

Statistical Mechanics: Lecture 2

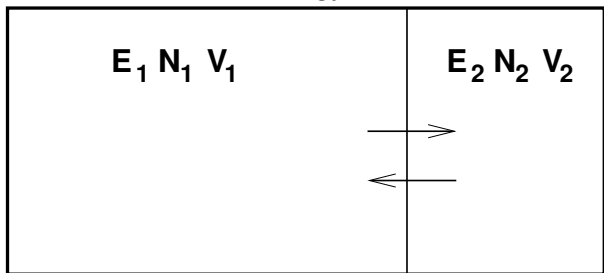
Microcanonical ensemble and entropy

We consider a system which is thermally isolated from its surroundings. Here only those microstates will be allowed which satisfy the fixed energy constraint, $H(p, q) = E$. The microstates of such a system, all equally probable, form an ensemble called *microcanonical ensemble*. The volume of the phase space enclosed by a very thin constant-energy "shell" should be a measure of the number of microstates. However, since p and q are continuous variables, there will be infinitely many points inside the shell. From the quantum mechanical uncertainty principle, we know that the product of the uncertainties Δp and Δq cannot be more precise than \hbar . So, the smallest cell in a 2-dimensional phase space will have size \hbar . This is the phase volume of one microstate for a single particle. For a $6N$ -dimensional phase space, the volume of one microstate will be \hbar^{3N} .

Now the total number of microstates for a gas of N particles with energy E , in a volume V can be written as

$$\Omega(E, N, V) = \frac{1}{\hbar^{3N}} \int_E \prod_i dp_i dq_i, \quad (1)$$

where the integrals over p 's and q 's are subject to the constraint that the total energy is fixed to be E .



Let us now consider two systems 1 and 2, with energy E_1 and E_2 , volume V_1 and V_2 , number of particles N_1 and N_2 , respectively. The total energy is fixed, $E_1 + E_2 = E_T$. Let the two systems be isolated to start with. The number of microstates of the two systems are denoted by $\Omega_1(E_1, N_1, V_1)$ and $\Omega_2(E_2, N_2, V_2)$. The total number of microstates of the combined system is given by

$$\Omega(E_1, N_1, V_1, E_2, N_2, V_2) = \Omega_1(E_1, N_1, V_1)\Omega_2(E_2, N_2, V_2) \quad (2)$$

Let the two systems now come into thermal contact with each other. They will exchange energy so that E_1 and E_2 will change, but E_T will remain unchanged. Equilibrium will be attained for that value of E_1 or E_2 which maximizes the number of microstates of the combined system. To obtain that condition we put

$\partial\Omega/\partial E_1$ equal to zero.

$$\frac{\partial\Omega}{\partial E_1} = \frac{\partial\Omega_1}{\partial E_1}\Omega_2 + \Omega_1 \frac{\partial\Omega_2}{\partial E_1} = 0 \quad (3)$$

$$\begin{aligned} \frac{\partial\Omega_1}{\partial E_1}\Omega_2 &= -\Omega_1 \frac{\partial\Omega_2}{\partial E_1} \\ &= -\Omega_1 \frac{\partial E_2}{\partial E_1} \frac{\partial\Omega_2}{\partial E_2} \\ &= \Omega_1 \frac{\partial\Omega_2}{\partial E_2} \\ \frac{1}{\Omega_1} \frac{\partial\Omega_1}{\partial E_1} &= \frac{1}{\Omega_2} \frac{\partial\Omega_2}{\partial E_2} \\ \frac{\partial \log(\Omega_1)}{\partial E_1} &= \frac{\partial \log(\Omega_2)}{\partial E_2} \end{aligned} \quad (4)$$

From thermodynamics we know that in such a situation, equilibrium is attained when the temperature of the two systems becomes equal, $T_1 = T_2$. In thermodynamics, temperature is defined as

$$\frac{1}{T} = \frac{\partial S}{\partial E}$$

Thus the condition of equilibrium should be

$$\frac{\partial S_1}{\partial E_1} = \frac{\partial S_2}{\partial E_2} \quad (5)$$

Comparing (4) and (5) we infer

$$S \propto \log(\Omega) \quad (6)$$

Since the relation between thermodynamics and mechanics should be fundamental, Boltzmann postulated that the proportionality constant in the above equation should be a universal constant, independent of any particular system. This constant is Boltzmann's constant k , sometimes also written as k_B . Thus we obtain the expression for entropy, which is of central importance in statistical mechanics

$$S = k \log(\Omega). \quad (7)$$

Probability of macrostates

From the preceding analysis, it is clear that the probability of a *macrostate* depends on how many *microstates* are there in it. Let us quantify this statement now. Suppose there is a configuration of the gas, which we denote by Γ . The macrostate Γ could, for example, denote a particular momentum distribution of the particles, or it could denote a particular position distribution of the particles. Let us assume that the number of *microstates* associated with Γ is denoted by Ω_Γ . Then the probability of the macrostate Γ is given

by

$$P_{\Gamma} = \frac{\Omega_{\Gamma}}{\Omega(E, V, N)}, \quad (8)$$

where $\Omega(E, V, N)$ is the total number of microstates of the gas. Since every microstate is equally probable, the above equation is very obvious. It just says that the probability of a state Γ is equal to the number of microstates in Γ divided by the total number of microstates.

In terms of phase space, the number of microstates can be written as

$$\begin{aligned} \Omega_{\Gamma} &= \frac{1}{h^{3N}} \int_{\Gamma} \prod_i dp_i dq_i \\ \Omega(E, N, V) &= \frac{1}{h^{3N}} \int_E \prod_i dp_i dq_i, \end{aligned} \quad (9)$$

where \int_{Γ} denotes integral over the region of phase-space described by Γ . It of course also respects the constraint of a fixed energy E .

An example here would make things clearer. Let us consider an *ideal* gas of N particles, enclosed in a volume V , and with a total energy E . We want to know, what is the probability of the whole gas spontaneously occupying only one particular half of the box. We

know that this practically never happens, so its probability should be negligible. Let us calculate it. Γ now denotes the state of the gas with all particles in one particular half of the box. We know that there is huge number of ways this is possible, because eventhough the particles are in one half of the box, they have many microstates corresponding to them shuffling their positions and velocities. In eqn (9), the integral over space can be carried out easily. For each particle, the volume integral gives a V , for $\Omega(E, N, V)$, and it gives a $V/2$ for Ω_Γ . Integrals over momenta are identical for Ω_Γ and $\Omega(E, N, V)$. Thus the probability of the gas occupying one half of the volume of the box is given by

$$\begin{aligned}
 P_\Gamma &= \frac{\frac{1}{h^{3N}} (V/2)^N \int_\Gamma \prod_i dp_i}{\frac{1}{h^{3N}} (V)^N \int_E \prod_i dp_i} \\
 &= \frac{1}{2^N} \tag{10}
 \end{aligned}$$

We see that the probability of all the particles spontaneously occupying one particular half of the box is $1/2^N$. Even for just 100 particles this number is negligibly small. For $N \sim 10^{23}$, the probability will be so very tiny that one can wait till the end of the world, and still such a state will never come up. On the other hand, if the gas has just, say, 5 particles, the probability of

such a state occurring is 0.03125. In this case, one can actually observe all particles by chance coming to one half of the box, with some patience.

So now we understand why equilibrium is what it looks like. It is just a macrostate which has the maximum number of microstates associated with it.

