Unit 2-17: The Grand Canonical Ensemble and the Grand Potential

Recall, the Grand Potential $\Phi(T,V,\mu)$, which we introduced as the Legendre transform of $E(S,V,N)$ from S to T and from N to μ, can also be related to a Legendre transform of $S(E,V,N)$.

To refresh this point, recall $\Phi = E - TS - \mu N \;\Rightarrow\; -\Phi/T = S - E/T + (\mu/T)N$, where $(\partial S/\partial E)_{V,N} = 1/T$ and $(\partial S/\partial N)_{E,V} = -\mu/T$. So $-\Phi/T$ is the Legendre transform of S from E to $1/T$ and from N to $-\mu/T$. We have that E and $1/T$ are conjugate variables, and N and $-\mu/T$ are conjugate variables.

By the properties of Legendre transforms, we then have,

$$E = -\left(\frac{\partial(-\Phi/T)}{\partial(1/T)}\right)_{V,\mu/T} \qquad \text{and} \qquad N = -\left(\frac{\partial(-\Phi/T)}{\partial(-\mu/T)}\right)_{1/T,V} \tag{2.17.1}$$

If we introduce $\beta \equiv \dfrac{1}{k_BT}$ and $\alpha \equiv \dfrac{\mu}{k_BT}$, then we can write the above as,

$$E = -\left(\frac{\partial(-\Phi/k_BT)}{\partial\beta}\right)_{V,\alpha} \qquad \text{and} \qquad N = \left(\frac{\partial(-\Phi/k_BT)}{\partial\alpha}\right)_{\beta,V} \tag{2.17.2}$$

Now consider $\ln\mathcal{L}$, with $\mathcal{L}$ the grand canonical partition function,

$$\mathcal{L} = \sum_i \mathrm{e}^{-(E_i-\mu N_i)/k_BT} = \sum_i \mathrm{e}^{-\beta E_i}\,\mathrm{e}^{\alpha N_i} \tag{2.17.3}$$

We have,

$$\left(\frac{\partial \ln\mathcal{L}}{\partial\beta}\right)_{V,\alpha} = \frac{1}{\mathcal{L}}\left(\frac{\partial\mathcal{L}}{\partial\beta}\right)_{V,\alpha} = \frac{1}{\mathcal{L}}\sum_i \mathrm{e}^{-\beta E_i}\,\mathrm{e}^{\alpha N_i}(-E_i) \tag{2.17.4}$$

$$= -\frac{1}{\mathcal{L}}\sum_i \mathrm{e}^{-\beta(E_i-\mu N_i)}E_i = -\sum_i \mathcal{P}_i\,E_i = -\langle E\rangle \tag{2.17.5}$$

where we used $\mathcal{P}_i = \dfrac{\mathrm{e}^{-\beta(E_i-\mu N_i)}}{\mathcal{L}}$ is the probability to be in state i in the grand canonical ensemble.

Similarly,

$$\left(\frac{\partial \ln\mathcal{L}}{\partial\alpha}\right)_{\beta,V} = \frac{1}{\mathcal{L}}\left(\frac{\partial\mathcal{L}}{\partial\alpha}\right)_{\beta,V} = \frac{1}{\mathcal{L}}\sum_i \mathrm{e}^{-\beta E_i}\,\mathrm{e}^{\alpha N_i}(N_i) \tag{2.17.6}$$

$$= \frac{1}{\mathcal{L}}\sum_i \mathrm{e}^{-\beta(E_i-\mu N_i)}\,N_i = \sum_i \mathcal{P}_i\,N_i = \langle N\rangle \tag{2.17.7}$$

Comparing Eqs. (2.17.5) and (2.17.7) with Eq. (2.17.2) leads to the identification,

$$\ln\mathcal{L} = -\frac{\Phi}{k_BT} \qquad \Rightarrow \qquad \boxed{\Phi = -k_BT\ln\mathcal{L}} \tag{2.17.8}$$

This is analogous to the relation between the canonical partition function Q_N and the Helmholtz free energy, $A = -k_BT\ln Q_N$.

