

Unit 2-8: The Canonical Ensemble

Consider a system of interest in contact with a thermal reservoir – i.e. the system of interest is separated from the reservoir by a fixed, impermeable, but thermally conducting wall. We will refer to this as the “combined system.” Let E be the energy of the system of interest and $E_T - E$ be the energy of the reservoir. The total energy E_T of the combined system plus reservoir is fixed. We now wish to compute the probability that the system of interest will be found to have energy E .

Consider the microcanonical ensemble for the combined system. The number of states available to the combined system at energy E_T is,

$$\Omega_T(E_T) = \int_0^{E_T} \frac{dE}{\Delta E} \Omega(E)\Omega_R(E_T - E) \quad (2.8.1)$$

Where $\Omega(E)$ is the number of states available to the system of interest and $\Omega_R(E_T - E)$ is the number of states available to the reservoir.

Since all states of the combined system are assumed to be equally likely in the microcanonical ensemble, then the probability for the system of interest to have energy E is proportional to the number of states of the combined system for which the system of interest has energy E ,

$$\mathcal{P}(E) \propto \Omega(E)\Omega_R(E_T - E) = \Omega(E)e^{S_R(E_T - E)/k_B} \quad (2.8.2)$$

where we used $S_R = k_B \ln \Omega_R$ is the entropy of the reservoir.

Since the reservoir is large, $E \ll E_T$, we can expand,

$$\Omega_R(E_T - E) = \exp \left\{ \frac{S_R(E_T - E)}{k_B} \right\} = \exp \left\{ \frac{1}{k_B} \left[S_R(E_T) - \left(\frac{\partial S_R}{\partial E_R} \right) \Big|_{E_R=E_T} E + \dots \right] \right\} \quad (2.8.3)$$

$$= \exp \left\{ \frac{1}{k_B} \left[S_R(E_T) - \frac{E}{T_R} + \dots \right] \right\} = \text{const } e^{-E/k_B T} \quad (2.8.4)$$

Here we used $(\partial S_R / \partial E_R)|_{E_T} = 1/T_R$. In the last step we used that the temperature of the system of interest must be equal to that of the reservoir, $T = T_R$, because the two are in equilibrium, and also that temperature of the reservoir T_R is independent of how much energy it shares with the system of interest by definition of its being a reservoir (i.e. $T_R(E_T) = T_R(E_T - E)$ is independent of the energy E of the system of interest). And lastly that $e^{S_R(E_T)/k_B}$ is a constant independent of E .

So finally we conclude that the probability that the system of interest has energy E is proportional to,

$$\mathcal{P}(E) \propto \Omega(E)e^{-E/k_B T} \quad (2.8.5)$$

Normalizing $\mathcal{P}(E)$ so that $\int dE \mathcal{P}(E) = 1$, we have for the probability density for the system of interest to have energy E ,

$$\boxed{\mathcal{P}(E) = \frac{\Omega(E) e^{-E/k_B T}}{\Delta E Q_N(T, V)}} \quad \text{with} \quad \boxed{Q_N(T, V) \equiv \int \frac{dE}{\Delta E} \Omega(E) e^{-E/k_B T}} \quad (2.8.6)$$

where $Q_N(T, V)$ is called the *canonical partition function*.

We will soon see that the partition function is the key quantity of the canonical ensemble, from which we can find the Helmholtz free energy, and hence all thermodynamic properties. [Note: in some texts, the partition function is denoted as Z . We will use the notation Q of Pathria and Beale.]

Using the density of states,

$$g(E) = \frac{1}{N!} \frac{1}{h^{3N}} \int dq_i dp_i \delta(\mathcal{H}[q_i, p_i] - E) \quad \text{with} \quad \Omega(E) = g(E) \Delta E \quad (2.8.7)$$

we can rewrite the above as,

$$\mathcal{P}(E) = \frac{g(E) e^{-E/k_B T}}{Q_N(T, V)} \quad \text{and} \quad Q_N(T, V) = \int dE g(E) e^{-E/k_B T} \quad (2.8.8)$$

Inserting $g(E)$ into the above expression for the partition function we get,

$$Q_N(T, V) = \int dE \frac{1}{N!} \frac{1}{h^{3N}} \int dq_i dp_i \delta(\mathcal{H}[q_i, p_i] - E) e^{-E/k_B T} \quad (2.8.9)$$

Interchanging the order of the integrations on E and on the $\{q_i, p_i\}$, we can do the integral over E trivially using the delta function to get,

$$Q_N(T, V) = \frac{1}{N!} \frac{1}{h^{3N}} \int dq_i dp_i e^{-\mathcal{H}[q_i, p_i]/k_B T} \quad (2.8.10)$$

Although they are equivalent, note the important distinction between the expressions for $Q_N(T, V)$ given in Eqs. (2.8.6) and (2.8.8) from that given in Eq. (2.8.10). In Eqs. (2.8.6) and (2.8.8) one first needs to compute the microcanonical number of states $\Omega(E)$ or the density states $g(E)$. This involves doing the constrained integration over phase space given in Eq. (2.8.7), where the constraint restricts one to the constant energy surface $\mathcal{H}[q_i, p_i] = E$. Carrying out the integration subject to such a constraint is in general not easy. However in Eq. (2.8.10) we compute the partition function by carrying out an *unconstrained* integration over all of phase space, weighting each point in phase space by its Boltzmann factor $e^{-\mathcal{H}/k_B T}$. Computing $Q_N(T, V)$ by using Eq. (2.8.10) is therefore, in general, much easier to carry out. Because it is usually *much* easier to compute $Q_N(T, V)$ using Eq. (2.8.10) than it is to compute $\Omega(E)$, this is why one usually prefers to work in the canonical ensemble rather than the microcanonical ensemble.

