

LECTURE 4

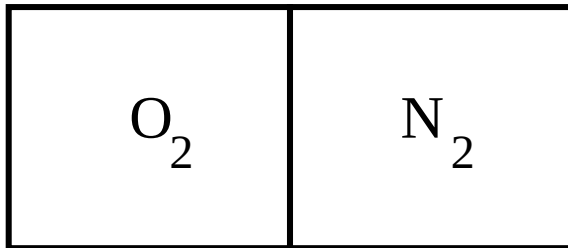
Reversible and Irreversible Processes

Consider an isolated system in equilibrium (i.e., all microstates are equally probable), with some number of microstates Ω_i that are accessible to the system. Suppose some *internal* constraint is removed but the total energy and particle number remain constant. Now the system can be in any of the Ω_i microstates *plus* whatever new microstates become available when the constraint is removed. The total number of accessible microstates after the constraint is removed is Ω_f .

Note that the system is *not* in equilibrium *immediately* after removing the constraint. Only a fraction of the states Ω_i/Ω_f are occupied. By the H theorem, the system now evolves in time (approaches equilibrium) in such a manner as to make more equal the probability of the system being found in any of the Ω_f microstates. (If some constraint on an isolated system is removed, the parameters readjust in such a way that $\Omega(y_1, \dots, y_n) \rightarrow$ maximum.)

Note also that if $\Omega_f > \Omega_i$, then after final equilibrium is achieved, simply restoring the initial constraint may not restore the system to its initial condition. In such a case we talk about an irreversible process.

As an example, consider a box divided into two parts by a partition.



Removing the partition increases the number of microstates accessible to the system as the volume accessible to each molecule increases. After the new equilibrium is reached, simply restoring the partition will not return the system to its original condition.

To summarize, if some constraint (or constraints) is removed in an isolated system in equilibrium, then the number of microstates accessible to the system can either remain constant or increase, i.e., $\Omega_f \geq \Omega_i$. If $\Omega_f = \Omega_i$, then the process is reversible. If $\Omega_f > \Omega_i$, the process is irreversible.

Dependence of Density of States on External Parameters

We have already shown that the equilibrium condition for two thermally interacting systems is that the β parameters of both systems be equal. We now want to determine the equilibrium conditions for two systems that interact thermally and mechanically. We will need, and therefore must derive, the relationship

$$\frac{\partial \ln \Omega}{\partial x_\alpha} = \beta \bar{X}_\alpha \quad (1)$$

where x_α is an external parameter and the generalized work is

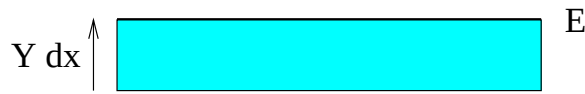
$$\overline{X}_\alpha = -\frac{\overline{\partial E}}{\partial x_\alpha} = -\frac{\partial \overline{E}}{\partial x_\alpha} \quad (2)$$

In other words, we want to know how the number of states Ω changes when work is done on the system, i.e., when the external parameters are changed. When the external parameters are changed, the energy levels shift. For example, consider standing waves or resonant modes in a cavity. If we change the size of the cavity, the wavelength of the standing waves changes, and the associated energy levels change. (Quantum mechanically, the frequency and energy go as $1/\lambda$ where λ is the wavelength.) This is why a piccolo has a higher pitch than a flute or a tuba.

Consider Ω as a function of E and x . (Let's drop the subscript α for a moment and concentrate on one external parameter.) Then how does Ω depend on x ? When x is changed by an amount dx , the energy $E_r(x)$ of each microstate is changed by an amount $(\partial E_r/\partial x)dx$. Let $\Omega_Y(E, x)$ be the number of states which have an energy between E and $E + \delta E$ when the external parameter is x and which are such that the derivative $\partial E_r/\partial x$ is between Y and $Y + \delta Y$. The total number of states is

$$\Omega(E, x) = \sum_Y \Omega_Y(E, x) \quad (3)$$

Consider a particular energy E . When the external parameter is changed, some states which originally had an energy less than E will acquire an energy greater than E and vice-versa. Those states for which $\partial E_r/\partial x$ has the particular value Y change their energy by Ydx . Hence all those states located within an energy Ydx below E will change their energy from a value smaller than E to one greater than E .



