TLL question 5:
A fundamental equation for the Grand Canonical Potential Function is expressed as:
\[ \Xi (T, V, \mu) \]
(a) write the Euler equation for this potential.
(b) write the corresponding Gibbs-Duhem equation.
(c) express the extremum principle for this function.

ChatGPT4 answer:
The Grand Canonical Potential, also called the Grand Potential, is a function \( \Xi (T, V, \mu) \) of temperature \( T \), volume \( V \), and chemical potential \( \mu \). It's used in statistical mechanics to describe a system in the grand canonical ensemble.

(a) The Euler equation for this potential is given by:
\[ \Xi = TS - PV + \mu N \]
where \( S \) is the entropy, \( P \) is the pressure, and \( N \) is the number of particles in the system.

(b) The Gibbs-Duhem equation in the context of the grand canonical potential is:
\[ SdT + VdP - Nd\mu = 0 \]
This equation is the thermodynamic identity corresponding to the Euler equation and states that at equilibrium, the infinitesimal changes in the system's variables must satisfy this relation.

(c) The extremum principle for the Grand Canonical Potential is that at equilibrium, the Grand Canonical Potential \( \Xi \) will be minimized with respect to its natural variables \( T, V, \) and \( \mu \). This means that for a small change in these variables, the change in the potential must be zero:
\[ d\Xi = 0 \]
If the system is not at equilibrium, it will evolve in such a way to minimize the grand potential. This is analogous to the principle of least action in classical mechanics.

TLL follow-up:
I think your response to part a is incorrect. The Euler for \( U \) is: \( U = TS - PV + \mu N \). Legendre transforming \( U \) to get \( \Xi \) we get: \( \Xi = U - TS - \mu N \). Substituting for \( U \) we get the Euler for \( \Xi: \Xi = -PV \). Can you explain the discrepancy in our answers?
The Grand Canonical Potential, $\Xi$, is indeed defined through the Legendre transformation of the Internal Energy, $U$. This is done to switch the natural variables from $(S, V, N)$ to $(T, V, \mu)$.

The relation is:
$$\Xi = U - TS - \mu N$$

To clarify, the Euler relation for $U$ is:
$$U = TS - PV + \mu N$$

Substituting this into the definition of $\Xi$ yields:
$$\Xi = -PV$$

This is the correct Euler relation for the Grand Canonical Potential.

Again, I apologize for the oversight in my original response. Your understanding is correct.

TLL follow-up:
Do you want to rethink your response to part b given your new answer to part a?

ChatGPT4 answer:
Absolutely, thank you for your patience.

Given the corrected Euler relation $\Xi = -PV$ for the Grand Canonical Potential, the Gibbs-Duhem equation, which relates the natural variables of the system, is expressed in this context as:
$$VdP = 0$$

However, please note that while this form of the Gibbs-Duhem equation is mathematically correct in the context of the Grand Canonical Potential, it doesn't carry as much physical information as the original Gibbs-Duhem equation for a system described by the thermodynamic potential $U$. The reason is that, in the grand canonical ensemble, the system is in equilibrium with a reservoir, which fixes the temperature, volume, and chemical potential, so there are no independent variations of these parameters. In contrast, the original Gibbs-Duhem equation, $SdT + VdP - Nd\mu = 0$, is derived under the assumption that these parameters can vary independently, which is not the case in the grand canonical ensemble.

TLL follow-up:
What Gibbs-Duhem equation do you get if you equate the total differential of the Euler equation from part a: $d\Xi = -PV = \cdot \cdot \cdot dP$ with the total differential of the equation for $\Xi$ obtained from the Legendre transformation of $U$: $\Xi = U - TS - \mu N$ taking the differential: $d\Xi = dU - TdS - SdT - \mu dN - Nd\mu = TdS - \mu dN - TdS - SdT - \mu dN - Nd\mu = -SdT - PdV - Nd\mu = -PdV - VdP$ so

ChatGPT4 answer:
I apologize for the confusion, but there is an error in your derivation. The total differential of the Grand Canonical Potential $\Xi$ (given the relation $\Xi = U - TS - \mu N$), taking into account that the internal energy $U$ is a function of entropy $S$, volume $V$ and number of particles $N$, is:
$$d\Xi = dU - TdS - SdT - \mu dN - Nd\mu$$

And because $dU = TdS - PdV + \mu dN$ (by the fundamental thermodynamic relation), the total differential of $\Xi$ can be rewritten as:
$$d\Xi = TdS - PdV + \mu dN - TdS - SdT - \mu dN - Nd\mu$$

This simplifies to:
$$d\Xi = -SdT - PdV - Nd\mu$$

This is the total differential of the Grand Canonical Potential. When this is equated to the differential of the Euler equation ($d\Xi = -PdV - VdP$), we get:
$$-SdT - PdV - Nd\mu = -PdV - VdP$$

Rearranging, we get the Gibbs-Duhem equation for the Grand Canonical Potential:
$$SdT + VdP = Nd\mu$$

This shows how the differential changes in the thermodynamic variables are related in the grand canonical ensemble.
TLL follow-up:

But you lost a negative sign on your -SdT term...should be -SdT + VdP = Ndµ

ChatGPT4 answer:

Yes, you're correct. I apologize for the mistake.

Here is the correct derivation:

Starting with the total differential of the Grand Canonical Potential Ξ (given the relation Ξ = U - TS - µN),

\[ dΞ = dU - TdS - SdT - µdN - Ndµ \]

And knowing that \( dU = TdS - PdV + µdN \) (by the fundamental thermodynamic relation), the total differential of Ξ can be rewritten as:

\[ dΞ = TdS - PdV + µdN - TdS - SdT - µdN - Ndµ \]

This simplifies to:

\[ dΞ = -SdT - PdV - Ndµ \]

This is the total differential of the Grand Canonical Potential. When this is equated to the differential of the Euler equation (\( dΞ = -PdV - VdP \)), we get:

\[ -SdT - PdV - Ndµ = -PdV - VdP \]

Rearranging, we get the Gibbs-Duhem equation for the Grand Canonical Potential:

\[ -SdT + VdP = Ndµ \]

This correctly expresses how the differential changes in the thermodynamic variables are related in the grand canonical ensemble. Again, I apologize for the error in the previous response.