] *Hanging pendulum in equilibrium*

Fig. B-5 illustrates a pendulum hanging at rest while suspended from the ceiling of a room.

(a) Is the pendulum bob then really not moving at all, or is it fluctuating slightly about its equilibrium position?

(b) The pendulum bob is constantly bombarded by the molecules of air in the room. Explain qualitatively why this random bombardment can lead to fluctuations in the pendulum bob's position.

(c) If the air in the room is pumped out, the pendulum is no longer bombarded by any air molecules. Would the position of the pendulum bob then still fluctuate? Explain why. <h-5> <a-6>

Fig. B-5. A pendulum suspended from the ceiling.

[B-3] *Brownian motion*

A microscope can be used to observe small particles (about 10^{-6} m in size) immersed in a liquid. It is found that these particles are not at rest, but move about so that their positions change in random ways.

(a) Explain why one would expect to observe such fluctuations in position.

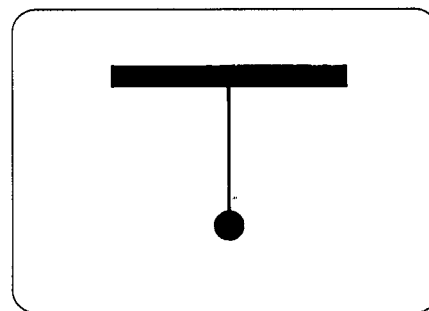(b) Would you expect these fluctuations to be larger or smaller if the particles are larger and have larger masses? Why? <a-10>

Such random motions of pollen grains were first observed in 1827 by the Scottish botanist Robert Brown (1773-1858). This "Brownian motion" was quantitatively explained by Albert Einstein in 1905.

C. Approach to equilibrium

Suppose that an isolate macroscopic system is in a situation where it is *not* with equal probability in each of its possible basic states. According to the fundamental equilibrium postulate (3B-2), the system is then *not* in equilibrium. Hence the system will change until it ultimately reaches an equilibrium situation where it is found with equal probability in each of its basic states.

Example of a gas approaching equilibrium

Fig. C-1a shows a box divided into two halves by a partition. A gas is initially in equilibrium inside the left half of the box and the partition is then suddenly removed. The situation immediately afterwards is illustrated in Fig. C-1b. It is now possible for each molecule to be located *anywhere* in the

entire box. However, in the actual situation illustrated in Fig. C-1b, each molecule is equally likely to be anywhere in the left half of the box, but has zero probability of being in the right half. This is thus clearly *not* an equilibrium situation.

What then happens? As the molecules move about, it is exceedingly unlikely that they all remain in the left half of the box. Instead, they will gradually spread out throughout the entire box until they reach the equilibrium situation illustrated in Fig. C-1c where each molecule is equally likely to be anywhere in the entire box.

Time required to reach equilibrium

The preceding argument, based on the statistical equilibrium postulate (3B-2), allows us to infer how the gas will change and what final equilibrium situation will thereby be reached. However, it does *not* make any statements about how long a time is required for this equilibrium situation to be reached.

Indeed, the change illustrated in Fig. C-1 would occur quite rapidly. On the other hand, consider the similar situation illustrated in Fig. C-2 where the partition is not removed, but a small hole is made in it. All positions throughout the entire box become thereby again available to each molecule. Hence the molecules again spread out and finally reach the *same* equilibrium situation as before (where each molecule is equally likely to be anywhere in the box). But the time required for this equilibrium situation to be reached depends crucially on the size of the hole and could be quite large if the hole is small.

Problems

[C-1] *Ink drop falling into water*

A drop of ink, containing 10^{21} ink molecules, falls into a glass containing 100 cm^3 of water.

(a) Will the drop of ink remain near the surface of the water or will the ink gradually spread out throughout the entire glass of water?

(b) How many molecules of ink per cm^3 of water will there be in the final equilibrium situation? *<a-1>*

[C-2] *Thermal interaction between two copper blocks*

A block of copper, consisting of N copper atoms and having an internal energy E, is placed on top of another block of copper consisting of a different number N' copper atoms and having an internal energy E'. (See Fig. C-3.) The entire system, consisting of both blocks, is thermally insulated from its surroundings.

(a) In an equilibrium situation, is it most likely that the average energy each of the copper atoms is the same, or is it more likely that some copper atoms have significantly larger energies than some other copper atoms?

(b) Suppose that the average energy E/N of an atom in the top block is initially larger that the average energy E'/N' of an atom in the bottom block. Will this situation persist or will it change? If it changes, will the internal energy of the top block increase, decrease, or remain the same? Will the internal energy of the bottom block increase, decrease, or remain the same? Will the total internal energy of both blocks increase, decrease, or remain the same?

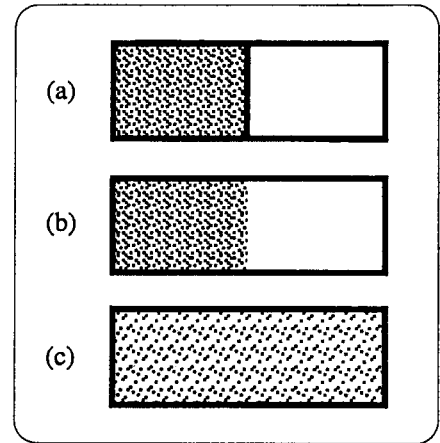**Fig. C-1.** A gas inside a box. (a) Initially confined to the left half by a partition. (b) Immediately after the partition is removed. (c) Final equilibrium situation.
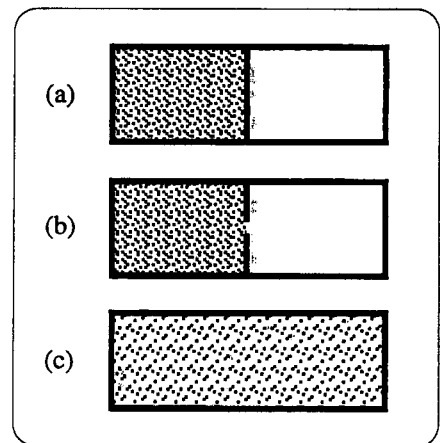

Fig. C-2. A gas inside a box. (a) Initially confined to the left half by a partition. (b) Immediately after a hole is made in the partition. (c) Final equilibrium situation.
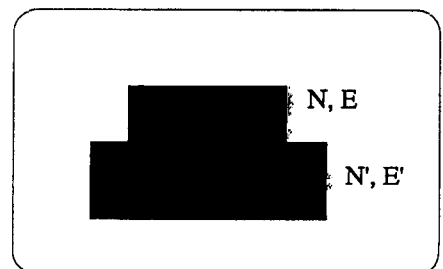

Fig. C-3. A copper block placed on top of another copper block.

(c) Is the heat absorbed by the top block positive or negative? Is the heat absorbed by the bottom block positive or negative? Is the magnitude of the heat absorbed by the top block larger than, smaller than, or equal to the magnitude of the heat absorbed by the bottom block?

(d) After the entire system has reached equilibrium, is the final internal energy E_f of the top block equal to the final internal energy E'_f of the bottom block? If, not what is the relation between these two energies?

(e) What is the final internal energy of each of the blocks? (Express your answer in terms of their initial energies E and E' and the numbers N and N' of atoms in the two blocks.)

(f) Suppose that a sheet of paper is initially placed between the top block and the bottom block. Would the answers to the preceding questions then be different or would they be essentially the same? Would the time required to reach the final equilibrium situation then be longer, shorter, or the same? <a-7>

D. Irreversibility

In science and in everyday life we observe many processes occurring in the course of time. To what extent do these processes indicate a preferred direction of time, i.e., to what extent do they allow us to distinguish the future from the past?

To make this question more specific, imagine that one makes a movie of any of these processes. One can then use a projector to play the movie either forward or backward. By watching the movie, can one then distinguish whether the movie is being played forward or backward? If one *cannot* distinguish which way the movie is being played, one says that the process is *reversible* (i.e., that it does *not* indicate a preferred direction of time). But if one *can* distinguish which way the movie is being played, one says that the process is *irreversible* (i.e., that it *does* indicate a preferred direction of time).

