

## ChatGPT-4 &amp; Questions from a Materials Thermodynamics Course

## Question 5: Alternate Energy Functions

**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?

### ChatGPT4 answer:

I apologize for the confusion. You are correct.

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:  $d\Xi = -(PV) = -PdV - VdP$  with the total differential of the equation for  $\Xi$  obtained from the Legendre transformation of  $U$ :  $\Xi = U - TS - \mu N$  taking the differential:  $d\Xi = dU - TdS - SdT - \mu dN - Nd\mu = TdS - PdV + \mu dN - TdS - SdT - \mu dN - Nd\mu = -SdT - PdV - Nd\mu = -PdV - VdP$  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  $-SdT + VdP = Nd\mu$

## 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  $\Xi$  (given the relation  $\Xi = U - TS - \mu N$ ),

$$d\Xi = dU - TdS - SdT - \mu dN - Nd\mu$$

And knowing that  $dU = TdS - PdV + \mu dN$  (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 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.