The number $\sigma_Y(E)$ of such states is thus given by the number per unit energy multiplied by the energy range Ydx , i.e., by

$$\sigma_Y(E) = \frac{\Omega_Y(E, x)}{\delta E} Y dx \quad (4)$$

Different states have their energy changed by different amounts Ydx . Hence the total number of states $\sigma(E)$ whose energy is changed from a value less than to a value greater than E is given by summing over all possible values of Y :

$$\sigma(E) = \sum_Y \sigma_Y(E) = \sum_Y \frac{\Omega_Y(E, x)}{\delta E} Y dx = \frac{\Omega(E, x)}{\delta E} \overline{Y} dx \quad (5)$$

where the mean value of Y is

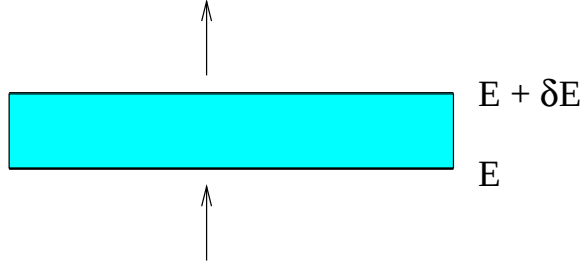
$$\overline{Y} = \frac{1}{\Omega(E, x)} \sum_Y \Omega_Y(E, x) Y \quad (6)$$

Note that

$$\overline{Y} = \frac{\overline{\partial E_r}}{\partial x} = -\overline{X} \quad (7)$$

where X is the generalized force conjugate to the external parameter x .

Let us now consider the total number of states $\Omega(E, x)$ between E and $E + \delta E$. When the parameter x changes from x to $x + dx$, the number of states changes by $[\partial\Omega(E, x)/\partial x]dx$ which must be due to [the number of states which enter this range from below by having their energy changed from a value less than E to one greater than E] minus [the number of states that leave through the top by having their energy changed from a value less than $E + \delta E$ to one greater than $E + \delta E$]:



$$\frac{\partial\Omega(E, x)}{\partial x} dx = \sigma(E) - \sigma(E + \delta E) = -\frac{\partial\sigma}{\partial E}\delta E \quad (8)$$

Using (5), this becomes

$$\frac{\partial\Omega}{\partial x} = -\frac{\partial}{\partial E}(\Omega\overline{Y}) \quad (9)$$

or

$$\frac{\partial\Omega}{\partial x} = -\frac{\partial\Omega}{\partial E}\overline{Y} - \Omega\frac{\partial\overline{Y}}{\partial E} \quad (10)$$

Dividing both sides by Ω , we have

$$\frac{\partial \ln \Omega}{\partial x} = -\frac{\partial \ln \Omega}{\partial E}\overline{Y} - \frac{\partial\overline{Y}}{\partial E} \quad (11)$$

The second term on the right is negligible since $\ln \Omega \sim f$ where the number of degrees of freedom f is on the order of 10^{23} . So we can write

$$\frac{\partial \ln \Omega}{\partial x} = -\frac{\partial \ln \Omega}{\partial E}\overline{Y} = \beta\overline{X} \quad (12)$$

since $\beta = \partial \ln \Omega / \partial E$. If we have several external parameters, we can easily generalize this to the desired relation:

$$\frac{\partial \ln \Omega}{\partial x_\alpha} = \beta\overline{X}_\alpha \quad (13)$$

From (12) and the definition of the entropy $S = k_B \ln \Omega$, we can write

$$\frac{\partial S}{\partial x_\alpha} = \frac{\overline{X}_\alpha}{T} \quad (14)$$