Reversible behavior of simple systems

Consider a pendulum swinging back and forth (under conditions of no friction.) If one takes a movie of this situation and plays it backward, it looks just as natural as if it were being played forward. It simply displays the familiar situation of a pendulum swinging back and forth — and there is no way of telling whether the movie is being played forward or backward. The motion of the swinging pendulum is thus a reversible process.

As another example, consider the planets moving around the sun in their elliptical orbits. If one takes a movie of this situation and plays it backward, it again looks just as natural as if it were being played forward. It merely displays the familiar situation of planets moving around the sun — and there is no way of telling whether the movie is being played forward or backward. The motion of the planets around the sun is thus also a reversible process.

The preceding conclusions are not surprising because nothing in the laws of mechanics indicates a preferred direction of time.

Indeed, consider Newton's law $m\vec{a} = \vec{F}_{tot}$ where the total force is due to fundamental forces (like gravitational or electromagnetic forces). This law remains unchanged if the sign of the time t is reversed, (i.e., if t is replaced by −t).

Fig. D-1. Successive movie frames of a gas of 40 molecules inside a box. These frames show the gas molecules becoming concentrated in the left half of the box. The frames in the next Fig. D-2 show the molecules spreading out throughout the entire box. The successive frames in both of these figures show an extreme fluctuation where all the molecules of the gas in equilibrium become at one time (in frame 0) spontaneously concentrated in the left half of the box. [The figure was produced by a computer-generated simulation of a gas of 40 molecules colliding with each other and with the walls of the box.]
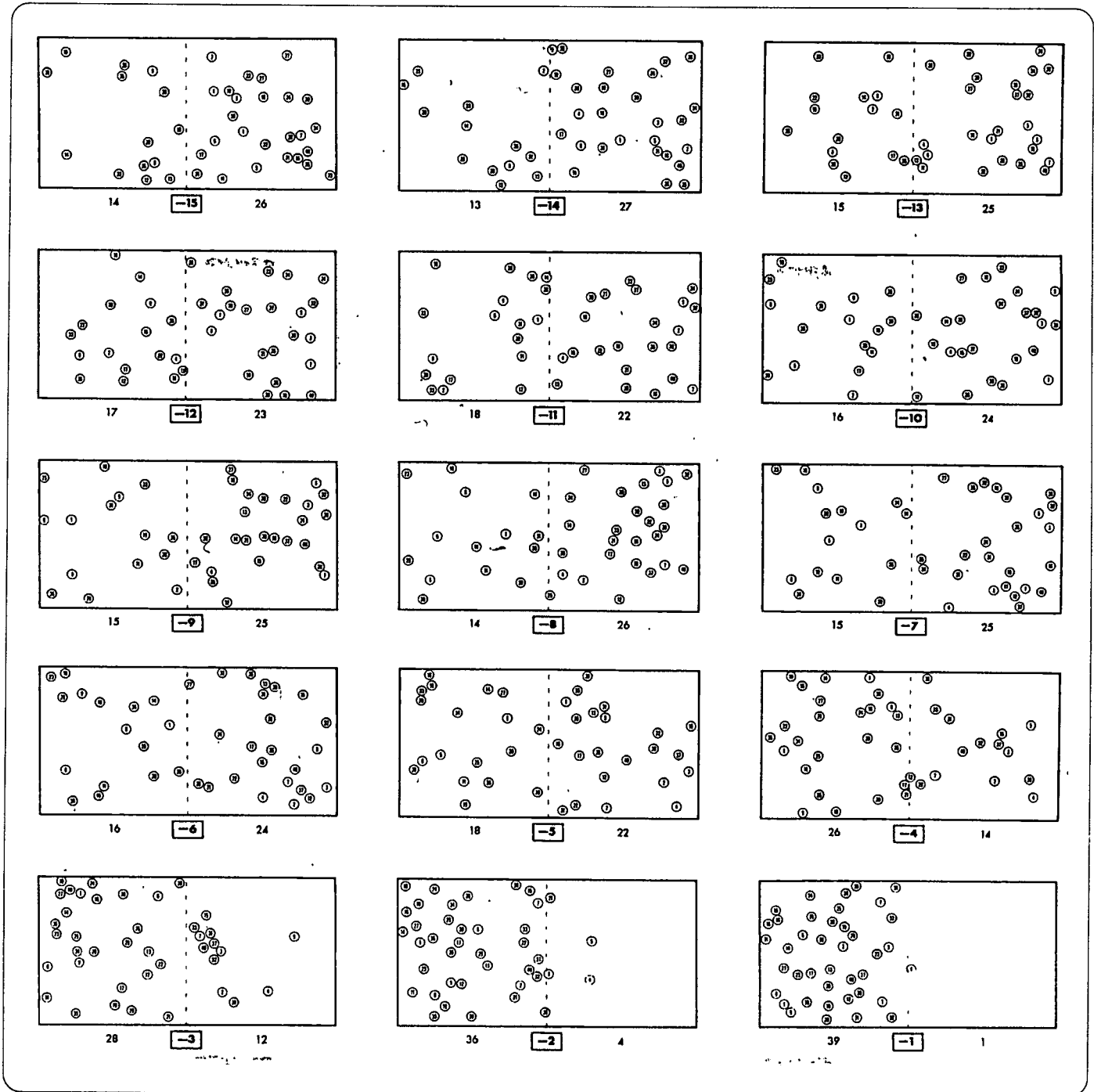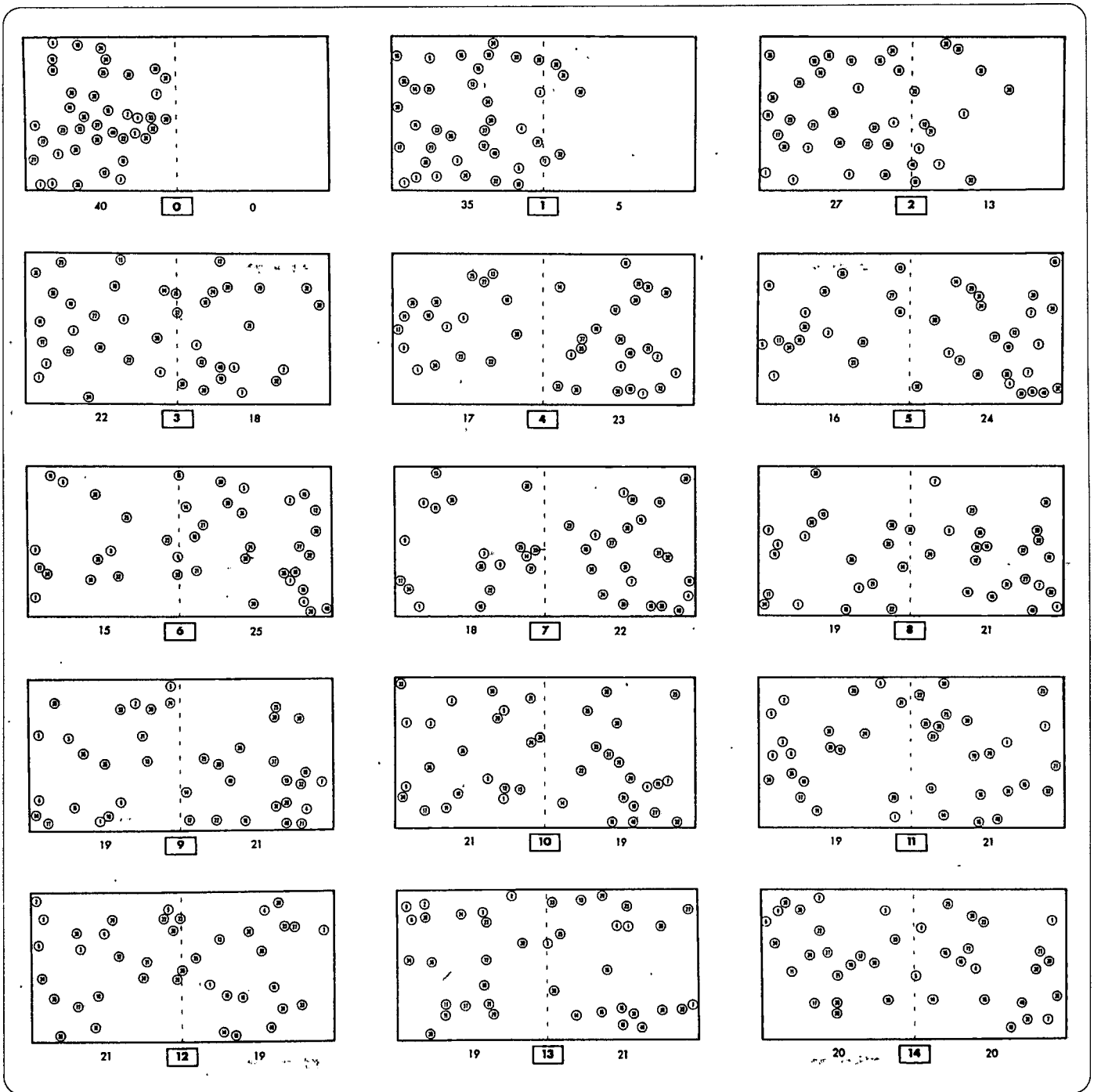
Fig. D-2. Successive movie frames of a gas of 40 molecules inside a box. These frames show the gas molecules, initially in the left half of the box, spreading out throughout the entire box. The frames in the preceding Fig. D-1 showed the molecules becoming concentrated in the left half of the box. The successive frames in both of these figures show an extreme fluctuation where all the molecules of the gas in equilibrium become at one time (in frame 0) spontaneously concentrated in the left half of the box. [The figure was produced by a computer-generated simulation of a gas of 40 molecules colliding with each other and with the walls of the box.]

