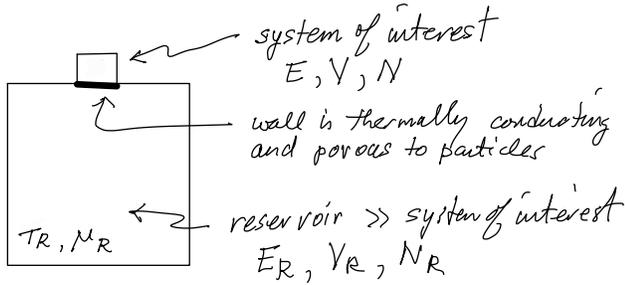
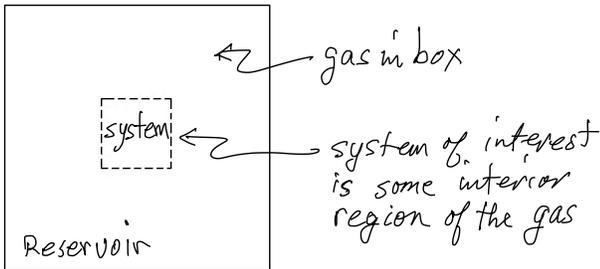


Unit 2-16: The Grand Canonical Ensemble

Consider a system of interest which is in contact with both a thermal *and* a particle reservoir.



The system of interest (henceforth “the system”) has energy, volume, and number of particles, E , V , and N . The reservoir has E_R , V_R and N_R . The wall separating the two allows the exchange of both energy *and* particles.



One way such a situation may arise physically is if “the system” is just a certain volume immersed in a much larger volume of the same stuff, and the walls about “the system” are just are mental constructs.

The reservoir is so large that, no matter how much energy or how many particles the system exchanges with the reservoir, the reservoir’s temperature T_R and chemical potential μ_R do not change – this is just what we mean by a reservoir!

We see this as we argued before. If heat $\Delta Q = T\Delta S$ is exchanged with the reservoir, then the change in temperature is,

$$\Delta T_R = \left(\frac{\partial T_R}{\partial S_R} \right) \Delta S = \left(\frac{\partial^2 E_R}{\partial S_R^2} \right) \Delta S \lesssim \frac{N}{N_R} T_R \quad \text{since } E_R \sim T_R S_R \sim T_R N_R, S_R \sim N_R, \text{ and } \Delta S \lesssim N. \quad (2.16.1)$$

So if $N \ll N_R$, then $\Delta T_R \ll T_R$.

Similarly, if ΔN is exchanged with the reservoir, then the change in the chemical potential is,

$$\Delta \mu_R = \left(\frac{\partial \mu_R}{\partial N_R} \right) \Delta N = \left(\frac{\partial^2 E_R}{\partial N_R^2} \right) \Delta N \lesssim \frac{N}{N_R} \mu_R \quad \text{since } E_R \sim \mu_R N_R, \text{ and } \Delta N \lesssim N. \quad (2.16.2)$$

So if $N \ll N_R$, then $\Delta \mu_R \ll \mu_R$.

So we regard T_R and μ_R of the reservoir as fixed. Then, because the system is in equilibrium with the reservoir, we also have for the temperature and chemical potential of the system, $T = T_R$ and $\mu = \mu_R$.

The ensemble in which both energy and number of particles can fluctuate, subject to the constraints of a fixed T and μ , is called the *grand canonical ensemble*.

Now, although the system can exchange energy and particles with the reservoir, the total energy and number of particles in the combined system plus reservoir is fixed.

$$E_T = E + E_R, \quad N_T = N + N_R, \quad V, V_R \quad \text{are all held fixed.} \quad (2.16.3)$$

Similar to what we did for the canonical ensemble, the number of states for the combined system plus reservoir is

given by,

$$\Omega_T(E_T, V, V_R, N_T) = \sum_{N=0}^{N_T} \int_0^{E_T} \frac{dE}{\Delta E} \Omega(E, V, N) \Omega_R(E_T - E, V_R, N_T - N) \quad (2.16.4)$$

$$= \sum_{N=0}^{N_T} \int_0^{E_T} \frac{dE}{\Delta E} \Omega(E, V, N) e^{S_R(E_T - E, V_R, N_T - N)/k_B} \quad (2.16.5)$$

where we integrate over all possible divisions of the energy, and sum over all possible divisions of the number of particles, between the system and the reservoir.

