Thermodynamics and Statistical Mechanics Qualifying Exam
June 12, 2014

Please work 4 of the following 6 questions. If you answer more than four you must clearly mark which four you want to have graded.

1. Think of the internal energy $E$ and the entropy $S$ as functions of the temperature $T$ and the volume $V$ of a system. The number of particles is fixed.

   a. For a quasi-static or reversible process rigorously show that

   \[
   \left( \frac{\partial E}{\partial T} \right)_V \left( T \frac{\partial S}{\partial T} \right)_V
   \]

   b. For a quasistatic or reversible process find a similar expression for

   \[
   \left( \frac{\partial E}{\partial V} \right)_T
   \]

   Again provide a rigorous derivation of your result.

   c. Use the results of parts (a) and (b) to derive one of the Maxwell relations.

2. If you have a system in equilibrium with both a heat and a pressure bath so that the variables that specify a macrostate of the system are $T$, $P$, and $N$, then the probability for a given microstate $s$ is

   \[
   P_s = \frac{e^{-\beta(E_s+PV_s)}}{Z}
   \]

   Here $E_s$ is the energy of the system and $V_s$ is the volume of the system in microstate $s$. $P$ is the pressure of the system and $Z$ is the partition function, and $\beta = 1/(kT)$. The Gibbs free energy in this case is taken to be

   \[
   G = -kT \ln Z
   \]

   a. Derive an expression for $Z$. You must show your work for full credit. Hint: This is not a long calculation.

   b. Find expressions for the average volume $\bar{V}$ and the average energy $\bar{E}$.

   c. Using the fact that in classical thermodynamics $G = E - TS + PV$, derive an expression for the entropy $S$ in terms of $k$, $T$, $Z$, and one or more derivatives of $Z$.

   d. Using your result for part (c) verify that the formula $S = -k \sum_s P_s \ln P_s$ is correct.
3. The diagram above shows a plot of the temperature ($T$) versus entropy ($S$) for a cyclic 3 step process of an ideal gas of $N$ monoatomic particles. Your answers to the following questions can be expressed in terms of the values of temperature ($T_1$, $T_2$, $T_3$) and entropy ($S_1$ and $S_2$).

(a) Find the heat added to or subtracted from the system for each of the steps – $Q_{AB}$, $Q_{BC}$, and $Q_{CA}$.

(b) Find the magnitude of the net work $|W|$ done on the system.

(c) Find the total amount of the heat $Q_{in}$ that is added to the system.

(d) Find the efficiency of each cycle

\[
\epsilon = \frac{|W|}{Q_{in}}
\]

(e) For a Carnot cycle operating between the same maximum and minimum temperatures and the same maximum and minimum entropies, find the corresponding efficiency $\epsilon_{Carnot}$. Comment on the value of $\epsilon_{Carnot}$ relative to $\epsilon$. 
4. Consider a system of 3 identical non-interacting particles each having two possible total (kinetic, potential, etc.) energies: $\epsilon_1$ and $\epsilon_2$ with $\epsilon_2 > \epsilon_1$. Assume that the particles are in equilibrium with a heat bath held at temperature $T$.

(a) Suppose that the 3 particles are indistinguishable particles obeying Fermi statistics and each has a spin with possible (degenerate) states $\uparrow$ and $\downarrow$.
   i. Write the canonical partition function for this case as a function of the temperature $T$.
   ii. Evaluate the average internal energy of the system for $T \to 0$.
   iii. Evaluate the average internal energy of the system for $T \to \infty$.

(b) Suppose that the 3 particles are indistinguishable particles obeying Bose statistics and each has no internal spin.
   i. Write the canonical partition function for this case as a function of the temperature $T$.
   ii. Evaluate the average internal energy of the system for $T \to 0$.
   iii. Evaluate the average internal energy of the system for $T \to \infty$.

(c) Suppose that the 3 particles are distinguishable particles obeying Boltzmann statistics and each has no internal spin.
   i. Write the canonical partition function for this case as a function of the temperature $T$.
   ii. Evaluate the average internal energy of the system for $T \to 0$.
   iii. Evaluate the average internal energy of the system for $T \to \infty$. 
5. Consider a one-dimensional chain on a two-dimensional flat surface composed of $N \gg 1$ sites. Each site has one of two energy states: it can be straight (with energy $h_{\text{bend}} = 0$) or it can bend by $90^\circ$ (on the right or on the left) with energy $h_{\text{bend}} = \epsilon > 0$, independently of the bending direction. Compute the entropy of the system, $S(E, N)$, for a fixed total bending energy $E = m\epsilon$ ($m$ is an integer number such that $m \gg 1$). Also, determine the internal energy as a function of the temperature and the resulting heat capacity $C_N$, under the assumption that $(Nm) \gg 1$. Finally, determine the behaviour of the internal energy in the limits of low and high temperatures.

6. A simple model of DNA consists of two filaments intersecting one with each other so as to form a double helix. However, the geometry of the double helix is not important for this problem. Let the system be at a fixed temperature $T$ and label the two filaments $(a, b)$. On each filament there are $N$ sites, each of which contains a molecular fragment. The molecular fragment on a given site of strand $a$ can only form a bond with the molecular fragment at the same site on strand $b$. There is only one way that this can occur. However, if at a particular site the molecular fragment on strand $a$ does not form a bond with the corresponding molecular fragment on strand $b$ then the energy of the system is larger by an amount $\epsilon > 0$ than it would be if there was a bond. Further, if no bond is formed then the molecular fragment on strand $a$ has $G$ directions that it can point in, all with the same energy. The same is true for the molecular fragment on strand $b$.

The system presents various configurations, including the configuration for which all sites have bonds, and configurations with any number $p$ of sites with no bonds, up to $N - 1$. At least one site must have a bond. Write down the canonical partition function and determine the average number of sites without bonds $\langle p \rangle$. Is there a critical temperature $T_c$ above which the canonical ensemble gives a divergent partition function for large $N$? Hint: Defining the quantity $x = G^2e^{-\beta\epsilon}$ will make the computations easier.