Now, $\mathcal{P}(E)$ is the probability density *per unit energy* that the system of interest (henceforth just “the system”) is found to have energy E . So $\mathcal{P}(E) \Delta E$ is the probability that the system has energy E' within the range $E - \Delta E/2 \leq E' \leq E + \Delta E/2$. Within this range there are $\Omega(E)$ possible microscopic states for the system and, by the assumption of the microcanonical ensemble, each of these is equally likely. So the probability that the system is in any particular one of those states is just,

$$\frac{\mathcal{P}(E) \Delta E}{\Omega(E)} = \frac{e^{-E/k_B T}}{Q_N(T, V)} \quad (2.8.11)$$

Each of those states, by our method of counting, occupies a volume h^{3N} in phase space. So we can write for the probability density *per unit volume of phase space*, at point $\{q_i, p_i\}$ in phase space, is,

$$\rho(q_i, p_i) = \frac{e^{-\mathcal{H}[q_i, p_i]/k_B T}}{h^{3N} Q_N(T, V)} = \frac{e^{-\mathcal{H}[q_i, p_i]/k_B T}}{\frac{1}{N!} \int dq_j dp_j e^{-\mathcal{H}[q_j, p_j]/k_B T}} \quad (2.8.12)$$

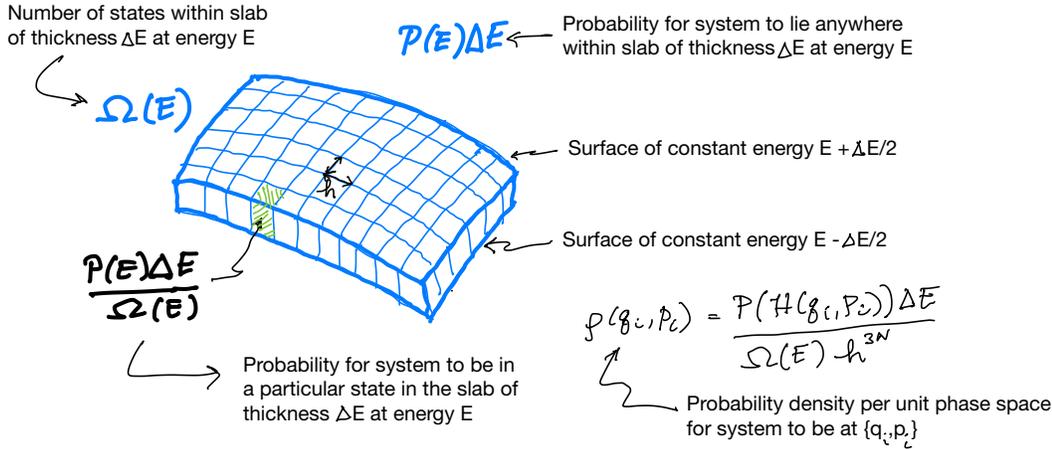
Note, $\rho(q_i, p_i)$ is normalized so that $\frac{1}{N!} \int dq_i dp_i \rho(q_i, p_i) = 1$, where the prefactor $1/N!$ is because we have identical particles and don't want to over count phase space.

If we wished to normalize so that $\int dq_i dp_i \rho(q_i, p_i) = 1$, then we should absorb the $1/N!$ factor into ρ so that

$$\rho(q_i, p_i) = \frac{e^{-\mathcal{H}[q_i, p_i]/k_B T}}{\int dq_j dp_j e^{-\mathcal{H}[q_j, p_j]/k_B T}} \quad (2.8.13)$$

Referring back to Notes 2-2, we see that the expression for $\rho(q_i, p_i)$ of Eq. (2.8.13) is just the density matrix for the canonical ensemble.

The above discussion is illustrated in the sketch below.



The above discussion was given in terms of a system, such as a collection of classical particles, where phase space is a continuum and the possible energies E of the system span a continuous range of values. Consider, instead, the case where the states of the system are labeled by a discrete index i , and so the possible energies of the system are a discrete set of values E_i . The corresponding results for the probability that the system has energy E_i , and for the partition function are,

$$\mathcal{P}(E_i) = \frac{\Omega(E_i) e^{-E_i/k_B T}}{Q_N(T, V)} \quad \text{with} \quad Q_N(T, V) = \sum_{E_i} \Omega(E_i) e^{-E_i/k_B T} \quad \text{and} \quad \sum_{E_i} \mathcal{P}(E_i) = 1 \quad (2.8.14)$$

Here $\mathcal{P}(E_i)$ is a probability rather than a probability *density*, and the sums are over the different distinct values of E_i .