Irreversible behavior of macroscopic systems

Gas concentrated in one half of a box. Consider a gas which is initially in the left half of a box (e.g., a gas like that in Fig. C-1b) and then spreads out throughout the entire box. Suppose that one takes a movie of this process and then plays it backward. This backward movie would show a gas initially concentrated in one half of a box and then spontaneously concentrating completely in only one half of the box. This is a most unnatural process which one would never expect to observe in real life. Hence one could immediately conclude that the movie is being played backward. The motion of this gas is thus an *irreversible* process.

For example, Fig. D-2 shows successive movie frames (labeled 0, 1, 2, ...,14) of a simulated gas of 40 molecules. Fig. D-1 also shows successive movie frames (labeled −15, −14, −13, ..., −1) of such a simulated gas. The movie in Fig. D-2 looks natural because it merely indicates how the gas molecules, initially in the left half of a box, spread out throughout the entire box. But the movie in Fig. D-1 looks fake because it shows all the gas molecules spontaneously concentrating in the left half of the box. (Indeed, this figure has been deliberately constructed by reordering the frames in backward order.)

Reasons for observed irreversibility. Why is it that one can so readily decide whether a movie of the preceding gas is being played backward?

If one sees all the molecules of the gas concentrated in one half of the box, this can only be for one of the following two possible reasons:

(1) *Spontaneous fluctuation.* The isolated box of gas in equilibrium might, at some time, exhibit a large fluctuation where all the molecules spontaneously happen to move into the left half of the box. For example, Figs. D-1 and D-2 shows successive movie frames (labeled 15, 14, −13, ..., 13, 14) of a gas of 40 molecules in equilibrium. The frame labeled by −2 −1, 0 illustrate such an extreme fluctuation where all the molecules move into the left half of the box.

But such an extreme fluctuation would occur very rarely. For example, in the case of the gas of 40 molecules, such a fluctuation would, on average, occur in only one out of $2^{40} = 1.1 \times 10^{12}$ movie frames. (If the movie were taken at the rate of 30 frames per second, such a fluctuation would thus be observed less frequently than once in a thousand years). In the case of a real gas consisting of about 10^{24} molecules, such an extreme fluctuation would occur only one out of $2^{10^{24}}$ movie frames! (One would thus have to wait much longer than 10^{23} times the age of the universe before one could ever hope to observe such an extreme fluctuation!) Thus we can be certain that such an extreme fluctuation would *never* be observed in real life. If it is observed in a movie, we can thus confidently conclude that this movie is being played backward.

(2) *Prior outside intervention.* Suppose that all the molecules in the gas are ever observed in one half of the box. The only realistic reason for this can then *not* be a spontaneous fluctuation, but must be some prior external intervention. (For example, before the gas was ever observed, somebody might have used a

piston to compress the gas into one half of the box and could then have let the gas spread out throughout the entire box.) But, if it is clear that some external intervention must have occurred *before* the observations, it is also clear why one can distinguish the future from the past (i.e., why one can distinguish whether movies are played forward or backward).

Examples of irreversible processes. Most processes observed in daily life involve macroscopic systems and are irreversible. The following are some examples:

(1) *Bouncing ball.* When a ball is dropped, it bounces several times on the floor before it comes to rest. A movie of this process, when played backward, would show a ball which initially lies on the floor and then spontaneously starts bouncing up and down to reach ever increasing heights. Since this is never observed in real life, one would immediately conclude that the movie is being played backward (i.e., that the original process is irreversible).

Of course, it is *possible* that the process portrayed in the backward movie might actually happen. Indeed, it would only require that all the randomly moving atoms in the ball spontaneously start, at the same time, all moving in the same upward direction. However, this is so enormously *improbable* to happen that it never occurs in actuality.

(2) *Block sliding along the floor.* After being given a push, a block slides along the level floor and gradually comes to rest. A movie of this process, when played backward, would show a block which is initially at rest on the floor and which then spontaneously starts moving with increasing speed. Since this is never observed in real life, one would again conclude that the movie is being played backward (i.e., that the original process is irreversible).

(3) *Frictional interactions.* The preceding example may be described by introducing a friction force that accounts for the interactions of the block with the floor. These interactions result in slowing down the block because some of the macroscopic kinetic energy of the block is converted into random kinetic energies of the atoms near the surface where the block touches the floor. This process is much more probable than the reverse process where all these atoms start spontaneously moving in the same direction so as to increase the block's speed and macroscopic kinetic energy. Frictional interactions thus lead to irreversible processes.

Degree of irreversibility

The reverse process observed when a movie is played backwards is not really impossible; it is ordinarily just highly improbable. Since situations can be more or less improbable, there is no sharp distinction between reversible and irreversible processes. In other words, irreversibility is a matter of degree and is ordinarily more pronounced in systems involving a larger number of independently moving atomic particles.

