# Statistical Mechanics: Lecture 2

Canonical Ensemble

The microcanonical ensemble, which we studied in the previous lecture, is applicable to systems which are thermally insulated. However, in reality the systems are interacting with their surroundings. A typical jar of gas is not insulated, but can exchange energy with the surroundings. For this reason, and also that the microcanonical ensemble is often cumbersome to use, we formulate another ensemble which better describes realistic situations.

Most thermodynamic systems we study are isolated only in the sense that the particles cannot penetrate the walls of the enclosure, but energy can be exchange through the walls. The surroundings can be considered as a kind of *heat-bath* or *heat-reservoir*, which is much much larger than our system of interest. It is assumed to be so large that any exchange of energy with our system of interest, will not have any noticeable effect on it. The system of interest, and the heat-bath, taken together, is assumed to be a closed system such that
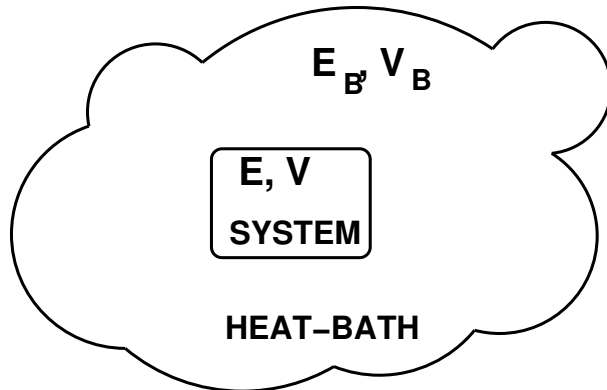
$$E + E_B = E_T, \tag{1}$$

where E is the energy of our system of interest, E_B is the energy of the heat-bath, and their sum is E_T. E and E_B are supposed to be variable, but E_T is fixed. Total number of microstates of the combined system is

$$\Omega = \int \Omega_S(E)\Omega_B(E_B)dE \tag{2}$$

where the integral is a sum over possiblities of various amounts of energy exchanges between the system and the heat-bath. For example, the term $E = 0$ in the integral would correspond to a situation where the system transfers all its energy to the heat-bath. The total system is closed, and can be treated in microcanonical ensemble.

Now, the number of microstates corresponding to the system having energy E is given by

$$\begin{aligned}
\Omega(E) &= \Omega_S(E)\Omega_B(E_B) \\
&= \Omega_S(E)\Omega_B(E_T - E)
\end{aligned} \tag{3}$$

One should convince oneself that if there are two systems with, say, 3 microstates each, the combined system will have $3 \times 3 = 9$ microstates. Microstates of the combined system should have been labelled by E and E_B, but since there is only one independent variable, it suffices to label it by E. We now write $\Omega_B(E_T - E)$ in terms of the entropy of the heat-bath, using the Boltzmann definition of entropy $S = k \log \Omega$:

$$\begin{aligned}
\Omega(E) &= \Omega_S(E)e^{\log(\Omega_B(E_T - E))} \\
&= \Omega_S(E)e^{\frac{1}{k}k \log(\Omega_B(E_T - E))} \\
&= \Omega_S(E)e^{\frac{1}{k}S_B(E_T - E))}
\end{aligned} \tag{4}$$

where S_B is the entropy of the heat-bath. Since the heat-bath is much much larger than our system of interest, it is obvious that $E \ll E_B, E_T$. The entropy of the heat-bath can now be expanded in a Taylor series in E:

$$S_B(E_T - E) = S_B(E_T) + E \left.\frac{\partial S_B}{\partial E}\right|_{E=0} + \frac{E^2}{2!} \left.\frac{\partial^2 S_B}{\partial E^2}\right|_{E=0} + \dots \tag{5}$$

We ignore the E^2 and higher order terms in the series, assuming E to be small, and plug in this expression in (4)

$$\Omega(E) \approx \Omega_S(E) \exp\left[\frac{1}{k}S_B(E_T) + \frac{1}{k}E\frac{\partial S_B}{\partial E}\right] \tag{6}$$

But

$$\frac{\partial S_B}{\partial E} = \frac{\partial E_B}{\partial E}\frac{\partial S_B}{\partial E_B} = -\frac{\partial S_B}{\partial E_B} = -\frac{1}{T}, \tag{7}$$

where T is the temperature of the heat-bath. Strictly speaking, this should be the temperature of the heat-bath when the system has tranferred all its energy to the heat-bath because $\frac{\partial S_B}{\partial E}$ in the above equation is actually $\left.\frac{\partial S_B}{\partial E}\right|_{E=0}$. However, since the heat-bath is assumed to be much larger that the system, its temperature will not change noticeable when it exchanges energy with the system.

