PHY541 Problem Set 1. Due September 2, 2014.

1. a. Practice using Jacobians and show that (at constant N)

$$\left.\frac{\partial E}{\partial V}\right|_T - T \left.\frac{\partial p}{\partial T}\right|_V = -p \tag{1}$$

   b. If you knew that a thermodynamic system satisfied $pV = NT$, what would this relationship tell you about the dependence of $E(T, V, N)$ on N, V and T?

2. a. Practice using Jacobians and show that (at constant N)

$$C_p - C_V = \left[p + \left.\frac{\partial E}{\partial V}\right|_T\right] \left.\frac{\partial V}{\partial T}\right|_p \tag{2}$$

   b. Substitute the result of problem 1 for the energy derivative, and evaluate this difference as a function of N, V and T, for the ideal gas equation of state, $p(n, T) = nT$, and the Van der Waals equation of state, $p(n, T) = \frac{nT}{1-bn} - an^2$, where $n = \frac{N}{V}$ is the number density, a and b are parameters typically fit to data or calculations.[1]

3. Practice using Jacobians and show that

$$\left.\frac{\partial E}{\partial V}\right|_{\frac{\mu}{T}, \frac{1}{T}} + \frac{1}{T} \left.\frac{\partial p}{\partial (\frac{1}{T})}\right|_{\frac{\mu}{T}, V} = -p\,. \tag{3}$$

4. a. You measure the energy E of a system as a function of temperature $T_0 \leq T \leq T_1$ at fixed volume and particle number. Write an expression for the Helmholtz free energy $F(T_1)$ at temperature T_1 in terms of the Helmholtz free energy at T_0 and the measured $E(T)$.

   b. You measure the pressure p of a system as a function of its volume $V_0 \leq V \leq V_1$, at fixed temperature and particle number. Write an expression for the Helmholtz free energy $F(V_1)$ at volume V_1 in terms of the Helmholtz free energy at V_0 and the measured pressure, $p(V)$.

   c. Think about and write on your own, but do not write an answer for me, how you could use these results to publish the value of the Helmholtz free energy, as a function of temperature and volume for fixed N, of a new material that you have discovered how to synthesize and which you have measured in your lab. To be explicit, any answer you give to this question on the turned in homework will give negative points. Feel free to discuss or ask questions about this in class after the homework deadline.

[1] Physically, a is the volume excluded by one particle, and b is the volume integral of the average attractive potential energy.