Fig. D-3. Successive movie frames of a gas of 4 molecules inside a box. These frames show the gas molecules becoming concentrated in the left half of the box. The frames in the next Fig. D-4 show the molecules spreading out throughout the entire box. The successive frames in both of these figures show an extreme fluctuation where all the molecules of the gas in equilibrium become at one time (in frame 0) spontaneously concentrated in the left half of the box. [The figure was produced by a computer-generated simulation of a gas of 4 molecules colliding with each other and with the walls of the box.]
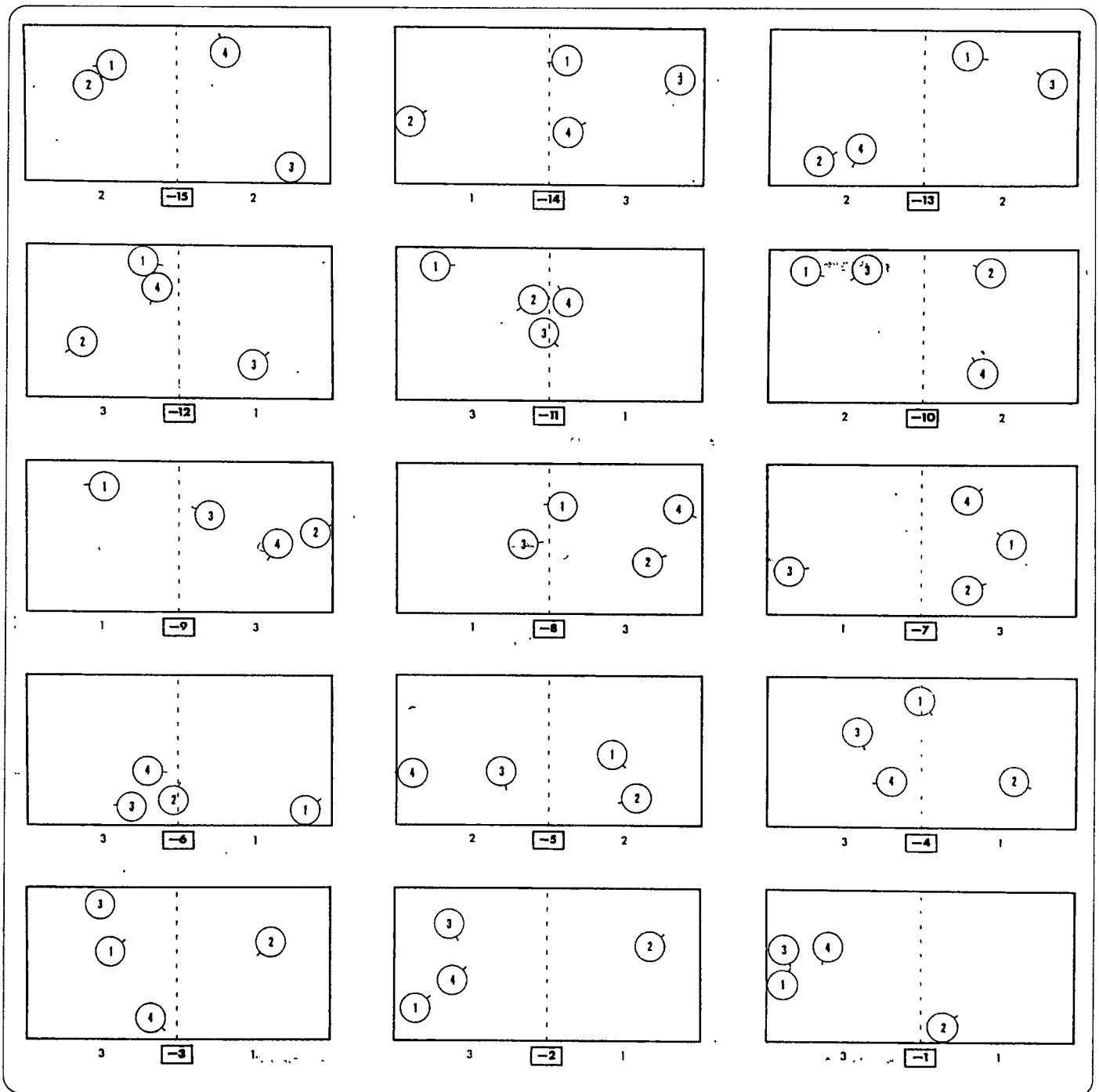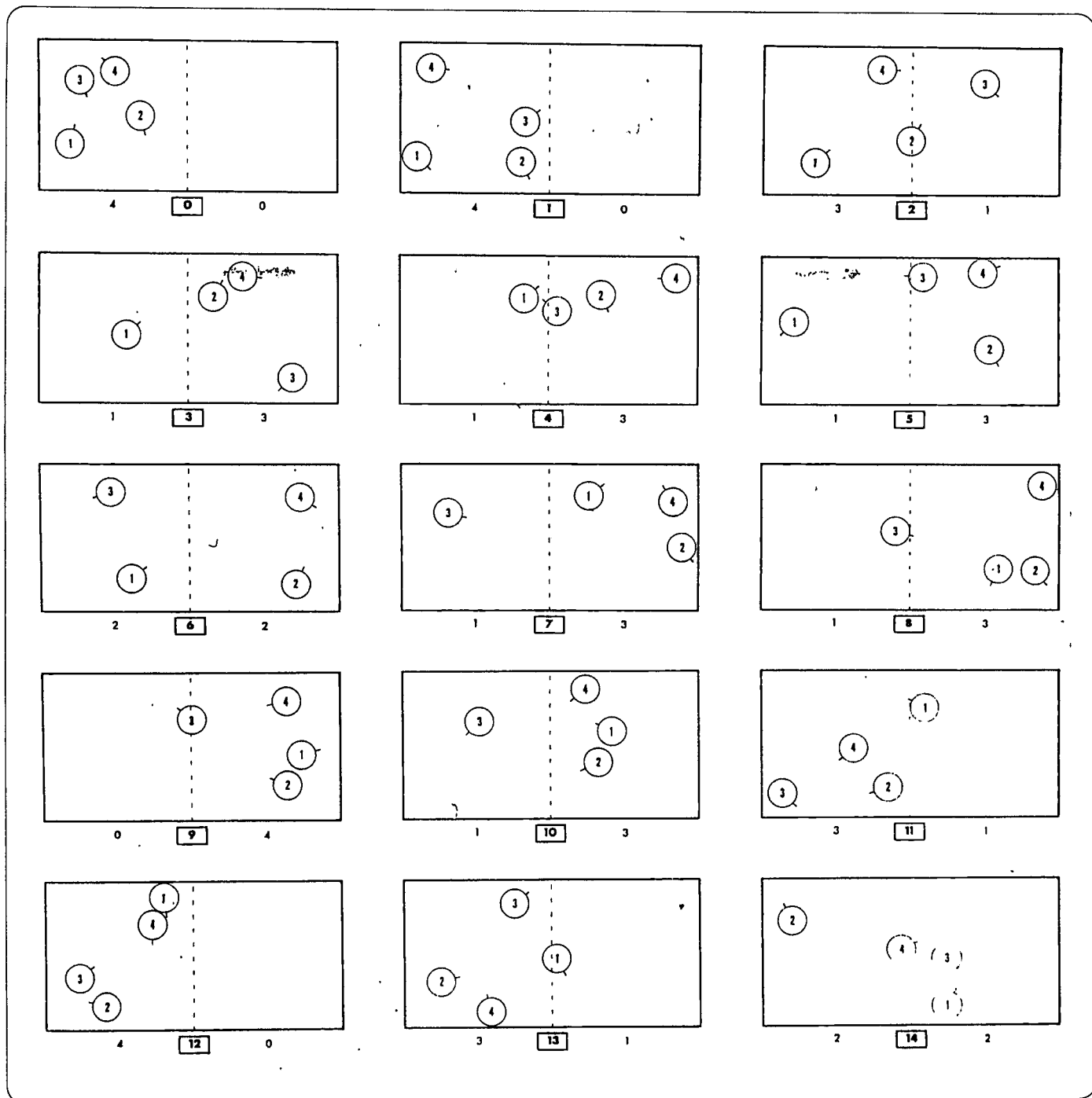
Fig. D-4. Successive movie frames of a gas of 4 molecules inside a box. These frames show the gas molecules, initially in the left half of the box, spreading out throughout the entire box. The frames in the preceding Fig. D-3 showed the molecules becoming concentrated in the left half of the box. The successive frames in both of these figures show an extreme fluctuation where all the molecules of the gas in equilibrium become at one time (in frame 0) spontaneously concentrated in the left half of the box. [The figure was produced by a computer-generated simulation of a gas of 4 molecules colliding with each other and with the walls of the box.]

Example: Gas of four molecules

Fig. D-2 illustrated a highly irreversible process where a gas of 40 molecules, initially in the left half of a box, spreads out throughout the entire box. For the sake of contrast, consider a gas of only 4 molecules which are initially in the left half of a box and then spread out throughout the entire box. (See Fig. D-4.) If a movie of this process is played backward, it does not look unnatural at all. Indeed, even if such a small gas in equilibrium, as many as one out of $2^4 = 16$ frames would, on the average, show all molecules in the left half of the box.

This extreme situation occurs thus actually quite frequently. Fluctuations of this kind are thus commonly observed (as illustrated in Figs. D-3 and D-4 by the successive movie frames labeled −15, −14, ..., 13, 14.), Correspondingly, a movie played backward looks just about as realistic as one played forward, i.e., the original process may be considered reversible.

Problems

[D-1] *Deciding whether a movie is being played backward*

Several movies portray the situations described below. In each case, do the following:

(1) Decide whether the process observed in the movie is one which could occur in actuality or which is very unlikely to occur in actuality. Is the movie being played backward or can't one tell?

(2) For each of these movies, describe the actual process that was filmed Is this a reversible or irreversible process?

The following situations are seen in the movies:

(a) A box, lying on the floor, rises and lands on the top of a table.
(b) Two billiard balls collide and move off in different directions.
(c) A small chicken crawls into a broken egg shell and the egg shells then reassemble themselves to form an intact egg. *<a-14>*

[D-2] *Reversible and irreversible processes*

Consider each of the processes described below.

(1) In each case, describe the process that would be observed in a backward-running movie of this process.

(2) Is this a process which could be observed in actuality or which is very unlikely to occur in actuality? Is the original process reversible or irreversible?

