Systems with a Variable Number of Particles

Chemical Potential in Thermodynamics

The fundamental relation of TD is generalised for a variable number of particles to:

$$dU = TdS - pdV + \mu dN$$

where μ is the chemical potential defined as

$$\mu = \left(\frac{\partial U}{\partial N}\right)_{S,V}$$

This is the TD definition of chemical potential.
We will now try and find the analogous statistical definition.

Condition for Particle Equilibrium

If you remember in previous chapters, we had the equilibrium condition:

$$d\sigma = \left.\frac{\partial \sigma}{\partial V_A}\right|_{E_A} dV_A + \left.\frac{\partial \sigma}{\partial E_A}\right|_{V_A} dE_A = 0$$

we now generalise this to:

$$d\sigma = \left.\frac{\partial \sigma}{\partial V_A}\right|_{E_A, N_A} dV_A + \left.\frac{\partial \sigma}{\partial E_A}\right|_{V_A, N_A} dE_A + \left.\frac{\partial \sigma}{\partial N_A}\right|_{E_A, V_A, N_A} dN_A = 0$$

As before, we split each partial derivative up since $\sigma = \sigma_A + \sigma_B$:

$$d\sigma = \left[\left.\frac{\partial \sigma_A}{\partial V_A}\right|_{E_A, N_A} - \left.\frac{\partial \sigma_B}{\partial V_B}\right|_{E_A, N_A}\right] dV_A$$

$$+ \left[\left.\frac{\partial \sigma_A}{\partial E_A}\right|_{V_A, N_A} - \left.\frac{\partial \sigma_B}{\partial E_B}\right|_{V_A, N_A}\right] dE_A$$

$$+ \left[\left.\frac{\partial \sigma_A}{\partial N_A}\right|_{V_A, E_A} - \left.\frac{\partial \sigma_B}{\partial N_B}\right|_{V_A, E_A}\right] dN_A = 0$$

Since this scenario is in complete TD equilibrium, we have $\tau_A = \tau_B$ $P_A = P_B$ and particle equilibrium:

$$\mu_{s,A} = \mu_{s,B}$$

which defines statistical chemical potential μ_s:

$$-\frac{\mu_s}{\tau} = \frac{\partial \sigma}{\partial N}\bigg|_{U,V}$$

In fact, just as $\tau = k_B T$ $\Pi = p$, we find $\mu_s = \mu$ since $s = k_B \sigma$ and $\tau = k_B T$

Consider now the process of approaching particle equilibrium while thermal and mechanical equilibrium have already been reached:

$$\frac{d\sigma}{dt} = -\frac{1}{\tau}\frac{dN_A}{dt}(\mu_A - \mu_B) > 0 \qquad \text{since entropy has to increase}$$

So there is a net flow of particles from higher chemical potential system to lower chemical potential system, until particle equilibrium is reached $\mu_A = \mu_B \Rightarrow \frac{dN_A}{dt} = 0$

Thermodynamic Potentials

Let's generalise our thermodynamic potentials.

Helmholtz Free Energy:
  This was $F = U - TS$, but now:

$$dF = -SdT - pdV + \mu dN \qquad \text{so} \qquad F = F(T, V, N)$$

$$\therefore \quad \underline{\mu = \left(\frac{\partial F}{\partial N}\right)_{V,T}} \qquad \text{This definition is often more convenient.}$$

In a system with constant volume and temperature, it can be shown F tends to a minimum in irreversible processes. i.e $\frac{\partial F}{\partial N} \leq 0$ if constant V and T

If N can vary, system chooses N for which F is minimised.

$\left(\frac{\partial F}{\partial N}\right)_{V,T} = 0$ at equilibrium

since $\mu = \left(\frac{\partial F}{\partial N}\right)_{V,T}$ then $\mu = 0$ at equilibrium for particles with no conservation laws (like photons).