Since E_T is held fixed, the combined system plus reservoir is described by the microcanonical ensemble, and so all states of the combined system plus reservoir are equally likely. The probability density for the system to have energy E and N particles is therefore just proportional to the number of states of the combined system plus reservoir that have the system with E and N ,

$$\mathcal{P}(E, N) \propto \frac{\Omega(E, V, N)}{\Delta E} e^{S_R(E_T - E, V_R, N_T - N)/k_B} \quad (2.16.6)$$

Now since $E \ll E_T$ and $N \ll N_T$, we can expand,

$$S_R(E_T - E, V_R, N_T - N) \approx S_R(E_T, V_R, N_T) + \left(\frac{\partial S_R}{\partial E_R} \right) (-E) + \left(\frac{\partial S_R}{\partial N_R} \right) (-N) \quad (2.16.7)$$

$$= S_R - \frac{E}{T} + \frac{\mu N}{T} \quad (2.16.8)$$

since $(\partial S_R / \partial E_R) = 1/T_R = 1/T$, and $(\partial S_R / \partial N_R) = \mu_R/T_R = \mu/T$. Here $S_R = S_R(E_T, V_R, N_T)$ is a constant independent of E and N .

We thus have,

$$\mathcal{P}(E, N) \propto \frac{\Omega(E, V, N)}{\Delta E} e^{-(E - \mu N)/k_B T} \quad (2.16.9)$$

Normalizing so that,

$$\sum_{N=0}^{N_T} \int_0^{E_T} dE \mathcal{P}(E, N) = 1 \quad (2.16.10)$$

we have,

$$\mathcal{P}(E, N) = \frac{\frac{\Omega(E, V, N)}{\Delta E} e^{-(E - \mu N)/k_B T}}{\sum_{N=0}^{N_T} \int_0^{E_T} \frac{dE}{\Delta E} \Omega(E, V, N) e^{-E/k_B T} e^{\mu N/k_B T}} \quad (2.16.11)$$

The denominator in the above expression for $\mathcal{P}(E, N)$ defines the grand canonical partition function \mathcal{L} ,

$$\begin{aligned} \mathcal{L}(T, V, \mu) &= \sum_{N=0}^{\infty} \left[\int_0^{\infty} \frac{dE}{\Delta E} \Omega(E, V, N) e^{-E/k_B T} \right] e^{\mu N/k_B T} \\ &= \sum_{N=0}^{\infty} Q_N(T, V) e^{\mu N/k_B T} = \sum_{N=0}^{\infty} Q_N(T, V) z^N \end{aligned} \quad \begin{array}{l} \text{the grand canonical} \\ \text{partition function} \end{array} \quad (2.16.12)$$

where $z \equiv e^{\mu/k_B T}$ is called the *fugacity*. Note, in principle the sum should go up to N_T and the integral up to E_T , however in the thermodynamic limit these both go to infinity.

Note, $\mathcal{L}(T, V, \mu)$ is just the discrete Laplace transform of $Q_N(T, V)$ from N to $-\mu/k_B T$. This is consistent with $-\mu/T$ being the conjugate variable to N in the entropy formulation. And, as we will soon see, \mathcal{L} determines the Grand Potential by $-\Phi/T = k_B \ln \mathcal{L}$. Thus the process of going from the canonical ensemble to the grand canonical ensemble is analogous to the process of going from the microcanonical ensemble to the canonical ensemble.

The above discussion had in mind a system with a continuum phase space and a continuous spectrum of allowed energies E . Consider now that we have discrete states (for example by dividing phase space into discrete cells of volume h^{3N}) labeled by the index i , such that state i has energy E_i and number of particles N_i . Considering the phase space to now include all states with any number of particles N , we can write,

$$Q_N(T, V) = \sum_{\substack{i \text{ such that} \\ N_i = N}} e^{-E_i/k_B T} \quad \text{canonical partition function} \quad (2.16.13)$$

and so,

$$\mathcal{L}(T, V, \mu) = \sum_N \left[\sum_{\substack{i \text{ such that} \\ N_i = N}} e^{-E_i/k_B T} \right] e^{\mu N/k_B T} \quad (2.16.14)$$

$$\mathcal{L} = \sum_i e^{-(E_i - \mu N_i)/k_B T}$$

all states

$$\text{grand canonical partition function} \quad (2.16.15)$$

The probability for the system to have energy E_i and N_i particles is then,

$$\mathcal{P}(E_i, N_i) = \frac{\Omega(E_i, V, N_i) e^{-(E_i - \mu N_i)/k_B T}}{\mathcal{L}} \quad (2.16.16)$$

and since Ω just counts the number of states of the system with energy E_i and N_i particles, and all these states are equally likely, then the probability for the system to be in any particular state i is,

$$\mathcal{P}_i = \frac{e^{-(E_i - \mu N_i)/k_B T}}{\mathcal{L}} = \frac{e^{-(E_i - \mu N_i)/k_B T}}{\sum_j e^{-(E_j - \mu N_j)/k_B T}}$$

$$(2.16.17)$$

This is the obvious generalization of what we had earlier for the canonical ensemble.

Note, our expressions for \mathcal{P}_i , \mathcal{L} , etc., make no reference at all to the reservoir, except for $T = T_R$ and $\mu = \mu_R$.