The following are the processes to be filmed.

(a) A pendulum, suspended from the ceiling, swings back and forth by decreasing amounts until it finally comes to rest.
(b) A drop of ink, falling into a glass of water, spreads out so that all the ink gradually becomes diffused throughout the water.
(c) A car is rolling up along a ramp with decreasing speed.
(d) A house collapses into a pile of debris when it is being demolished by an explosion. *<a-5>*

E. Basic states and entropy

Importance of the number of basic states. As we have seen, the probability that a macroscopic system is in a given situation depends on the number of possible basic states in which the system can be (i.e., the number of

basic states *available* to the system). A knowledge of the number Ω of basic states available to a system is thus of central importance to all arguments about macroscopic systems. In particular, it is useful to know how the number Ω of basic states depends on important macroscopic quantities that describe the system (e.g., its volume V or total energy E).

Ideal gas. The following paragraphs examine this question in the case of simple gases. Suppose that the number of molecules per unit volume in such a gas is sufficiently small that these molecules are ordinarily far apart from each other. The molecules then interact with each other to an almost negligible extent as they move about, occasionally colliding with each other and with the walls of the confining container. Such a simple gas is called an *ideal* gas.

Def: | ***Ideal gas:*** A gas whose molecules are sufficiently far apart that they interact with each other to an almost negligible extent. | (E-1)

The potential energy U of interaction of the molecules in such an ideal gas is, therefore, negligible compared to the kinetic energy K associated with the center-of-mass motion of the molecules. If the molecules are *monatomic* (i.e., if each molecule consists of a single atom), so that one can ignore the internal energy of any molecule, the total energy E of the gas is then just equal to its total kinetic energy K.

For example, helium and argon are such monatomic gases (consisting, respectively, of He or A atoms).

Dependence of Ω on the volume of an ideal gas

Consider an ideal gas of N molecules in a container of volume V. Suppose that the volume of this container were 2 times as large (while the energy of the gas is the same). Then the number of possible positions available to each molecules would also be 2 times as large. (See Fig. E-1.)

Hence the number of position states available to the first molecule would be 2 times as large. When this first molecule is in any of these positions, the number of possible states available to the second molecule would also be 2 times as large. Hence the number of position states available to *both* of these molecules would be $2 \times 2 = 2^2$ as large. For each of these position states, the number of position states for the third molecule would also be 2 times as large. Hence the number of position states available to three molecules would be $2^2 \times 2 = 2^3$ times as large. By continuing this argument, we see that the number Ω of positions states available to all N molecules would be multiplied by 2^N.

Similarly, if the volume V of the container were 3 times as large, the number Ω of position states would be multiplied by 3^N. Hence we arrive at the general conclusion that the number Ω of position states available to the N molecules is proportional to V^N, i.e.,

for an ideal gas, $\qquad \Omega \propto V^N$ $\qquad\qquad$ (E-2)

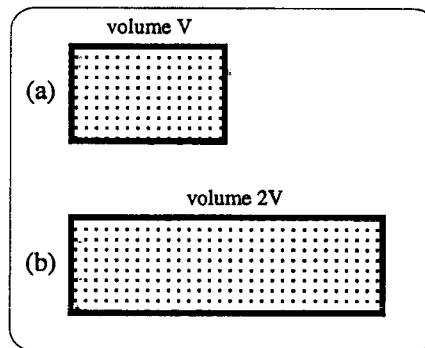where the symbol $\propto$ means "is proportional to".

Fig. E-1. (a) Points indicating the possible positions of a single gas molecule in a container of volume V. (Each point really indicates a digitized position, i.e., a small range of positions in a small cube surrounding this point.) (b) Possible positions in a container of 2 times larger volume.

The number N of molecules in a real gas is, of course, enormously large (e.g., typically there might be $N = 10^{24}$ such molecules). The exponent of V in (E-2) is thus enormously large. When the volume of the gas is increased, the number of basic position states available to all the molecules in the gas increases thus *extremely* rapidly.

Dependence of Ω on the energy of an ideal gas

Consider now an ideal gas of N *monatomic* molecules when the gas has some fixed volume and some known energy E (equal to its kinetic energy K). What happens to the number of possible basic states available to the gas if its kinetic energy is increased? Each of its molecules can then have a larger speeds and hence also more possible values of its velocity. Thus the number of possible values of the velocities of *all* the molecules in the gas is greatly increased. Indeed, reasoning similar to that leading to (E-2) shows that the number Ω of these states of possible velocities depends on the kinetic energy K so that

for an ideal gas, $\Omega \propto K^{3N/2}$.   (E-3)

(The reasoning leading to this result is outlined below.)

Since the number N of molecules in a real gas is typically as large as 10^{24}, the exponent of K in (E-3) is again enormously large. When the kinetic energy of the gas is increased, the number of basic velocity states available to all the molecules in the gas increases thus *extremely* rapidly.

Reasoning leading to the result (E-3)

Suppose that the kinetic energy of the gas were 2 times as large. Then the kinetic energy of each of its molecules would, on the average, also be 2 times as large. But this kinetic energy is equal to

$$\frac{1}{2} m (v_x^2 + v_y^2 + v_z^2)$$ (E-4)

where m is the mass of the molecule and v_x, v_y, v_z are the three components of its velocity. The square of each of each of these velocity components in (E-4) would then, on the average, also be 2 times as large. Hence the magnitude of each velocity component (e.g., of v_x) would be larger by a factor of $\sqrt{2}$.

As indicated in Fig. E-2, the number of possible values of v_x, having a magnitude less than this, would then also be $\sqrt{2}$ times as large. For each of these values, there would similarly be $\sqrt{2}$ times as many possible values of v_y; and for each of these, there would similarly be $\sqrt{2}$ times as many possible values of v_z. Thus the number of possible values of velocity components for a single molecule would be larger by a factor of

$$\sqrt{2} \times \sqrt{2} \times \sqrt{2} = (\sqrt{2})^3 = 2^{3/2}.$$

For each of these values, a second molecule in the gas would also have $2^{3/2}$ as many possible values of its velocity components. For each of these, a third molecules would also have $2^{3/2}$ as many possible
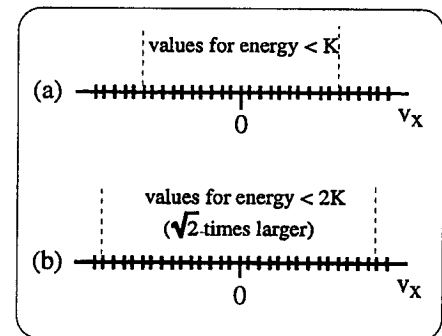

Fig. E-2. Marks indicating the identifiable digitized values of the velocity component v_x of a single molecule. (a) Average range of available values when the kinetic energy of the gas is less than K. (b) Average range of available values when this kinetic energy is less than 2K.

values of its velocity components. All the N molecules of the gas would then have

$$2^{3/2} \times 2^{3/2} \times 2^{3/2} \times \ldots = (2^{3/2})^N = 2^{3N/2}$$

as many velocity components.

If the kinetic energy K of the gas were 3 times larger, the number of possible values of velocity components of all molecules in the gas would similarly be larger by $3^{3N/2}$. In general, therefore, the number Ω of possible velocity states of the gas depends on its total kinetic energy so that

$$\Omega \propto K^{3N/2}. \tag{E-5}$$

Strictly speaking, the preceding reasoning is about the number Φ of velocity states corresponding to a kinetic energy *less* than K and leads to the conclusion that $\Phi \propto K^{3N/2}$. The number Ω of states in any small range between K and K + dK is then equal to $(d\Phi/dK)\, dK$ and is thus proportional to $K^{3N/2\,-1}$. But since N is as large as 10^{24}, 1 is utterly negligible compared to 3N/2. Hence the result (E-5) is correct.

Entropy

Dealing with unimaginably large numbers. The number N of atomic particles in a macroscopic system is extremely large (e.g., as large as 10^{24}). When one considers the number Ω of basic states available to such a system, one is then led to numbers which are even enormously larger. Indeed, as indicated by results like (E-3) and (E-4), one may be forced to work with numbers as unimaginably large as $2^{10^{24}}$.