Enthalpy :

This was $H = U + pV$ but now :

$dH = TdS + Vdp + \mu dN$ so $H = H(S, p, N)$

Gibbs Function:

This was $G = U - TS + pV$ but now :

$dG = -SdT + Vdp + \mu dN$ so $G = G(T, p, N)$

$$\mu = \left(\frac{\partial G}{\partial N}\right)_{p, T}$$

$\Rightarrow G = \mu N$ why is this true? Since G is extensive, like all TD potentials:

$G \rightarrow \lambda G$ as $N \rightarrow \lambda N$

$\therefore G(T, p, \lambda N) = \lambda G(T, p, N) = N f(p, T)$

from which it follows $G = \mu N$

from $G = U - TS + pV$: $\mu N = U - TS + pV$

$\Rightarrow S = \frac{U + pV - \mu N}{T}$ letting $s = \frac{S}{V}$ $u = \frac{U}{N}$ $n = \frac{N}{V}$

$s = \frac{u + p - \mu n}{T}$

Please turn over

We now introduce an important TD potential:

grand potential is

$$\phi_G = U - TS - \mu N = F - \mu N$$

$$d\phi_G = -SdT - pdV - Nd\mu \qquad so \qquad \phi_G = \phi_G(T, V, \mu)$$

so: $S = -\left(\dfrac{\partial \phi_G}{\partial T}\right)_{V, \mu}$

$p = -\left(\dfrac{\partial \phi_G}{\partial V}\right)_{T, \mu}$

$N = -\left(\dfrac{\partial \phi_G}{\partial \mu}\right)_{T, V}$ This is particularly useful.
We will use it later.

$\phi_G = U - TS - G$ after inserting $G = \mu N$

so using $G = U - TS + pV$ we get:

$$\phi_G = -pV$$

Grand Canonical Ensemble

Let's recap on the microcanonical and canonical ensembles:

Microcanonical Ensemble:

E, N, V fixed. The system is isolated and there is no reservoir.

Canonical Ensemble:

T, N, V fixed. The system is in thermal contact with a reservoir and can exchange energy with it.
Reservoir has constant T, system has variable E

Grand Canonical Ensemble :

Here, T U μ are fixed. The system is in thermal contact with a reservoir and can exchange energy and particles with it. The reservoir has constant T and μ , system has variable E and N

The Grand Canonical distribution is:

$$w(E,N) = A' e^{-\frac{E-\mu N}{\tau}}$$ where A' is the normalisation constant.

The Grand Partition Function is:

$$Z_G = \sum_{N=0}^{N_{max}} \int e^{-\frac{E-\mu N}{\tau}} \, dW(N)$$

The normalisation condition: $\sum_{N=0}^{N_{max}} \int w(E,N) \, dW(N) = 1$

from which we find $Z_G = A'^{-1}$

so

$$w(E,N) = \frac{1}{Z_G} e^{-\frac{E-\mu N}{\tau}}$$

The Importance of the Grand Potential

In the canonical ensemble, we saw $F = -k_B T \ln Z$ hence how F and Z are related.

In the grand canonical ensemble, we use $\phi_G = F - \mu N$ instead of F and grand partition function instead of partition function

$$\phi_G = -k_B T \ln Z_G$$

where Z_G here is grand partition function

This is a generalisation of $F = -k_B T \ln Z$.

Let's prove this.

The mean number of particles in a quantum discrete system is:

$$\langle N \rangle = \sum_i N_i P_i = \sum_i N_i \frac{e^{\beta(\mu N_i - E_i)}}{Z_G}$$

$$\Rightarrow \quad \langle N \rangle = \frac{1}{\beta Z_G} \frac{\partial}{\partial \mu} \sum_i e^{\beta(\mu N_i - E_i)} = \frac{1}{\beta Z_G} \frac{\partial}{\partial \mu} Z_G$$

$$= k_B T \frac{\partial \ln Z_G}{\partial \mu}$$

Earlier we saw $\quad N = -\left(\frac{\partial \Phi_G}{\partial \mu} \right)_{T, V}$

Setting $\langle N \rangle = N$, we find:

$$k_B T \frac{\partial \ln Z_G}{\partial \mu} = -\frac{\partial \Phi_G}{\partial \mu}$$

$$\Rightarrow \quad \underline{\Phi_G = -k_B T \ln Z_G}$$

We can also derive internal energy U.

