

Statistical Mechanics: Lecture 7

Grand Canonical Ensemble

The canonical ensemble, which we studied in the previous lectures, is applicable to systems which are thermally interacting with a heat-bath, but are physically isolated. Now we wish to study that class of systems which are open in the sense of particles freely moving between the system and the heat-bath. Physical examples are many, an electron gas for example, has electrons being absorbed and released by the walls. Same things happens for a photon gas, where the number of photons is not fixed. To study such systems, we introduce an ensemble where only the volumes is fixed, and the energy and number of particles can vary. Such an ensemble is called *grand canonical ensemble*.

Again, we consider a system characterized by energy, volume and number of particles E, V, N , interacting with a much larger heat-bath, characterized by E_B, V_B, N_B . However the system can exchange energy with the heat-bath through the walls. In addition, the walls of the system are supposed to be porous so that particles can also pass from the system to the heat-bath, and vice-versa. The heat-bath is assumed to be so large that any exchange of energy and number of particles 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

$$E + E_B = E_T, \quad N + N_B = N_T \quad (1)$$

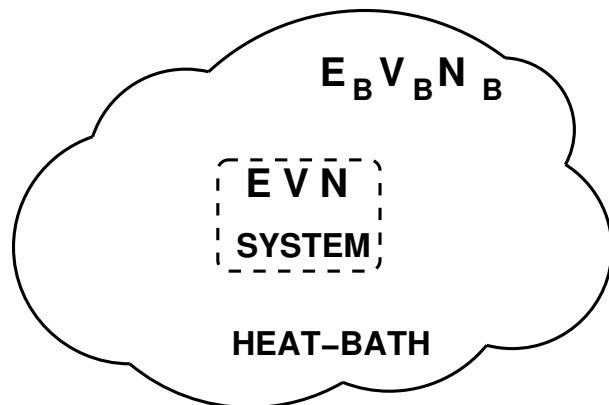
where E_T and N_T are total energy and number of particles, respectively, of the system and the heat-bath, taken together, and are supposed to be fixed. Total number of microstates of the combined system is

$$\Omega = \sum_N \int \Omega_S(E, N) \Omega_B(E_B, N_B) dE \quad (2)$$

where the integral is a sum over possibilities of various amounts of energy exchanges between the system and the heat-bath, and the sum over N represents various particle exchanges between the system and the heat-bath. For example, the term $E = 0, N = 0$ would correspond to a situation where the system transfers all its energy and particles 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 and number of particles is given by

$$\begin{aligned} \Omega(E, N) &= \Omega_S(E, N) \Omega_B(E_B, N_B) \\ &= \Omega_S(E, N) \Omega_B(E_T - E, N_T - N) \end{aligned} \quad (3)$$

Microstates of the combined system should have been labelled by E, E_B, N and N_B , but because of the constraint (1), E, N can be taken to be the only independent variables.



We now write $\Omega_B(E_T - E, N_T - N)$ in terms of the entropy of the heat-bath, using the Boltzmann definition of entropy $S = k \log \Omega$:

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

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 $E \ll E_B, E_T$ and $N \ll N_B, N_T$. The entropy of the heat-bath can now be expanded in a Taylor series in E and N :

$$S_B(E_T - E, N_T - N) = S_B(E_T, N_T) + E \left. \frac{\partial S_B}{\partial E} \right|_{E=0} + N \left. \frac{\partial S_B}{\partial N} \right|_{N=0} + \dots \quad (5)$$

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

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

But

$$\frac{\partial S_B}{\partial E} = \frac{\partial E_B}{\partial E} \frac{\partial S_B}{\partial E_B} = - \frac{\partial S_B}{\partial E_B} = - \frac{1}{T}, \quad (7)$$

and

$$\frac{\partial S_B}{\partial N} = \frac{\partial N_B}{\partial N} \frac{\partial S_B}{\partial N_B} = - \frac{\partial S_B}{\partial N_B} = \frac{\mu}{T}, \quad (8)$$

where T is the temperature of the heat-bath, and μ its chemical potential.