Note: From the Euler relation, $E = TS - pV + \mu N$, and the Legendre transform $\Phi = E - TS - \mu N$, we had $\Phi = -pV$, so now we can write,

$$\boxed{p = \frac{k_BT}{V}\ln\mathcal{L}(T,V,\mu)} \tag{2.17.9}$$

Note: Taking a derivative at constant $\alpha = \dfrac{\mu}{k_B T} = \ln z$ is *not* the same as taking a derivative at constant μ. For example,

$$\left(\frac{\partial \ln \mathcal{L}}{\partial \beta}\right)_{V,\mu} = \frac{1}{\mathcal{L}}\left(\frac{\partial \mathcal{L}}{\partial \beta}\right)_{V,\mu} = \frac{1}{\mathcal{L}}\sum_i \frac{\partial}{\partial \beta}\left(\mathrm{e}^{-\beta(E_i-\mu N_i)}\right) = \frac{1}{\mathcal{L}}\sum_i \mathrm{e}^{-\beta(E_i-\mu N_i)}(-E_i+\mu N_i) \tag{2.17.10}$$

$$= -\sum_i \mathcal{P}_i(E_i - \mu N_i) = -\langle E\rangle + \mu\langle N\rangle \tag{2.17.11}$$

Similarly, taking a derivative with respect to μ is not the same as taking a derivative with respect to $\alpha = \mu/k_B T$,

$$\left(\frac{\partial \ln \mathcal{L}}{\partial \mu}\right)_{\beta,V} = \frac{1}{\mathcal{L}}\sum_i \frac{\partial}{\partial \mu}\left(\mathrm{e}^{-\beta(E_i-\mu N_i)}\right) = \frac{1}{\mathcal{L}}\sum_i \mathrm{e}^{-\beta(E_i-\mu N_i)}\beta N_i \tag{2.17.12}$$

$$= \sum_i \mathcal{P}_i\, \beta N_i = \beta\langle N\rangle \tag{2.17.13}$$

Sometimes it is useful to view $z = \mathrm{e}^{\alpha} = \mathrm{e}^{\beta\mu}$ as the variable instead of α or μ. We therefore have,

$$\left(\frac{\partial \ln \mathcal{L}}{\partial \beta}\right)_{V,z} = -\langle E\rangle \tag{2.17.14}$$

(since differentiating at constant z is the same as differentiating at constant α), but since $d\alpha = d(\ln z) = dz/z$ we can write,

$$\langle N\rangle = \left(\frac{\partial \ln \mathcal{L}}{\partial \alpha}\right)_{\beta,V} = z\left(\frac{\partial \ln \mathcal{L}}{\partial z}\right)_{\beta,V} \tag{2.17.15}$$

To summarize, we have:

$$\boxed{\begin{aligned} \langle N\rangle &= \left(\frac{\partial \ln \mathcal{L}}{\partial \alpha}\right)_{\beta,V} = z\left(\frac{\partial \ln \mathcal{L}}{\partial z}\right)_{\beta,V} = \frac{1}{\beta}\left(\frac{\partial \ln \mathcal{L}}{\partial \mu}\right)_{\beta,V} \\ \langle E\rangle &= -\left(\frac{\partial \ln \mathcal{L}}{\partial \beta}\right)_{V,\alpha} = -\left(\frac{\partial \ln \mathcal{L}}{\partial \beta}\right)_{V,z} \quad \text{but} \quad \langle E\rangle - \mu\langle N\rangle = -\left(\frac{\partial \ln \mathcal{L}}{\partial \beta}\right)_{V,\mu} \end{aligned}} \tag{2.17.16}$$

All these relations are consistent with $\Phi(T,V,\mu) = -k_B T \ln \mathcal{L}(T,V,\mu)$.

Analogous to what we did in comparing the canonical and the microcanonical ensembles, we now want to show that in the thermodynamic limit, $N \to \infty$, computing in the grand canonical ensemble, with a fixed μ determining an average $\langle N\rangle$, gives the same result as computing in the canonical ensemble with fixed $N = \langle N\rangle$.

Thus one can use the grand canonical ensemble even if the physical system of interest in *not* in contact with a reservoir. Just choose a T and a μ to give the desired E and N as the average energy and average number of particles. Because, as $N \to \infty$, the probability for a state in the grand canonical ensemble to have some E' and N' is so sharply peaked about the averages $\langle E\rangle$ and $\langle N\rangle$, the difference between using the grand canonical ensemble vs the microcanonical ensemble at fixed E and N will be negligible. We will find that it is particularly useful to employ this conclusion when we treat quantum ideal gases.

Fluctuations of Particle Number and of Energy

To demonstrate that the grand canonical and the canonical ensembles are equivalent in the thermodynamic limit, we want to show that the relative fluctuations in both N and E will vanish as $N \to \infty$.

