Don’t Panic

Undergraduate Thermodynamics

If \( \frac{\partial f}{\partial x} \bigg|_y \frac{\partial f}{\partial y} \bigg|_x \), then \( f \) is a function of \( x \) and \( y \). The conjugate of \( x \) is \( \frac{\partial f}{\partial x} \bigg|_y \) and the conjugate of \( y \) is \( \frac{\partial f}{\partial y} \bigg|_x \).

1. If \( \partial U = T\partial S - P\partial V + \mu \partial n \), then what are the natural variables of \( U \) and the corresponding conjugates of those natural variables?

2. If \( \partial U = T\partial S - P\partial V + \mu \partial n \), and I use it to derive: \( \partial S = \ldots \), then what are the natural variables of \( S \) and the corresponding conjugates of those natural variables?

3. How can I calculate the temperature of a system using \( U \) and \( S \)? Do I need to hold something constant?

4. If I write a new function: \( g = f - \frac{\partial f}{\partial y} \bigg|_x \cdot y \), what is \( g \) a function of (what are the natural variables)? Hint: derive what \( \partial g \) is. Double hint: this is a Legendre Transform.

5. What are the natural variable of the function: \( H = U - (P) \cdot V = U + PV \)? Hint: show me what \( \partial H \) is.

6. I hope you know that entropy is a first order homogeneous function of \( U \) (internal energy), \( V \) (volume), and \( n \) (number of moles). Stated mathematically, this means that \( \lambda S = S(\lambda U, \lambda V, \lambda n) \). Note that \( S \) is 0 J/K at 0K (3\text{rd} Law of thermodynamics) and rises with temperature. Can you show that for the following two equations that describe some arbitrary system:

   a. \( S = [n \cdot V \cdot U]^{1/2} \) satisfies all three criterias above?

   b. \( S = n \cdot \ln \left( \frac{U \cdot V}{n^2} \right) \) does not satisfy all three (there must have been a mistake when deriving it!).

   Hint: you have to calculate \( S(T) \) via \( \frac{\partial U}{\partial S} \) to show that \( S=0 \) J/K when \( T=0 \) K and that \( S(T) \) rises with temperature.

7. The following is a Legendre transform of entropy: \( S = (1/T) \cdot U \)

   It still represents entropy but represents a form of entropy that depends on different natural variables. What are the natural variables of this function?
Graduate Statistical Mechanics

Let’s introduce the concept of statistical mechanics. Here, \( S = k_B \ln(W) \), where \( W \) is the number of states.

8. If possible, a thermodynamic system will evolve over time to a) lower its energy and/or to b) maximize its entropy. One of these statements (a or b) is more true than the other. Which one, and why? If you get it right, you won’t need a 2\(^{nd}\) opinion!

9. I am doing a molecular dynamics simulation in the microcanonical ensemble, where \( U, V, n \) are constant. Each molecular configuration generated has equal probability to represent the system as any other. Why? Hint: think about how a system with a higher entropy is more likely to be observed (or is more representative), vs. a configuration with a lower entropy.

10. If I am performing a statistical analysis on a system where I want to keep the “entropy” function: \( S - (1/T) \cdot U \) constant, then what variables should I hold constant? What are the conjugates of those variables that fluctuate? Hint: this defines the canonical ensemble.

11. We can work with a system of units such that \( k_B = 1 \). Concerning the Helmholtz energy: \(-A/T = S - (1/T) \cdot U = \ln(W) - (1/T) \cdot U\) Please cast this equation: \( \ln(W) - (1/T) \cdot U \) into the form: \( \ln(Q) \). To answer the question, just tell me what \( Q \) is. Hint: \( f(x) = \ln(e^{f(x)}) \), and \( Q \) is the canonical partition function.

12. If \( W \) is the number of microstates of a thermodynamic system, where each microstate has a different internal energy \( U_i \), then can you justify the idea that:
\[
\ln(e^W) \cdot f(U_i) = \sum_{i=1}^{\#\text{states}} f(U_i)
\]

13. Given that the canonical partition function is \( Q = \sum_{i=1}^{\#\text{states}} e^{-U_i/T} \), can you prove that
\[
\langle U \rangle = \frac{-\partial \ln(Q)}{\partial (1/T)}
\]
You should know that the probability \( (P_i) \) of observing a system with an internal energy \( U_i \) is: \( P_i = \frac{e^{-U_i/T}}{\sum_{i=1}^{\#\text{states}} e^{-U_i/T}} \).

Hint: how do you determine the average value of anything though probability?