LECTURE 9  MICROSCOPIC DESCRIPTION OF EQUILIBRIUM STATES AND PROCESSES

Text Sections  21.1, 21.6
Sample Problems  21.6
Suggested Questions  None
Suggested Problems  67P, 69P

Summary  States, configurations and microstates
          Equilibrium
          Entropy
          Natural processes

Specific objectives

• Explain the relation between macroscopic entropy and microscopic disorder or complexity of a system
States, configurations and microstates

Consider, for example, a quantity of an ideal monatomic gas at equilibrium in a container (see Fig 21-1). Suppose that a barrier is removed (stopcock is opened) allowing the gas to expand into another identical container and come to equilibrium again. In this new equilibrium state the gas molecules can move freely from one container to the other.

The gas system can be completely described in a macroscopic sense by specifying a set of parameters such as \( n \) (the number of moles), \( V \) and \( T \) for each of the two equilibrium states. By definition these equilibrium thermodynamic quantities do not change with time.

If we were able to keep track of individual gas molecules we could provide more precise microscopic descriptions of the system in the second equilibrium state.

We could specify the configuration of the system. This is done by specifying \( N_L \) and \( N_R \) (the numbers of molecules in the left and right containers), \( V \) and \( K \) (the average kinetic energy of the gas molecules). Remember that \( K = \frac{1}{2} k T \). At this level of detail we would expect that \( N_L \) might change slightly with time (and \( N_R \) change by a compensating amount since their sum must remain constant) since the molecules move freely from one container to the other. Thus the system moves from one configuration to another.

Alternatively we could go into even greater detail and specify the microstate of the system. This is done by labelling the gas molecules and specifying which particular molecules are in the left-hand container (and hence which are in the right), \( V \) and \( K \). At this (Olympian) level of detail, the system moves rapidly from one microstate to another with time since individual molecules move quickly from one container to the other. It is possible, for example, that all of the molecules might move back into the left-hand container (which corresponds to the first equilibrium state before the barrier was removed).

How are these three descriptions of the same system related to one another? The answer is provided by statistical mechanics and the theory of probability.

The basic assumption of statistical mechanics is that if we observe the system for a long time then it is equally probable that we will find the system in any microstate consistent with the laws of motion (i.e. those that have the same value of \( K \) in this example). Since the configurations have different numbers of microstates associated with them, the configurations are NOT equally probable.
To illustrate this, consider a system with only 4 gas molecules (see Table 21-1). There are 16 microstates of this system and 5 configurations with $N_L$ equal to 0, 1, 2, 3 and 4 respectively. From the Table, the multiplicities, $W$ (or numbers of microstates) of these configurations are 1, 4, 6, 4 and 1 respectively. Thus there is 1 chance in 16 of finding all 4 molecules in the left hand container, 4 in 16 of finding 3 there, etc. The most likely configuration, 6 chances in 16, is the one with 2 molecules in each of the containers.

In general, the probability of a configuration is $W$ divided by the total number of microstates.

For our two container system the theory of probability gives

$$W = \frac{(N_L + N_R)!}{N_L! \ N_R!}$$

and the total number of microstates is $2^N$ where $N$ is equal to $N_L + N_R$.

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Equilibrium

A much more realistic number of molecules is $10^{22}$ rather than 4. The values for the total number of microstates and for $W$ for the configuration where $N_L$ is equal to $N_R$ are both unimaginably large (about 10 raised to the power of $3 \times 10^{21}$).

Fig 21-15 is a sketch of the multiplicities for configurations with various values of $N_L$. It peaks very very sharply (much more than shown in Fig 21-15!) at the configuration where half the gas molecules are in each of the two containers. The width of the peak is typically about $\sqrt{N}$ or about $1/\sqrt{N}$ of the length $N$ of the horizontal axis.

Thus in the case where $N$ equals $10^{22}$ the probability of finding $N_L$ differing from $N_R$ by more than about $10^{11}$ (i.e. by more than one part in $10^{11}$) is negligibly small.

By similar statistical arguments, the probability of finding any thermodynamic parameter such as $p$ varying by more than one part in $10^{11}$ from the equilibrium value is also negligibly small.

The (macroscopic) thermal equilibrium state corresponds to the most probable configuration of the system. The most probable configuration is the one associated with the greatest possible number of microstates. At macroscopic level, the system remains in equilibrium even though at microscopic level it moves through an enormous number of microstates.
Note that the first equilibrium state with all molecules in the left-hand container corresponds to a possible configuration. The probability of the system returning to that configuration however is infinitesimally small and this does not occur in real life.

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Entropy

Configurations associated with large numbers of microstates are said to be more complex or more disordered than those with fewer microstates. The equilibrium state of a system is the most disordered configuration available. The Austrian physicist Ludwig Boltzmann introduced a measure of disorder called the entropy defined by

\[ S = k \ln W \]

where \( k \) is the Boltzmann constant and \( \ln \) is the natural logarithm (to the base e). Note that \( S \) has the same units as \( k \), i.e. J . K\(^{-1}\).

This important equation provides a microscopic interpretation of \( S \) which, as we shall see in the next few lectures, is one of the key thermodynamic parameters. The equation ranks with \( F = ma \) and \( E = mc^2 \) and is carved on Boltzmann’s tombstone.

For the first equilibrium state in the example, \( N_L = N \) and \( N_R = 0 \) and hence \( W = 1 \). Therefore \( S = 0 \).

For the second equilibrium state, \( N_L = N_R = N/2 \) and so

\[ S = k \ln \left[ \frac{N!}{(\frac{1}{2}N)! (\frac{1}{2}N)!} \right] = k \ln (N!) - 2k \ln \left[ (\frac{1}{2}N)! \right] \]

The logarithms can be evaluated using Stirling’s approximation

\[ \ln (N!) = N \ln (N) - N \]

so that

\[ S = kN \ln (2) = nR \ln (2) \]

This is also the entropy difference between the two equilibrium states.
Natural processes

Energy is conserved in all processes. Why then are all natural processes one-way?

For example, the internal energies of the above two equilibrium states are the same but the system always moves from the first to the second and not vice-versa.

Other examples

Heat flow is always from hot bodies to cold ones and not vice-versa.

Cold water does not spontaneously transform into ice and hot water.

If we drill a hole in a material with a blunt drill bit, the bit and the material become hot, i.e. mechanical energy has been converted to thermal energy. We do not see the reverse process where the bit and the material return to their original temperature returning mechanical energy to the drill!

Mechanical energy corresponds to ordered motion. All “adjacent” parts of a moving object have essentially the same velocity.

Thermal energy corresponds to disordered motion. Molecules in the object have random velocities that are superimposed on any ordered motion they may have.

It is very highly improbable that the disordered motion will become ordered motion and this does not occur in natural processes. The natural direction is for ordered motion to become disordered.