Fluctuations of the Particle Number N

We first consider the fluctuations of particle number, $\langle N^2\rangle - \langle N\rangle^2$, in the grand canonical ensemble.

From Eq. (2.17.16) we have,

$$\langle N\rangle = \frac{1}{\beta}\left(\frac{\partial \ln \mathcal{L}}{\partial \mu}\right)_{T,V} \tag{2.17.17}$$

Now consider,

$$\frac{1}{\beta}\left(\frac{\partial \langle N\rangle}{\partial \mu}\right)_{T,V} = \frac{1}{\beta^2}\left(\frac{\partial^2 \ln \mathcal{L}}{\partial \mu^2}\right)_{T,V} = \frac{1}{\beta^2}\frac{\partial}{\partial \mu}\left(\frac{1}{\mathcal{L}}\frac{\partial \mathcal{L}}{\partial \mu}\right)_{T,V} \tag{2.17.18}$$

$$= \frac{1}{\beta^2}\left[\frac{1}{\mathcal{L}}\left(\frac{\partial^2 \mathcal{L}}{\partial \mu^2}\right)_{T,V} - \frac{1}{\mathcal{L}^2}\left(\frac{\partial \mathcal{L}}{\partial \mu}\right)^2_{T,V}\right] \tag{2.17.19}$$

Since $\dfrac{1}{\beta\mathcal{L}}\left(\dfrac{\partial \mathcal{L}}{\partial \mu}\right)_{T,V} = \dfrac{1}{\beta}\left(\dfrac{\partial \ln \mathcal{L}}{\partial \mu}\right)_{T,V} = \langle N\rangle$, the second term above is $\langle N\rangle^2$.

The first term is,

$$\frac{1}{\beta^2\mathcal{L}}\left(\frac{\partial^2 \mathcal{L}}{\partial \mu^2}\right)_{T,V} = \frac{1}{\beta^2\mathcal{L}}\frac{\partial^2}{\partial \mu^2}\left(\sum_i \mathrm{e}^{-\beta E_i}\,\mathrm{e}^{\beta\mu N_i}\right)_{T,V} = \frac{1}{\beta^2\mathcal{L}}\sum_i \mathrm{e}^{-\beta(E_i-\mu N_i)}(\beta N_i)^2 = \sum_i \mathcal{P}_i\, N_i^2 = \langle N^2\rangle \tag{2.17.20}$$

So we have for the variance of N,

$$\sigma_N^2 \equiv \langle N^2\rangle - \langle N\rangle^2 = \frac{1}{\beta}\left(\frac{\partial \langle N\rangle}{\partial \mu}\right)_{T,V} \sim N \quad \text{since } \beta \text{ and } \mu \text{ are intensive} \tag{2.17.21}$$

So the relative fluctuation in N is,

$$\frac{\sigma_N}{\langle N\rangle} \sim \frac{\sqrt{N}}{N} \sim \frac{1}{\sqrt{N}} \to 0 \qquad \text{as } N \to \infty. \tag{2.17.22}$$

Since the relative fluctuation in N vanishes in the thermodynamic limit, the grand canonical ensemble becomes equivalent to the canonical ensemble as $N \to \infty$.

Just like we saw in the canonical ensemble, that the fluctuations in energy σ_E^2 are related to the specific heat C_V, here we can express the fluctuations in the number of particles σ_N^2 in terms of the familiar response function κ_T, the isothermal compressibility.

$$\sigma_N^2 = \frac{1}{\beta}\left(\frac{\partial \langle N\rangle}{\partial \mu}\right)_{T,V} \tag{2.17.23}$$

Write $v = V/N$ and so $N = V/v$. Then,

$$\left(\frac{\partial \langle N\rangle}{\partial \mu}\right)_{T,V} = \left(\frac{\partial (V/v)}{\partial \mu}\right)_{T,V} = V\left(\frac{\partial (1/v)}{\partial \mu}\right)_{T,V} = -\frac{V}{v^2}\left(\frac{\partial v}{\partial \mu}\right)_{T,V} \tag{2.17.24}$$

By the Gibbs-Duhem relation, $N d\mu = V dp - S dT$, so $d\mu = v dp - s dT$. So at constant T we have $d\mu = v dp$. So,

$$\left(\frac{\partial \langle N\rangle}{\partial \mu}\right)_{T,V} = -\frac{V}{v^2}\left(\frac{\partial v}{\partial \mu}\right)_{T,V} = -\frac{V}{v^2}\left(\frac{\partial v}{v\partial p}\right)_{T,V} = -\frac{N^2}{V}\frac{1}{v}\left(\frac{\partial v}{\partial p}\right)_{T,V} \tag{2.17.25}$$

