PHYS 301: The Grand Canonical Potential and Extensive vs. Intensive Quantities

Prof. Cyr-Racine

1 The Grand Canonical Potential

Last week, we introduced the grand partition function:

$$\mathcal{Z} = \sum_n e^{-\beta(E_n - \mu N_n)} \tag{1}$$

where $\beta = \frac{1}{k_B T}$.

This serves as the normalization factor for the probability distribution governing a system in equilibrium with a large reservoir at temperature T and chemical potential μ. The probability of finding the system in a specific microstate n is:

$$p(n) = \frac{e^{-\beta(E_n - \mu N_n)}}{\mathcal{Z}} \tag{2}$$

1.1 Entropy in the Grand Canonical Ensemble

What about the entropy of this system? We can compute it using the Gibbs entropy formula:

$$S = -k_B \sum_n p(n) \ln p(n) \tag{3}$$

Substitute the probability distribution $p(n)$ into the natural logarithm:

$$\begin{aligned} S &= -k_B \sum_n p(n) \ln \left[\frac{e^{-\beta(E_n - \mu N_n)}}{\mathcal{Z}} \right] \\ &= -k_B \sum_n p(n) \left[-\beta(E_n - \mu N_n) - \ln \mathcal{Z} \right] \\ &= k_B \beta \sum_n E_n p(n) - k_B \beta \mu \sum_n N_n p(n) + k_B \ln \mathcal{Z} \sum_n p(n) \end{aligned}$$

Recognizing that $\sum E_n p(n) = \langle E \rangle$, $\sum N_n p(n) = \langle N \rangle$, and $\sum p(n) = 1$, we get:

$$S = k_B \beta \langle E \rangle - k_B \beta \mu \langle N \rangle + k_B \ln \mathcal{Z} \tag{4}$$

Since $\beta = \frac{1}{k_B T}$, we can rewrite this as:

$$S = \frac{\langle E \rangle}{T} - \frac{\mu}{T} \langle N \rangle + k_B \ln \mathcal{Z} \tag{5}$$

1.2 Defining the Grand Canonical Potential (Φ)

Multiply the entire entropy equation by T and rearrange the terms:

$$TS = \langle E\rangle - \mu\langle N\rangle + k_B T \ln \mathcal{Z} \tag{6}$$

$$-k_B T \ln \mathcal{Z} = \langle E\rangle - TS - \mu\langle N\rangle \tag{7}$$

Recall that the Helmholtz free energy is defined as $F = \langle E\rangle - TS$. Substituting F into the equation gives us a new thermodynamic potential, the **Grand Canonical Potential**, denoted by Φ:

$$\boxed{\Phi \equiv F - \mu\langle N\rangle = -k_B T \ln \mathcal{Z}} \tag{8}$$

Mathematically, Φ is the **Legendre transform** of the Helmholtz free energy F, switching the particle number N for the chemical potential μ:

$$F(T, V, N) \longrightarrow \Phi(T, V, \mu) \tag{9}$$

1.3 Thermodynamic Relations for Φ

To find the thermodynamic relations, we take the total differential of $\Phi = F - \mu\langle N\rangle$:

$$d\Phi = dF - \langle N\rangle d\mu - \mu dN \tag{10}$$

Remember the fundamental thermodynamic identity for dF is $dF = -SdT - PdV + \mu dN$. Substituting this in:

$$\begin{aligned} d\Phi &= (-SdT - PdV + \mu dN) - \langle N\rangle d\mu - \mu dN \\ &= -SdT - PdV - \langle N\rangle d\mu \end{aligned}$$

From this total differential, we can easily read off the partial derivatives:

$$S = -\left(\frac{\partial \Phi}{\partial T}\right)_{V,\mu} \tag{11}$$

$$P = -\left(\frac{\partial \Phi}{\partial V}\right)_{T,\mu} \tag{12}$$

$$\langle N\rangle = -\left(\frac{\partial \Phi}{\partial \mu}\right)_{T,V} \tag{13}$$

2 Extensive and Intensive Quantities

Consider a large macroscopic system at equilibrium with fixed energy E, fixed particle number N, and fixed volume V.

Now, consider a small, mathematically defined subset of this system with volume $V_0 = \lambda V$, where $\lambda < 1$ is a scaling factor. Clearly, the energy and number of particles are smaller in this subset. In fact, if E and N are uniformly distributed within the big system (which is required to maximize entropy), then the subsystem contains:

$$\begin{aligned} E_0 &= \lambda E \\ N_0 &= \lambda N \end{aligned}$$

2.1 Extensive Quantities

What about the entropy in the small subsystem? Because entropy is a measure of the system's multiplicity and is additive for independent subsystems, it must also scale directly with the size of the system:

$$S_0 = S(\lambda E, \lambda V, \lambda N) = \lambda S(E, V, N) \tag{14}$$

We can rigorously check this using the Sackur-Tetrode equation for an ideal gas:

$$\begin{aligned} S_0 &= (\lambda N)k_B \left[\ln \left(\frac{(\lambda V)}{(\lambda N)} \left(\frac{4\pi m(\lambda E)}{3(\lambda N)h^2} \right)^{3/2} \right) + \frac{5}{2} \right] \\ &= \lambda N k_B \left[\ln \left(\frac{V}{N} \left(\frac{4\pi m E}{3N h^2} \right)^{3/2} \right) + \frac{5}{2} \right] \\ &= \lambda S(E, V, N) \end{aligned}$$

Notice how the scaling factor λ perfectly cancels out inside the intensive arguments of the logarithm!

Variables that scale linearly with the size of the system (like volume V, particle number N, energy E, and entropy S) are called **extensive quantities**.

2.2 Intensive Quantities

What about the temperature? We know from its thermodynamic definition that:

$$\frac{1}{T} = \frac{\partial S}{\partial E} \tag{15}$$

Intuitively, if the whole system is in thermal equilibrium, the temperature must be the exact same in the small subsystem as it is in the big system.

To see this mathematically, note that temperature is defined as a ratio (a derivative) of two extensive quantities. For the subsystem:

$$\frac{1}{T_0} = \frac{\partial S_0}{\partial E_0} = \frac{\partial(\lambda S)}{\partial(\lambda E)} = \frac{\lambda}{\lambda} \frac{\partial S}{\partial E} = \frac{\partial S}{\partial E} = \frac{1}{T} \tag{16}$$

Therefore, $T_0 = T$.

Quantities that are independent of the system size are called **intensive quantities**. They often emerge as ratios or derivatives of extensive quantities. Other examples include:

- Pressure: $P = T\left(\frac{\partial S}{\partial V}\right)$
- Chemical Potential: $\mu = -T\left(\frac{\partial S}{\partial N}\right)$