One can avoid the difficulties of dealing with such gigantic numbers by working with their *logarithms*. For example, if $\Omega = 2^{10^{24}}$, $\ln\Omega$ (i.e., the natural logarithm of Ω) is $10^{24} \times \ln 2 = 0.69 \times 10^{24}$. Although this may still be a large number, it is at least a manageably large number!

A review of logarithms can be found in Appendix B. We shall work with the *natural* logarithm (the logarithm to the base e) since it arises in many theoretical calculations. However ln x (the natural logarithm of any number x) is very simply related to log x (its logarithm to base 10) so that ln x ≈ 2.30 log x.

Definition of entropy. Instead of working with the number Ω of available states, it is thus usually much more convenient to work with its logarithm. We shall call $\ln\Omega$ the *basic entropy* of a system in accordance with the following definition:

Def: | **Basic entropy:** The basic entropy of a system is $\ln\Omega$ (where Ω is the number of basic states available to the system). | (E-6)

The quantity S, which is conventionally called the *entropy* of a system, differs from this basic entropy only by a constant k.

Def: | **Entropy:** $S = k \ln\Omega$ | (E-6)

This constant k, which is called "Boltzmann's constant", has no fundamental theoretical significance, but is only introduced for the convenience of some measurements. (Chapter 6 will discuss the particular international conventions adopted to specify the numerical value of this constant.)

Ludwig Boltzmann (1844-1906) was an Austrian physicist who first formulated a statistical theory of gases and thus laid the foundation for an atomic theory of macroscopic systems. The atomic specification of entropy, $S = k \ln\Omega$, was also first introduced by him.

Entropy as a measure of randomness. The entropy provides a convenient and precise way of specifying the degree of *randomness* of a system. Indeed, a situation where a system can be in any one of a large number of possible basic states is said to be more random than a situation where it can be in only a few such states.

For example, a situation where the molecules of a gas are equally distributed in the two halves of a box corresponds to many more possible positions of the molecules than a situation where all the molecules are in only one half of the box. Thus one would say that the first situation is much more random than the second. The entropy $\ln \Omega$ is correspondingly larger is the first situation than in the second and provides a quantitative measure of the degree of randomness of the gas.

Problems

[E-1] *Randomness in everyday life*

The notion of randomness is also encountered in everyday life and there too is related to the number of possible ways that a situation can be realized. The following are some examples.

(a) In the game of bridge, each player is dealt a hand consisting of 13 cards. Consider a situation A in which all the cards in such a hand are spades, and another situation B where a hand contains some spades, some clubs, some hearts, and some diamonds. (1) Which of these situations can be realized in more possible ways? (2) Which of these situations is more random and which is less random (i.e., more orderly)

(b) Compare the number of ways that four letters can be used to form meaningful words and the number of ways that four letters can be used to form nonsense words. (1) Which of these numbers is larger? (2) Does a meaningful word correspond to a more random or less random arrangement of the letters? <a-9>

[E-2] *Entropy of very small systems*

(a) Consider a very small system X which can only be in any one of 3 possible basic states. What is the basic entropy of this system?

(b) Consider another very small system Y which can only be in any one of 5 possible basic states. What is the basic entropy of this system?

(c) Consider the composite system consisting of both X and Y. In how many possible basic states can this system be? What then is the corresponding basic entropy of this system? <h-1>

(d) How is the basic entropy of this composite system related to the basic entropies of its constituent systems X and Y? <a-18>

[E-3] *Entropy due to molecular positions in a gas*

Suppose that the position of every molecule in a gas is described with a precision of 0.010 mm (or 1.0×10^{-5} m). The possible positions of each molecule are then indicated by the points in Fig. E-3 where each point is at the center of a small cube having a side of 0.010 mm.

(a) What is the volume of each such small cube?

(b) Suppose that the box containing the gas has a volume of 1.0 m³. In how many possible positions can a single molecule of the gas then be found?

(c) What then is the number of possible positions available to all the N molecules of the gas?

(d) Suppose there are $N = 10^{24}$ molecules in the gas. What then is the basic entropy of the gas due to all the possible positions of its molecules? <a-3>

Fig. E-3. Points indicating the possible positions of a molecule in a gas.

[E-4] *Entropy of a gas*

There are Ω_{pos} basic states available to an ideal gas because of all the possible positions of its molecules. There are also Ω_{vel} basic states available to this gas because of all the possible velocities of its molecules.

(a) What then is the *total* number Ω of possible states available to the gas (both because of all the possible positions and also because of all the possible velocities of its molecules)? <h-4>
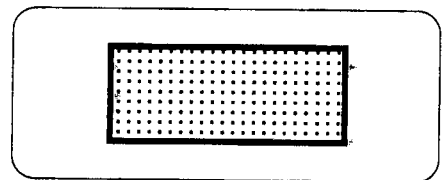
(b) How is the basic entropy $\ln \Omega$ of the gas related to the basic entropy $\ln \Omega_{pos}$ and to the basic entropy $\ln \Omega_{vel}$ due to velocities?

(c) For a ideal gas, the number Ω_{pos} of basic states due to possible positions depends on the volume V of the gas in the manner specified by (E-3). If the gas is monatomic, the number Ω_{vel} of basic states due to possible velocities depends on the energy E = K of the gas in the manner specified by (E-5). How then does the basic entropy $\ln \Omega$ of the gas depend on its volume V and its energy E? *<a-16>*

[E-5] *Typical magnitudes*

A consideration of macroscopic systems leads one to deal with numbers of very different sizes. Thus it is useful to distinguish the following kinds of numbers:

(1) Ordinary numbers (like 5 or 100).

(2) Huge numbers (like 10^{25}).

(3) Gigantic numbers (like $10^{10^{25}}$).

State whether the typical magnitudes of the following quantities are ordinary, huge, or gigantic.

(a) The number of atoms in a macroscopic system (like a person or the air in a room).

(b) The basic entropy $\ln \Omega$ of such a macroscopic system. *<h-10>*

(c) The number Ω of possible basic states in which such a system can be?

(d) Suppose that the basic entropy of such a macroscopic system is increased by 0.1%. If its original entropy is $\ln \Omega$, its new entropy $\ln \Omega'$ is then such that

$$\ln \Omega' - \ln \Omega = 0.001 \ln \Omega.$$

The new number Ω' of basic states available to the system is then correspondingly larger than the original number Ω of basic states available to the system. To assess how much larger it is, determine whether the ratio Ω'/Ω is an ordinary number, a huge number, or a gigantic number. *<a-25>*

F. Properties of the entropy

Dependence of entropy on energy

Entropy of a monatomic ideal gas. If the volume of a macroscopic system remains unchanged, its entropy depends on the internal energy E of the system. For example, consider the simple case of a monatomic ideal gas where the internal energy E is just equal to the total kinetic energy K of the molecules. According to (E-§), the number of basic states available to the gas, because of the different possible velocities of its molecules, is then proportional to $E^{3N/2}$, i.e.,

$$\Omega = c\, E^{3N/2}$$

where c is some constant. Hence the basic entropy of this gas depends on its internal energy E so that

for ideal monatomic gas, $\ln \Omega = \ln c + \dfrac{3N}{2} \ln E.$ (F-1)

The basic entropy of such a gas thus increases with its energy E in the manner illustrated in Fig. F-1.

Entropy of any system. Most macroscopic systems are, of course, more complex than ideal gases because their atoms or molecules interact appreciably with each other. Thus their internal energy E = K + U includes also appreciable potential energy U of interactions among atomic particles. But all these systems contain many moving atomic particles. If the internal energy E of such a system is increased, the kinetic energy of these moving particles is also increased. As in the case of the ideal gas, the number of possible velocities of these particles is then correspondingly also greatly increased.

The number Ω of basic states available to *any* macroscopic system is thus greatly increased if its internal energy E is increased. The basic entropy $\ln\Omega$ of any macroscopic system then increases with its energy E again roughly in the fashion indicated in Fig. F-1 (although the exact dependence on the energy will be more complex than in the case of an ideal gas).

Fig. F-1. Qualitative graph showing how the basic entropy $\ln\Omega$ of a system depends on its internal energy E.

This conclusion is not true if one ignores the velocities of the particles in a system. (This may occasionally be done in special cases where one considers only the "spins" of atomic particles.)