Now since both v and p are intensive, they must be independent of N and V, and so $(\partial v/\partial p)_T$ is independent of N and V. So,

$$\frac{1}{v}\left(\frac{\partial v}{\partial p}\right)_{T,V} = \frac{1}{v}\left(\frac{\partial v}{\partial p}\right)_{T,N} = \frac{1}{v}\left(\frac{\partial (V/N)}{\partial p}\right)_{T,N} = \frac{1}{vN}\left(\frac{\partial V}{\partial p}\right)_{T,N} = \frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_{T,N} = -\kappa_T \tag{2.17.26}$$

Finally,

$$\sigma_N^2 = \frac{1}{\beta}\left(\frac{\partial\langle N\rangle}{\partial\mu}\right)_{T,V} = \frac{1}{\beta}\left(-\frac{N^2}{V}\right)(-\kappa_T) = \frac{N^2}{\beta V}\kappa_T \tag{2.17.27}$$

and

$$\boxed{\frac{\sigma_N}{\langle N\rangle} = \sqrt{\frac{k_B T \kappa_T}{V}}} \tag{2.17.28}$$

<u>Fluctuation of the Energy E</u>

We now consider the fluctuation of the energy, $\langle E^2\rangle - \langle E\rangle^2$, within the grand canonical ensemble. We will see that there are two contributions. One term arises from the fixed temperature, as we found in the canonical ensemble. An addition term arises due to the fluctuations in the number of particles N.

Recall that in the *canonical* ensemble we had,

$$\langle E^2\rangle - \langle E\rangle = -\frac{\partial\langle E\rangle}{\partial\beta} = -k_B\frac{\partial\langle E\rangle}{\partial(1/T)} = k_B T^2\frac{\partial\langle E\rangle}{\partial T} = k_B T^2 C_V \tag{2.17.29}$$

with C_V the specific heat at constant volume.

We now want to see how the fluctuations of N in the grand canonical ensemble will effect the fluctuation of E.

We have,

$$\mathcal{L} = \sum_i \mathrm{e}^{-\beta(E_i-\mu N_i)} = \sum_i \mathrm{e}^{-\beta E_i}\, z^{N_i} \qquad \text{where } z = \mathrm{e}^{\beta\mu} \text{ is the fugacity.} \tag{2.17.30}$$

Then,

$$-\left(\frac{\partial \ln\mathcal{L}}{\partial\beta}\right)_{V,z} = -\frac{1}{\mathcal{L}}\left(\frac{\partial\mathcal{L}}{\partial\beta}\right)_{V,z} = \frac{1}{\mathcal{L}}\sum_i \mathrm{e}^{-\beta E_i}\, z^{N_i}\, E_i = \sum_i \mathcal{P}_i\, E_i = \langle E\rangle \tag{2.17.31}$$

and,

$$\left(\frac{\partial^2 \ln\mathcal{L}}{\partial\beta^2}\right)_{V,z} = -\left(\frac{\partial\langle E\rangle}{\partial\beta}\right)_{V,z} = \frac{1}{\mathcal{L}}\left(\frac{\partial^2\mathcal{L}}{\partial\beta^2}\right)_{V,z} - \frac{1}{\mathcal{L}^2}\left(\frac{\partial\mathcal{L}}{\partial\beta}\right)_{V,z}^2 = \frac{1}{\mathcal{L}}\left(\frac{\partial^2\mathcal{L}}{\partial\beta^2}\right)_{V,z} - \langle E\rangle^2 \tag{2.17.32}$$

Now,

$$\frac{1}{\mathcal{L}}\left(\frac{\partial^2\mathcal{L}}{\partial\beta^2}\right)_{V,z} = \frac{1}{\mathcal{L}}\sum_i \mathrm{e}^{-\beta E_i}\, z^{N_i}\, E_i^2 = \sum_i \mathcal{P}_i\, E_i^2 = \langle E^2\rangle \tag{2.17.33}$$

So finally we have,

$$\left(\frac{\partial^2 \ln\mathcal{L}}{\partial\beta^2}\right)_{V,z} = -\left(\frac{\partial\langle E\rangle}{\partial\beta}\right)_{V,z} = k_B T^2\left(\frac{\partial\langle E\rangle}{\partial T}\right)_{V,z} = \langle E^2\rangle - \langle E\rangle^2 = \sigma_E^2 \tag{2.17.34}$$

Since E is extensive, while β is intensive, then we have $\sigma_E^2 \sim N$, and the relative fluctuation in energy is,

$$\frac{\sigma_E}{\langle E\rangle} \sim \frac{\sqrt{N}}{N} \sim \frac{1}{\sqrt{N}} \to 0 \qquad \text{as } N\to\infty. \tag{2.17.35}$$

So the relative fluctuation of E in the grand canonical ensemble vanishes in the thermodynamic limit.