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

$$\begin{aligned}\Omega(E, N) &= \Omega_S(E, N) \exp \left[\frac{1}{k} S_B(E_T, N_T) - \frac{E}{kT} + \frac{\mu N}{kT} \right] \\ &= \Omega_S(E, N) e^{S_B(E_T, N_T)/k} e^{-(E - \mu N)/kT}\end{aligned}\quad (9)$$

The term $e^{S_B(E_T, N_T)/k}$ is constant, as far as E and N are concerned. From microcanonical ensemble we know that all microstates (with same energy) are equally probable. This holds true here too, but only 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 and number of particles N , the heat-bath has $e^{S_B(E_T, N_T)/k} e^{-(E - \mu N)/kT}$ microstates. So, two microstates of the system with different E and N , 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 and number of particles, have different probability of occurrence*.

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

$$\Omega = \sum_N \int \Omega_S(E, N) e^{S_B(E_T, N_T)/k} e^{-(E - \mu N)/kT} dE \quad (10)$$

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

$$\begin{aligned}
 P(E, N) &= \frac{\Omega_S(E, N) e^{S_B(E_T, N_T)/k} e^{-(E-\mu N)/kT}}{\sum_N \int \Omega_S(E, N) e^{S_B(E_T, N_T)/k} e^{-(E-\mu N)/kT} dE} \\
 &= \frac{\Omega_S(E, N) e^{-E/kT}}{\sum_N \int \Omega_S(E) e^{-(E-\mu N)/kT} dE} \\
 &= \frac{\Omega_S(E, N) e^{-(E-\mu N)/kT}}{\mathcal{Z}}, \tag{11}
 \end{aligned}$$

where $\mathcal{Z} = \sum_N \int \Omega_S(E) e^{-(E-\mu N)/kT} dE$ is called the grand-canonical partition function or the grand partition function. For classical systems, we define the number of microstates of a system in terms of accessible phase-space volume,

$$\Omega_S(E, N) = \int_E \frac{dpdq}{\Delta}, \tag{12}$$

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. The probability of the system having energy E and N particles, can now be written as

$$P(E, N) = \frac{\frac{1}{\Delta} \int_E dpdq e^{-(E-\mu N)/kT}}{\sum_N \frac{1}{\Delta} \int dpdq e^{-(E-\mu N)/kT}} \tag{13}$$

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

We can thus define a *density function*

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

such that $\rho(p, q, N) dpdq$ gives the probability of the system to have N particles with momenta between p and $p + dp$ and positions between q and $q + dq$. Remember that integral over p here, represents $6N$ integrals over the 3 momentum components of N particles. Thus $\rho(p, q, N)$ describes the normalized density of microstates (of the system plus heat-bath) in phase space. The grand partition function is now written as

$$\mathcal{Z} = \sum_{N=0}^{\infty} \frac{1}{\Delta} \int e^{-(E-\mu N)/kT} dpdq \tag{15}$$

In the above expression, $e^{\mu N/kT}$ does not depend on p, q , and can be brought out of the integral

$$\mathcal{Z} = \sum_{N=0}^{\infty} e^{\mu N/kT} \frac{1}{\Delta} \int e^{-E(p, q, N)/kT} dpdq \tag{16}$$

But the term $\frac{1}{\Delta} \int e^{-E(p,q,N)/kT} dpdq$ is just the *canonical* partition function for N particles. The grand partition function can thus be represented as a sum over canonical partitions with different number of particles

$$\mathcal{Z} = \sum_{N=0}^{\infty} (e^{\mu\beta})^N Z_N \quad (17)$$

The quantity $e^{\mu\beta}$ is called *fugacity*, and sometimes represented by z . The thermal average of any quantity A can now be written as

$$\langle A \rangle = \sum_{N=0}^{\infty} \frac{1}{\Delta} \int A(p, q, N) \rho(p, q, N) dpdq = \frac{1}{\mathcal{Z}} \sum_{N=0}^{\infty} \frac{1}{\Delta} \int A e^{-(E-\mu N)/kT} dpdq \quad (18)$$

As in the case of canonical ensemble, it will turn out that various thermodynamic quantities can be represented in terms of the grand partition function. The energy and number of particles of the system can now be determined by calculating the corresponding ensemble averages $\langle E \rangle$ and $\langle N \rangle$.

If the system consists of indistinguishable particles, the canonical partition function for N particles, Z_N should be represented by $\frac{1}{N!} \frac{1}{\Delta} \int e^{-E(p,q,N)/kT} dpdq$ instead of $\frac{1}{\Delta} \int e^{-E(p,q,N)/kT} dpdq$.