Entropy change and absolute temperature

Small entropy change and basic temperature. Suppose that the volume of a macroscopic system is kept fixed, but its internal energy E is changed by a small amount dE. The basic entropy $\ln\Omega$ of the system is then correspondingly changed by the small amount

$$d \ln\Omega = \frac{d \ln\Omega}{dE} dE = \beta \, dE. \qquad \text{(F-2)}$$

Here we have used β (the Greek letter *beta)* to denote the quantity $d \ln\Omega/dE$ which is the rate of change of the basic entropy with energy. (This quantity indicates the slope of the graph in Fig. F-1.) We can call this quantity the *basic temperature* of the system.

Def: | **Basic temperature β:** $\qquad \beta = \dfrac{d \ln\Omega}{dE}.$ | (F-3)

By virtue of (E-§), this definition can also be expressed in terms of the conventional entropy $S = k \ln\Omega$. Thus

$$\beta = \frac{1}{k} \frac{dS}{dE}. \qquad \text{(F-4)}$$

According to the definition (F-3), *the basic temperature β specifies how rapidly a system's entropy (or randomness) changes with increasing energy.*

Absolute temperature. Since $\ln\Omega$ is just a number, the basic temperature β has units involving an energy. More specifically, $1/\beta$ has the units of an energy (e.g., joule). Hence it is convenient to introduce another quantity T, called the *absolute temperature*, related to the basic temperature β according to the following definition:
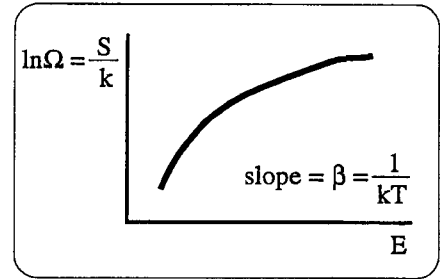
Def: | ***Absolute temperature T:*** $\quad kT = \dfrac{1}{\beta}$. | (F-5)

Note that the quantity kT has thus simply the units of an energy.

Equivalently, (F-3) allows one to express the basic temperature β in terms of the absolute temperature T. Thus

$$\beta = \frac{1}{kT}. \qquad \text{(F-6)}$$

Small entropy change and absolute temperature. The relation (F-2) specifies how much the entropy S of a system changes if its energy E is changed by a small amount (while its volume remains constant).. Thus it implies that

for constant volume, $\quad \dfrac{dS}{k} = \dfrac{1}{kT} dE$

or $\qquad\qquad\qquad dS = \dfrac{dE}{T}. \qquad \text{(F-7)}$

If the system's volume remains fixed so that no work is done on the system, the small energy change dE can only be due to a small amount of heat d'Q absorbed by the system. Equivalently, (F--7) can thus be written in the form

$$dS = \frac{d'Q}{T}. \qquad \text{(F-8)}$$

Internal energy and absolute temperature. The qualitative graph in Fig. F-1 indicates how the basic entropy of a system changes with its internal energy E.. As the energy E increases, the graph becomes less steep, i.e., its slope β decreases. The basic temperature β of a system thus *decreases* when its internal energy increases. Since $kT = 1/\beta$, this implies correspondingly that the absolute temperature T of a system *increases* when its internal energy increases.

Significance of the absolute temperature. According to (F-7), the absolute temperature T (or more precisely its reciprocal 1/T) indicates how rapidly the entropy of a system increases with increasing energy. For example, when the internal energy E of a system is small (and its absolute temperature T correspondingly also small), a small increase dE of its energy leads to a large increase dS of its entropy. But when the internal energy E of a system is large (and its absolute temperature T correspondingly also large), the same small increase dE of its energy leads to a smaller increase dS of its entropy.

Since β or T depend on the internal energy of a system, they can be used as indicators of this internal energy. According to the comments made in Chapter 2, one is thus well-justified in calling these quantities "temperatures". On the other hand, these quantities are not just related to the length of the column of liquid of some arbitrary thermometer. They have a more fundamental significance since they are directly related to the number of basic states available to a system. Indeed, the fundamental significance of the basic temperature (or absolute temperature) will become fully apparent in the next few chapters.

Entropy of a composite system

Consider a macroscopic system X which consists of two parts X_1 and X_2, as schematically indicated in Fig. F-2. Suppose that the part X_1 of this system can be in any one of Ω_1 possible basic states and that the other part X_2 of this system can be in any one of Ω_2 basic states. In how many basic states can the combined system X then be?

If X_1 is in any *one* of its basic states, X_2 can be in any one of its Ω_2 states. But X_1 can be in each of its Ω_1 states. Hence the number Ω of states available to the total system is

Fig. F-2. A system consisting of two parts.

$$\Omega = \underbrace{\Omega_2 \times \Omega_2 \times \Omega_2 \times \ldots \times \Omega_2}_{\Omega_1 \text{ factors}}$$

or $\Omega = \Omega_1 \, \Omega_2 \, .$ (F-9)

The basic entropy of the total system is thus

$$\ln\Omega = \ln\Omega_1 + \ln\Omega_2 \, . \tag{F-10}$$

If both sides of this relation are multiplied by k, one then obtains the result

$$\boxed{S = S_1 + S_2 \, .} \tag{F-11}$$

In other words, *the entropy of a system is the sum of the entropies of its parts.*

The preceding conclusion is equally true for a system consisting of any number of parts. Accordingly, it also implies that a system which consists of n *identical* parts has an entropy n times as large as that of one of its parts. The entropy of such a system (like the mass of the system) is thus proportional to the number of particles in the system. (For example, a copper block having a mass of 3 kg has an entropy 3 times larger than a copper block having a mass of 1 kg.)

Entropy and precision of description

To identify discrete basic states, we grouped neighboring values of positions or velocities into small ranges which could then be counted. As discussed in Section B of Chapter 3, each basic state corresponds thus to some small range of positions and velocities.

For example, one might specify each particle's position coordinate x within a range of 10^{-5} meter. However, if one is interested in greater precision, one could specify it within a range of 10^{-6} meter — and would thereby identify 10 times as many distinguishable values of x. If one increase the precision of description of all the positions or velocities, one thus multiplies the number Ω of identified basic states by some large factor.

However, the number Ω_A and Ω_B of basic states in any two macrostates A and B would be multiplied by the *same* factor. Hence the *ratio*

$$\frac{\Omega_A}{\Omega_B}$$ is independent of precision.

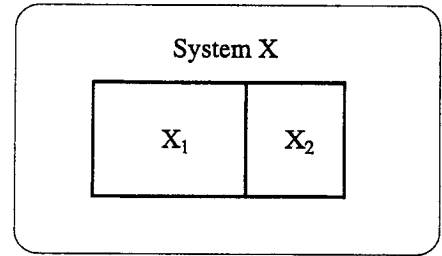The corresponding logarithm is thus also independent of precision, i.e.,

$\ln\Omega_A - \ln\Omega_B$ is independent of precision

so that

$S_A - S_B$ is independent of precision.

Thus one arrives at the following conclusion: *Although the entropy itself depends on the chosen precision of description of the basic states, the difference between any two entropies has a physical significance independent of the chosen precision.*

In a more accurate quantum-mechanical discussion of atomic particles, the basic states are unambiguously defined as quantum states. No precision needs then to be specified, i.e., the precision is ultimately specified by a constant of nature (Planck's constant). The more accurate quantum-mechanical description of atomic particles leads, therefore, to a uniquely defined value of the entropy.

Problems

[F-1] *Absolute temperature and energy of a monatomic ideal gas*

The relation (F-1) specifies how the basic entropy $\ln\Omega$ of a monatomic ideal gas depends on its internal energy $E = K$.

(a) Use the definition (F-3) of basic temperature to find how the basic temperature β of this gas depends on its energy E. *<h-8>*

(b) How then is the average energy E/N of a single molecules of this gas related to the absolute temperature T of the gas?

(c) If the absolute temperature of the gas is 3 times larger, how much larger is the average kinetic energy of one of its molecules? *<a-13>*

[F-2] *Energy and entropy changes in thermal interaction*

A system X is placed into contact with a system Y so that heat can be transferred from one to the other. (For example, X might be a spoon and Y a cup of tea.) The entire system, consisting of X and Y, is thermally insulated from its surroundings. The system X, which has initially a lower absolute temperature than the system Y, is then observed to absorb some positive amount of heat.

(a) Is the heat absorbed by the system Y positive, negative, or zero?