Since Eq. (2.17.34) for σ_E^2 involves $(\partial E/\partial T)_{V,z}$, one might think this is just proportional to C_V. However C_V is computed at constant V and N, while the derivative in Eq. (2.17.34) is computed at constant V and z. To express this derivative in terms of more familiar response functions we can do as follows. Regard E as a function of (T, V, N), which follows from,

$$E(T,V,N) = -\left(\frac{\partial(-A/T)}{\partial(1/T)}\right)_{V,N} \qquad \text{since } -A/T \text{ is the Legendre transform of } S \text{ from } E \text{ to } 1/T$$

Then regard N as a function of (T, V, z) by using,

$$N(T,V,\mu) = -\left(\frac{\partial \Phi}{\partial \mu}\right)_{T,V} \qquad \text{and then substituting in } \mu = k_B T \ln z \text{ to get } N(T,V,z)$$

We can then write $E(T, V, N) = E(T, V, N(T, V, z))$ and use the chain rule for differentiation to get,

$$\left(\frac{\partial\langle E\rangle}{\partial T}\right)_{V,z} = \left(\frac{\partial\langle E\rangle}{\partial T}\right)_{V,N} + \left(\frac{\partial\langle E\rangle}{\partial N}\right)_{T,V}\left(\frac{\partial\langle N\rangle}{\partial T}\right)_{V,z} \tag{2.17.36}$$

Now $\left(\frac{\partial\langle E\rangle}{\partial T}\right)_{V,N} = C_V$, the specific heat at constant volume. So the first term in Eq. (2.17.36) gives the same contribution to σ_E^2 as one finds in the canonical ensemble. The second term in Eq. (2.17.36) gives the additional fluctuation in E that arise because N is fluctuating.

For the second term one can show (proof left to reader),

$$\left(\frac{\partial\langle N\rangle}{\partial T}\right)_{V,z} = \frac{1}{k_B T^2}\Big[\langle EN\rangle - \langle E\rangle\langle N\rangle\Big] = \frac{1}{T}\left(\frac{\partial\langle E\rangle}{\partial \mu}\right)_{T,V} \tag{2.17.37}$$

(one can show this directly by taking appropriate derivatives of $\ln\mathcal{L}$, or one can recognize it as an appropriate Maxwell relation for the potential $-\Phi/T$ viewed as a function of the variables $(1/T, V, -\mu/T)$) and then use this to write,

$$\left(\frac{\partial\langle E\rangle}{\partial \mu}\right)_{T,V} = \left(\frac{\partial\langle E\rangle}{\partial N}\right)_{T,V}\left(\frac{\partial\langle N\rangle}{\partial \mu}\right)_{T,V} = \left(\frac{\partial\langle E\rangle}{\partial N}\right)_{T,V}\beta\sigma_N^2 \qquad \text{using Eq. (2.17.21) for } \sigma_N^2 \tag{2.17.38}$$

So finally we have,

$$\sigma_E^2 = k_B T^2\left[C_V + \left(\frac{\partial\langle E\rangle}{\partial N}\right)_{T,V}\frac{1}{T}\left(\frac{\partial\langle E\rangle}{\partial N}\right)_{T,V}\beta\sigma_N^2\right] \tag{2.17.39}$$

$$\boxed{\sigma_E^2 = k_B T^2 C_V + \left(\frac{\partial\langle E\rangle}{\partial N}\right)_{T,V}^2\sigma_N^2} \tag{2.17.40}$$

Note, $C_V \sim N$ is extensive, $(\partial\langle E\rangle/\partial N) \sim N/N$ is intensive, $\sigma_N^2 \sim N$ is extensive. Hence $\sigma_E^2 \sim N$ is extensive, and

$$\frac{\sigma_E}{\langle E\rangle} \sim \frac{\sqrt{N}}{N} \sim \frac{1}{\sqrt{N}} \tag{2.17.41}$$

as we saw before.