Equilibrium Conditions

Consider now two systems A and A' in contact which can exchange heat and do work on each other. A is described by the macroscopic parameters E and x , while A' is described by E' and x' where $E^o = E + E'$ and $x^o = x + x'$. Then

$$\Omega^o(E, x) = \Omega(E, x) \Omega'(E', x') \quad (15)$$

$$\ln \Omega^o(E, x) = \ln \Omega(E, x) + \ln \Omega'(E', x') \quad (16)$$

At equilibrium

$$d \ln \Omega^o = d(\ln \Omega + \ln \Omega') = 0 \quad (17)$$

But

$$\begin{aligned} d \ln \Omega &= \frac{\partial \ln \Omega}{\partial E} dE + \frac{\partial \ln \Omega}{\partial x} dx \\ &= \beta dE + \beta \overline{X} dx \end{aligned} \quad (18)$$

and

$$\begin{aligned} d \ln \Omega' &= \frac{\partial \ln \Omega'}{\partial E'} dE' + \frac{\partial \ln \Omega'}{\partial x'} dx' \\ &= -\beta' dE - \beta' \overline{X}' dx \end{aligned} \quad (19)$$

since $dE' = -dE$ and $dx' = -dx$. The equilibrium condition $d \ln \Omega^o = 0$ implies

$$(\beta - \beta') dE + (\beta \overline{X} - \beta' \overline{X}') dx = 0 \quad (20)$$

Both coefficients must vanish since E and x are independent variables. Hence the equilibrium conditions are

$$\beta = \beta' \quad (21)$$

and

$$\overline{X} = \overline{X}' \quad (22)$$

where $\overline{X}$ is any generalized force. So if $\overline{X}$ is the pressure p , then the pressures and temperatures are equal in equilibrium.

Quasi-Static Processes

Almost by definition, when a system undergoes a process and changes, it cannot be exactly described by equilibrium statistical mechanics or thermodynamics. However we can talk about a quasi-static process in which the system progresses slowly enough to be arbitrarily close to equilibrium throughout the process. We can think of the system

progressing through a series of equilibrium states infinitesimally separated from each other.

Consider first an infinitesimal quasi-static process in which a system A is brought from an equilibrium state described by mean energy E and external parameter x_α to an infinitesimally different equilibrium state described by $E + dE$ and $x_\alpha + dx_\alpha$ due to an interaction with system A'. Since $\Omega = \Omega(E, x_1, x_2, \dots, x_n)$, we can write

$$\begin{aligned} d \ln \Omega &= \frac{\partial \ln \Omega}{\partial E} dE + \sum_{\alpha=1}^n \frac{\partial \ln \Omega}{\partial x_\alpha} dx_\alpha \\ &= \beta \left(dE + \sum_{\alpha=1}^n \bar{X}_\alpha dx_\alpha \right) \end{aligned} \quad (23)$$

Let the *total* mechanical work done by the system be

$$dW = \sum_{\alpha=1}^n \bar{X}_\alpha dx_\alpha \quad (24)$$

Hence

$$d \ln \Omega = \beta(dE + dW) = \beta dQ \quad (25)$$

since

$$dQ = dE + dW \quad (26)$$

This statement is valid for any quasistatic process, even if work of any form is done by the system. But

$$TdS = \frac{1}{\beta} d \ln \Omega = dE + dW = dQ \quad (27)$$

or

$$dS = \frac{dQ}{T} \quad (28)$$

This statement is true for any infinitesimal quasi-static processes, even if work is done.

Note that if $dQ = 0$, then $dS = 0$. Thus entropy does not change in an infinitesimal, adiabatic process. An adiabatic process is one in which there is no heat transfer. We can extend this discussion to a finite process which proceeds quasi-statically through a series of equilibrium states, and obtain the result that if the external parameters of a *thermally isolated* system are changed *quasi-statically* by a finite amount, then

$$\Delta S = \int dS = 0 \quad (29)$$

In other words, the entropy is unchanged. Since $\Delta S = 0$, the number of accessible states is unchanged. This means that the process is reversible. However, it is worth emphasizing that even if a system is thermally isolated so that it absorbs no heat, its entropy will *increase* if processes take place which are *not* quasi-static.