(b) Does the internal energy of X increase, decrease, or remain the same?

(c) Does the internal energy of Y increase, decrease or remain the same?

(d) Does the internal energy of the entire system increase, decrease, or remain the same?

(e) Does the entropy of X increase, decease, or remain the same?

(f) Does the entropy of Y increase, decrease, or remain the same?

(g) Does the entropy of the entire system increase, decrease, or remain the same? *<h-7> <a-15>*

G. Summary

Definitions

Reversibility: A process is *reversible* if a backward-running movie of it shows a situation that could readily be observed in actuality. It is *irreversible* if such a movie shows a situation that would be exceedingly unlikely to occur in actuality.

Ideal gas: A gas whose molecules are sufficiently far apart that they interact with each other to an almost negligible extent.

Basic entropy: The basic entropy of a system is $\ln\Omega$ (where Ω is the number of basic states available to the system).

Entropy: $S = k \ln\Omega$ (k = Boltzmann's constant)

{The entropy provides a convenient measure of the degree of randomness of a system.}

Basic temperature: $\beta = \dfrac{d \ln\Omega}{dE}$.

{The basic temperature thus specifies how rapidly a systems' entropy changes with increasing energy.}

Absolute temperature T: $kT = \dfrac{1}{\beta}$.

Important knowledge

Probability of a macrostate: $P_A \propto \Omega_A$

{The probability that a macroscopic system in a particular macrostate is proportional to the number of basic states available to the system in this macrostate}.

Equilibrium values: Macroscopic quantities describing a macroscopic system in equilibrium have values very close to their most probable values, but exhibit small fluctuations around these.

Irreversibility of macroscopic processes: Processes involving macroscopic systems are predominantly irreversible (since they involve motions of many independently moving atomic particles).

Approach to equilibrium. If a macroscopic system is in a situation where it is not with equal probability in each of its available basic states, it will change until it reaches the equilibrium situation where these probabilities are equal.

Dependence of entropy on energy: The entropy of a macroscopic system increases with its internal energy.

Small entropy change (for fixed volume):

$$d\ln\Omega = \beta \, dE \qquad \text{or} \qquad dS = \frac{dE}{T} = \frac{d'Q}{T} \ .$$

Additivity of entropy: The entropy of a macroscopic system is the sum of the entropies of its parts.

New abilities

You should now be able to do the following:

(1) Calculate the probabilities of various spatial distributions of molecules in a gas if it consists of only very few molecules in equilibrium.

(2) Describe qualitatively equilibrium and non-equilibrium situations.

(3) Decide whether a process is reversible or irreversible.

(4) Find the absolute temperature of a system if you know how its entropy depends on its internal energy.

Problems

[G-1] *Spatial distribution of 3 gas molecules*

Fig. G-1 illustrates a very simple gas consisting of only three molecules inside a box. In equilibrium each of these molecules is then equally likely to be located in each third of the box.

(a) What is the probability P_0 that no molecule is located in the left third of the box?

(b) What is the probability P_1 that one molecule is located in the left third of the box?

(c) What is the probability P_2 that two molecules are located in the left third of the box?

(d) What is the probability P_3 that all three molecules are located in the left third of the box? <h-6> <a-17>

[G-2] *Spatial distribution of 5 gas molecules*

Fig. G-2 illustrates a very simple gas consisting of five molecules inside a box. In equilibrium each of these molecules is then equally likely to be located in each third of the box.

(a) What is the probability that *all* the molecules are located in the left third of the box?

(b) What is the probability that *no* molecules is located in the left third of the box?

(c) What is the probability that *two* molecules are located in the left third of the box? <a-11>

[G-3]† *Probability that any number of gas molecules are in one half of a box*

A gas of N molecules is in equilibrium inside a box so that every molecules is equally likely to be in the left half or the right half of the box.

(a) What is the total number of possible ways that the N molecules can be distributed over the two halves of the box?

(b) If there is one molecule in the left half, this molecule can be any one of the N molecules. If there is also a second molecules in the left half, this can be any of the remaining (N 1) molecules. In how many ways can one select theses two molecules so that they are at two distinct places in the left half of the box? In how many ways can one select them irrespective of where they are in the left half of the box?

(c) If there is also a third molecule in the left half, this can be any of the remaining (N − 2) molecules. If there is also a fourth molecule in the left half, this can be any of the remaining (N − 3) molecules. And so forth. If there are n molecules in the left half, in how many ways can one select these so that they are at n distinct places in the left half of the box?

(d) The actual places where these molecules are in the left half is irrelevant. In how many ways could the molecules be rearranged among the preceding places (and yet leave exactly the same molecules in the left half of the box)? <h-2>

(e) What then is the probability that n of the N molecules are found anywhere in the left half of the box?

(f) The preceding general result was used to calculate the probabilities listed in Fig. B-2 about a gas of 20 molecules. To check the general result, apply it to a gas of 6 molecules and find the probability that 3 of these molecules are in the left half of the box. Does your result agree with that which you found in Problem A-1? <a-20>
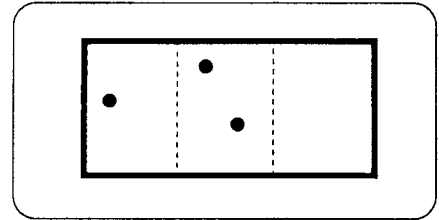

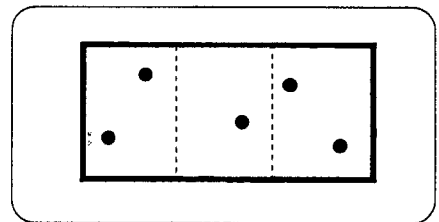**Fig. G-1.** A gas of three molecules in a box.

Fig. G-2. A gas of five molecules in a box.

[G-4] *Alternative listing of the positions of 4 molecules*

Fig. A-2 listed the possible ways in which 4 molecules can be located either in the left half or the right half of a box. This listing was done by focusing attention on either half of the box and listing which of the four molecules could be in this half. Alternatively, one could focus on each of the four molecules and list whether each of these is in the left half (L) or right half (R) of the box. (For example, the particular entry in the table of Fig. G-3 indicates that molecules 1, 2, and 3 are in the left half of the box and molecule 4 is in the right half of the box.)

Proceed in this manner to list in the table all the 16 possible ways in which the molecules can be distributed over the two halves of the box. *<a-4>*

[G-5] *Time-averaged value*

A macroscopic system can be observed in the course of time, e.g., by taking a movie of it. Some quantity n (like the number of gas molecules in one half of a box) can then be measured at several successive times. For example, if one looks at f successive frames of the movie, one might observe that n has the value n_1 in the first of these movie frames, the value n_2 in the second of these frames, the value n_3 in the third of these frames, and so forth. The time-average value $<n>_t$ of n, over these f successive frames, is then defined so that

$$<n>_t = \frac{n_1 + n_2 + n_3 + \ldots + n_f}{f}.$$

(a) The number n of molecules in one half of the box does not always have the same value, but fluctuates in the course of time. Does the time-averaged value of this number fluctuate more or less than n itself?

(b) If one averages of more frames (i.e., over a longer time), do the fluctuations in the time-averaged value become larger or smaller?

(c) Does this time averaged value of n change appreciably in the course of time if the gas is not in equilibrium? Does it change appreciably if the gas is in equilibrium? *<a-19>*

[G-6]† *Increase of number of gas states with energy*

The basic entropy of a monatomic ideal gas depends on its energy E in the manner specified by (F-1).

(a) Consider such a gas consisting of N molecules. What then is the change d $(\ln\Omega)$ of the basic entropy of this gas when its internal energy is increased by 0.1% ?

(b) What is this change if $N = 10^{24}$ molecules?

(c) Suppose that the gas can be in any of Ω possible states when its energy is E and that it can be in any of Ω' possible states when its energy is 0.1 larger. What then is ln (Ω'/Ω)?

(d) Correspondingly, what is the ratio Ω'/Ω? Does a small increase in the energy of the gas then produce a moderate increase in the number of possible states of this gas, a huge increase, or a gigantic increase? *<a-22>*

n	n'	molecule #
		1	2	3	4
3	1	L	L	L	R

Fig. G-3. A table with an entry specifying one particular arrangement of 4 molecules in two halves of a box.