The number of microstates of the combined system, corresponding to the system having energy E, can now be written as

$$\Omega(E) = \Omega_S(E) \exp\left[\frac{1}{k}S_B(E_T) - \frac{E}{kT}\right]$$
$$= \Omega_S(E)e^{S_B(E_T)/k}e^{-E/kT} \tag{8}$$

Let us reflect at this expression for a moment. The term $e^{S_B(E_T)/k}$ is constant, as far as E is concerned. From microcanonical ensemble we know that all microstates (with same energy) are equally probable. This holds true here too, but for the microstates of the *system plus heat-bath*. If one wants to concentrate only on the system, as we do because we it is the system we are studying, things are slightly different. Corresponding to a microstate of the system with energy E, the heat-bath has $e^{S_B(E_T)/k}e^{-E/kT}$ microstates. So, two microstates of the system with different energies, will have different number of microstates of the heat-bath associated with them. From the system's point of view, it will appear as if *microstates of the system with different energies, have different probability of occurance*.

Total number of microstates of the combined system can be written as

$$\Omega = \int \Omega_S(E)e^{S_B(E_T)/k}e^{-E/kT}dE \tag{9}$$

So, the probability of the system having energy E should be equal to the number of microstates corresponding to the system having energy E, divided by the total number of microstates

$$P(E) = \frac{\Omega_S(E)e^{S_B(E_T)/k}e^{-E/kT}}{\int \Omega_S(E)e^{S_B(E_T)/k}e^{-E/kT}dE} = \frac{\Omega_S(E)e^{-E/kT}}{\int \Omega_S(E)e^{-E/kT}dE} = \frac{\Omega_S(E)e^{-E/kT}}{Z}, \tag{10}$$

where $Z = \int \Omega_S(E) e^{-E/kT} dE$ is called the partition function. Earlier we had defined the number of microstates of a system in terms of accessible phase-space volume,

$$\Omega(E) = \int_E \frac{dpdq}{\Delta}, \tag{11}$$

where integral of $dpdq$ represents integral over all positions and momenta of all particles, over the constant energy surface with energy E, and Δ is the smallest phase-volume of one microstate. For example, for N particles in 3-dimensions, $\Delta = \hbar^{3N}$. The probability of the system having energy E can now be written as

$$P(E) = \frac{\frac{1}{\Delta} \int_E dpdq e^{-E(p,q)/kT}}{\frac{1}{\Delta} \int dpdq e^{-E(p,q)/kT}} \tag{12}$$

Notice that the integral in the numerator is over a constant energy surface with fixed energy E, while the that in the denominator is over all phase space.

We can thus define a *density function*

$$\rho(p,q) = \frac{e^{-E(p,q)/kT}}{\frac{1}{\Delta} \int dpdq e^{-E(p,q)/kT}} = \frac{e^{-E(p,q)/kT}}{Z}, \tag{13}$$

such that $\rho(p,q)dpdq$ gives the probability of the system having momentum between p and $p + dp$ and position between q and $q + dq$. Thus $\rho(p,q)$ describes the normalized density of microstates (of the system plus heat-bath) in phase space. The partition function is now written as

$$Z = \frac{1}{\Delta} \int e^{-E(p,q)/kT} dpdq \tag{14}$$

The partition function Z might not look very important as one might think that the information about microstates etc has already been summed over. However, the partition function turns out to be a singly most useful entity in statistical mechanics, and most measurable quantities can be expressed in terms of Z.

The thermal average of any quantity A can now be written as

$$\langle A \rangle = \frac{1}{\Delta} \int A(p,q) \rho(p,q) dpdq = \frac{1}{\Delta} \frac{1}{Z} \int A e^{-E/kT} dpdq \tag{15}$$

The stage is now set for us to study any system using canonical ensemble.