Note that while dQ is an inexact differential, dQ/T is an exact differential, i.e.,

$$S(\text{final}) - S(\text{initial}) = \int_i^f \frac{dQ}{T} \quad (30)$$

provided the path of integration is a series of equilibrium states. Only for equilibrium states is the entropy a defined concept. Entropy ($S = k_B \ln \Omega$) just depends on the equilibrium state of the system and not on how it got there. So the entropy difference is path independent. The inverse temperature ($1/T$) is thus an integrating factor for dQ . This, in fact, is another way mathematically to define the concept of temperature. The reciprocal temperature can be defined as the integrating factor of dQ .

Limiting Behavior of Entropy

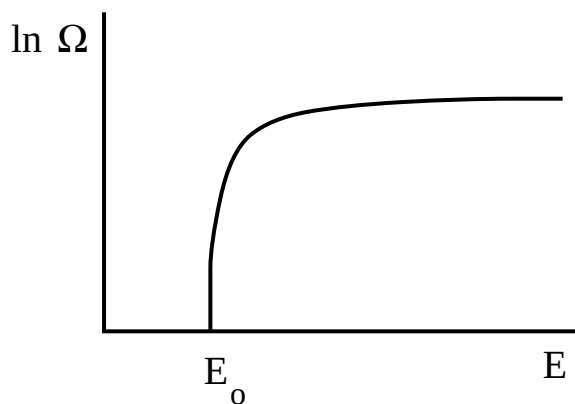
In quantum mechanics, as the energy of a system decreases, it goes towards its ground state. The lowest possible energy state of a system is called its ground state. Let's call the ground state energy E_o . Corresponding to this energy there is usually only one possible microstate of the system. Or there may be a relatively small number of such states, all with the same energy E_o ; in this case the ground state is then said to be "degenerate." If there is just one state with energy E_o , the ground state is nondegenerate. Then

$$S(E_o) = k_B \ln \Omega(E_o) = k_B \ln 1 = 0 \quad (31)$$

Even if the ground state is degenerate, $S \sim k_B \ln f$ which is negligibly small compared to the entropy at large energy. Since $\Omega(E) \sim E^f$ at large energies, $S = k_B \ln \Omega(E) \sim k_B f \ln E \sim k_B f$ which is much larger than S at low energies. In general at low energies S is vanishingly small and we can write

$$\text{as } E \rightarrow E_o, \quad S \rightarrow 0 \quad (32)$$

We can state this in terms of the temperature. Recall that we can think of the temperature roughly as the energy per degree of freedom. As the temperature drops, the energy of the system drops. If we plot the $\ln \Omega$ versus E , it looks something like:



The slope gives the inverse temperature $\beta = 1/k_B T$:

$$\beta = \frac{\partial \ln \Omega}{\partial E} \quad (33)$$

Notice that the slope gets steeper as $E \rightarrow E_o$. So

$$\frac{\partial \beta}{\partial E} < 0 \quad (34)$$

or

$$\frac{\partial T}{\partial E} > 0 \quad (35)$$

At E_o the slope is vertical, $\beta = \infty$, and $T = 0$. So as the temperature approaches zero, the system approaches its ground state, the energy approaches E_o and the entropy approaches zero.

$$\text{as } T \rightarrow 0, \quad S \rightarrow 0 \quad (36)$$

In applying this, one must be sure that equilibrium arguments apply to the system in question. Equation (36) is the third law of thermodynamics.

Ideal Gas

It is about time we applied a few of these ideas to a simple system. Perhaps the simplest nontrivial example of a large collection of particles is the ideal gas. We will come back to this example several times because of its simplicity. An ideal gas consists of a collection of noninteracting particles treated as mass points. The only energy available is the kinetic energy of the particles; no internal excitations, no internal vibrations, no rotation and no interactions. We will first treat the ideal gas as a simple classical system.