$$U = \frac{\sum_i E_i e^{-\beta E_i}}{\sum_i e^{-\beta E_i}} = \frac{\partial \ln Z}{\partial \beta} \qquad \text{from the canonical ensemble equations}$$

$$\Rightarrow \quad U = \frac{\sum_i E_i e^{\beta(\mu N_i - E_i)}}{\sum_i e^{\beta(\mu N_i - E_i)}} = -\left(\frac{\partial \ln Z_G}{\partial \beta} \right)_{\beta\mu = \text{constant}} \qquad \text{for grand canonical ensemble}$$

Note the condition $\beta\mu = \text{constant}$.

Ideal Gas

We will now discuss the ideal gas within the grand canonical ensemble. Let's start with:

$$\mathcal{Z}_g = \sum_{N=0}^{\infty} \int e^{\beta(\mu N - E)} \, dW(N) \qquad \text{where we have taken } N_{max} \to \infty$$

using $dW = \dfrac{d^{3N}p \, d^{3N}q}{h^{3N} N!}$ i.e relating number of microstates to volume of phase space:

$$Z_g = \sum_{N=0}^{\infty} \int \frac{d^{3N}p \, d^{3N}q}{h^{3N} N!} e^{\beta(\mu N - E)} = \sum_{N=0}^{\infty} e^{\beta \mu N} Z_N$$

where $Z_N = \int \dfrac{d^{3N}p \, d^{3N}q}{h^{3N} N!} e^{-E/\tau}$

using $e^x = \sum_{N=0}^{\infty} \dfrac{x^N}{N!}$ with $x = \left(e^{\beta\mu} \dfrac{V}{\lambda_{th}^3}\right)$, we can

rewrite this:

$$Z_g = \sum_{N=0}^{\infty} \frac{1}{N!} \left(e^{\beta\mu} \frac{V}{\lambda_{th}^3}\right)^N = \exp\left[e^{\beta\mu} \frac{V}{\lambda_{th}^3}\right]$$

We can now calculate grand potential $\Phi_G = -k_B T \ln Z_g$

$$\Phi_G = -k_B T e^{\beta\mu} \frac{V}{\lambda_{th}^3}$$

We can calculate the number of particles $N = -\left(\dfrac{\partial \Phi_G}{\partial \mu}\right)_{T,V}$

$$N = e^{\beta\mu} \frac{V}{\lambda_{th}^3}$$

Comparing expressions for Φ_G and N, we see $\underline{\Phi_G = -N k_B T}$

we can also see $\underline{\mu = k_B T \ln(n \lambda_{th}^3)}$

Since $U = -\left(\dfrac{\partial \ln Z_g}{\partial \beta}\right)$ we can also derive the internal energy

$$\underline{U = \frac{3}{2} N k_B T} \quad \text{the usual expression.}$$

$U = \frac{3}{2} N k_B T$

Since $p = -\left(\frac{\partial \Phi_G}{\partial V}\right)_{T,\mu}$ we can also calculate pressure

$\underline{p = n k_B T}$ where $n = \frac{N}{V}$ so $PV = N k_B T$ the expected equation

which gives us confirmation of $\Phi_G = -pV$

From $S = -\left(\frac{\partial \Phi_G}{\partial T}\right)_{V,\mu}$:

$S = \frac{\partial}{\partial T}\left[k_B T e^{\beta\mu} \frac{V}{\lambda_{th}^3}\right]_{V,\mu}$ After some algebra:

$S = k_B T N \left[\frac{5}{2T} + \mu \frac{d\beta}{dT}\right]$ which we can combine

with $\mu = k_B T \ln(n \lambda_{th}^3)$:

$\sigma = N\left[\frac{5}{2} - \ln(n\lambda_{th}^3)\right]$

But this is weird. If we consider $T \to 0$, neither S nor C_V vanish, as is required for 3rd Law of TD. So maybe we need some quantum magic!