Since $\Omega(E_i)$ is just the number of the discrete states that have energy E_i , we can write,

$$Q_N(T, V) = \sum_{E_i} \Omega(E_i) e^{-E_i/k_B T} = \sum_i e^{-E_i/k_B T} \quad (2.8.15)$$

Note that in the first sum we are summing over the allowed values of the energy E_i , and multiplying each term by the number of states $\Omega(E_i)$ that have that energy. In the second sum we are summing over the individual states i directly.

Since all states which have a given value of E_i are equally likely, and the number of such states are $\Omega(E_i)$, then the probability for the system to be in any particular one of those states i is just,

$$\mathcal{P}_i = \frac{\mathcal{P}(E_i)}{\Omega(E_i)} = \frac{e^{-E_i/k_B T}}{Q_N(T, V)} = \frac{e^{-E_i/k_B T}}{\sum_j e^{-E_j/k_B T}} \quad \text{with} \quad \sum_i \mathcal{P}_i = 1 \quad (2.8.16)$$

In the microcanonical ensemble, the system energy E is *fixed*, and the system entropy is given by $S = k_B \ln \Omega(E)$. In the canonical ensemble, the system energy E is *not* fixed, but fluctuates according to a probability distribution set by the fixed temperature T . The temperature determines the *average* energy $\langle E \rangle$. The canonical ensemble does *not* depend on any details of the reservoir, except for the assumption that the reservoir is very much larger than the system.

In thermodynamics, in the entropy formulation, we saw that when one wishes to use $1/T$ as the thermodynamic variable instead of the energy E , then the thermodynamic potential to use is the Legendre transform of S with

respect to E , which is $-A/T$ where $A(T, V, N)$ is the Helmholtz free energy. We will now see that there is a direct connection between $A(T, V, N)$ and the canonical partition function $Q_N(T, V)$.

In the canonical ensemble, the average energy of the system is given by,

$$\langle E \rangle = \int dE \mathcal{P}(E) E, \quad \text{with} \quad \mathcal{P}(E) = \frac{g(E) e^{-E/k_B T}}{Q_N(T, V)} \quad \text{and} \quad Q_N(T, V) = \int dE g(E) e^{-E/k_B T} \quad (2.8.17)$$

Defining $\beta = 1/k_B T$, we then have,

$$\langle E \rangle = \frac{\int dE g(E) e^{-\beta E} E}{\int dE g(E) e^{-\beta E}} = \frac{-\frac{\partial}{\partial \beta} \left[\int dE g(E) e^{-\beta E} \right]}{\int dE g(E) e^{-\beta E}} = -\frac{\partial}{\partial \beta} \left(\ln \left[\int dE g(E) e^{-\beta E} \right] \right)_{V, N} \quad (2.8.18)$$

so

$$\langle E \rangle = -\frac{\partial}{\partial \beta} \left(\ln Q_N(T, V) \right)_{V, N} \quad (2.8.19)$$

Recall now that, since $-A/T$ is the Legendre transform of S from E to $1/T$, then in thermodynamics we have,

$$E = -\left(\frac{\partial(-A/T)}{\partial(1/T)} \right)_{V, N} = -\left(\frac{\partial(-\beta A)}{\partial \beta} \right)_{V, N} \quad (2.8.20)$$

Comparing Eqs. (2.8.19) and (2.8.20) then suggests the identification,

$$-\beta A(T, V, N) = \ln Q_N(T, V) \quad \text{or} \quad \boxed{A(T, V, N) = -k_B T \ln Q_N(T, V)} \quad (2.8.21)$$

We can now make the following identifications:

$$\begin{aligned} \frac{-A(T, V, N)}{T} &= k_B \ln Q_N(T, V) & Q_N(T, V) \text{ is the } \textit{canonical} \text{ partition function} \\ S(E, V, N) &= k_B \ln \Omega(E, V, N) & \Omega(E, V, N) \text{ is the } \textit{microcanonical} \text{ partition function} \end{aligned} \quad (2.8.22)$$

and

$$\begin{aligned} \frac{-A}{T} &= S - \frac{E}{T} & \frac{-A}{T} \text{ is the Legendre transform of } S \text{ from } E \text{ to } 1/T \\ Q_N &= \int \frac{dE}{\Delta E} \Omega(E) e^{-\beta E} & Q_N \text{ is the Laplace transform of } \Omega \text{ from } E \text{ to } \beta = 1/k_B T \end{aligned} \quad (2.8.23)$$

We thus have that k_B times the ln of the partition function gives the corresponding thermodynamic potential (in the entropy formulation). When two thermodynamic potentials are related by a Legendre transform, then their corresponding partition functions are related by a Laplace transform. We will see that this is a general rule when we later consider the grand canonical ensemble, in which the number of particles N fluctuates and the chemical potential μ is fixed, as well as for a constant pressure ensemble, in which the volume V fluctuates while the pressure p is fixed.