Consider N particles with mass m and momentum $\vec{p}_i$. The particles are identical. The total energy is

$$E = \frac{1}{2m} \sum_{i=1}^N \vec{p}_i \cdot \vec{p}_i \quad (37)$$

In classical statistical mechanics, the total number of microstates is the total volume of the accessible phase space divided by the volume of a unit cell of phase space. N particles require $3N$ spatial coordinates and $3N$ components of momenta to specify a point in the $6N$ dimensional phase space. The number of microstates is

$$\Omega(E) = \frac{1}{h_o^{3N}} \int_0^V \int_E^{E+dE} (d^3\vec{r}_1 \dots d^3\vec{r}_N d^3\vec{p}_1 \dots d^3\vec{p}_N) \quad (38)$$

Now the coordinates and momenta are independent. Also each integration over $d^3\vec{r}_i$ yields a factor of V , the volume of the container in which the gas is contained. We obtain

$$\Omega(E) = V^N \chi(E) \quad (39)$$

where

$$\chi(E) = \frac{1}{h_o^{3N}} \int_E^{E+dE} (d^3\vec{p}_1 \dots d^3\vec{p}_N) \quad (40)$$

Thus

$$\ln \Omega(E) = N \ln V + \ln \chi(E) \quad (41)$$

The generalized force corresponding to the external parameter V is the pressure p . Thus

$$\bar{p} = \frac{1}{\beta} \frac{\partial \ln \Omega}{\partial V} = \frac{N}{\beta} \frac{\partial \ln V}{\partial V} = \frac{N}{\beta V} = \frac{N k_B T}{V} \quad (42)$$

or

$$p = n k_B T \quad (43)$$

where $n = N/V$ is the number of molecules per unit volume. Alternatively one can write $N = \nu N_a$ where ν is the number of moles of gas present and N_a is Avogadro's number. Then (43) becomes

$$pV = \nu RT \quad (44)$$

where $R = N_a k_B$ is called the “gas constant.” This equation is known as an equation of state. It relates the macroscopic parameters pressure, volume, and temperature. We will talk more about equations of state in our discussion of thermodynamics. In general equations of state relate p , V , and T . $pV = \nu RT$ is the equation of state for an ideal gas and it is the most famous one.

The parameter β is given by

$$\beta = \frac{\partial \ln \Omega}{\partial E} = \frac{\partial \ln \chi(E)}{\partial E} = \beta(E) \quad (45)$$

The temperature of an ideal gas is a function only of the total energy and does not depend on V . We can invert this to say that the mean energy is solely a function of the temperature

$$\bar{E} = \bar{E}(T) \quad (46)$$

For an ideal gas the mean energy $\bar{E}$ does not depend on the volume. Changing the volume of the container changes the mean distance between the particles and affects the strength of their mutual interaction. But in the case of an ideal gas, there are no interactions. Since the kinetic energies do not depend on the distances between particles, the mean energy is unaffected by the change in volume. Later we will find the complete relation between β and E , and find that

$$E = \frac{3}{2} N k_B T \quad (47)$$

The van der Waals gas

Just to show you that there is more than one equation of state, I would like to mention the van der Waals gas. The molecules in real gases interact with one another and one approximation to a real gas is known as a van der Waals gas. The equation of state for a van der Waals gas is

$$\left(p + \frac{a}{v^2}\right)(v - b) = RT \quad (48)$$

where $v = V/\nu$ is the molar volume. a and b are constants. This is an empirical equation known as the van der Waals equation. van der Waals interactions refer to spontaneous electronic charge fluctuations on a molecule which produces a short lived

dipole moment. These fluctuations induce complementary fluctuations on neighboring molecules and the molecules attract one another. So the molecules are a little closer together than noninteracting molecules, i.e., the gas is compressed a little bit; the term a/v^2 represents this additional positive pressure. On the other hand there are also short-range repulsive forces between the molecules which keep them apart sufficiently to prevent them from occupying the same place at the same time. The term b represents the volume occupied by the molecules themselves and which must thus be subtracted from the volume available to any one molecule in the container. Notice that for $a = b = 0$ or in the limit of a very dilute gas ($v \rightarrow \infty$), (48) reduces to the equation of state for an ideal gas.