Formulae that might be helpful

\[
\int_{-\infty}^{\infty} e^{-ax^2+bx} \, dx = \left( \frac{\pi}{a} \right)^{1/2} e^{b^2/4a}
\]

(1)

Relations between partial derivatives,

\[
\left( \frac{\partial x}{\partial y} \right) = 1/ \left( \frac{\partial y}{\partial x} \right); \quad \text{Inversion}
\]

(2)

\[
\left( \frac{\partial x}{\partial y} \right) = \left( \frac{\partial x}{\partial w} \right) \left( \frac{\partial w}{\partial y} \right) \quad \text{Addition of a variable}
\]

(3)

\[
\left( \frac{\partial x}{\partial y} \right) \left( \frac{\partial y}{\partial z} \right) \left( \frac{\partial z}{\partial x} \right) = -1; \quad \text{Triple Product}
\]

(4)

If \( A(x, y) \), then,

\[
\left( \frac{\partial A}{\partial x} \right) = \left( \frac{\partial A}{\partial x} \right) y + \left( \frac{\partial A}{\partial y} \right) x \quad \text{non-natural derivative}
\]

(5)

Response functions are defined as follows;

\[
C_V = \left( \frac{\partial Q}{\partial T} \right)_{V,N} = \left( \frac{\partial U}{\partial S} \right)_{V,N} \left( \frac{\partial S}{\partial T} \right)_{V,N} = T \left( \frac{\partial S}{\partial T} \right)_{V,N},
\]

(6)

\[
C_P = \left( \frac{\partial H}{\partial T} \right)_{P,N} = \left( \frac{\partial U}{\partial S} \right)_{P,N} \left( \frac{\partial S}{\partial T} \right)_{P,N} = T \left( \frac{\partial S}{\partial T} \right)_{P,N},
\]

(7)

\[
\kappa_S = -\frac{1}{V} \left( \frac{\partial V}{\partial P} \right)_{S,N} = - \left( \frac{\partial \ln V}{\partial P} \right)_{S,N},
\]

(8)

\[
\kappa_T = -\frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_{T,N} = - \left( \frac{\partial \ln V}{\partial T} \right)_{T,N},
\]

(9)

\[
\alpha_P = \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_{P,N} = \left( \frac{\partial \ln V}{\partial T} \right)_{P,N},
\]

(10)
1. (8 points)
(i) Write down the Boltzmann, Gibbs and von Neumann expressions for the entropy and show how the von Neumann form reduces to the Gibbs form.

**Solution.** The Boltzmann, Gibbs and von Neumann forms of the entropy are respectively,

\[ S = k_B \ln(\Omega(E)); \quad S = -k_B \sum_i p_i \ln(p_i); \quad S = -k_B \text{tr}(\hat{\rho} \ln(\hat{\rho})) \] (11)

By transforming to the basis of energy eigenstates, the von Neumann entropy of Corollary reduces to the entropy of Corollary,

\[ S = -k_B \text{tr}(\hat{\rho} \ln(\hat{\rho})) = -k_B \text{tr}(\hat{U} \hat{\rho} \hat{U}^\dagger \ln(\hat{\rho}) \hat{U}) \] (12)

where \( \hat{U} \) is the unitary matrix that diagonalizes both the Hamiltonian \( \hat{H} \) and the density matrix in the canonical ensemble is \( \hat{\rho} = \text{Exp}(-\beta \hat{H})/Z \). These matrices can be introduced into the trace formula as the trace formula is invariant under cyclic permutations of a matrix product, and the unitary matrix has the property \( \hat{U} \hat{U}^\dagger = \text{unit matrix} \).

In the (many body) eigenfunction basis, the von Neumann entropy is then,

\[ S = -k_B \text{tr}(\hat{U} \hat{\rho} \ln(\hat{\rho}) \hat{U}) = -k_B \sum_i p_i \ln(p_i) \] (13)

where, in the canonical ensemble, \( p_i = \text{exp}(-\beta E_i)/Z \), where \( Z = \sum_i \text{e}^{-\beta E_i} \). In carrying out this reduction, we also use the fact that \( \hat{\rho} \) and \( \ln(\hat{\rho}) \) commute and hence are diagonalized by the same unitary matrix.

(ii) A DNA chain with \( N \) binding sites allows binding at each site by three different proteins. Only one protein can bind to a site at a given time and the binding energy between a protein and a binding site is the same for all cases. If there are \( n_1 \) bound proteins of type one, \( n_2 \) bound proteins of type two and \( n_3 \) bound proteins of type three, with \( n_1 + n_2 + n_3 < N \) how many different protein binding configurations are there. From your expression find the configurational entropy of the system.

**Solution.** The number of configurations is given by the multinomial,

\[ \Omega(E) = \frac{N!}{n_1! n_2! n_3! (N - (n_1 + n_2 + n_3))!} \] (14)

Using Stirling’s approximation and the definitions \( p_i = n_i/N \), we find,

\[ S = -N k_B \ln(\Omega(E)) = N \ln(N) - N - [n_1 \ln(n_1) + n_2 \ln(n_2) + n_3 \ln(n_3) + (N - n_1 - n_2 - n_3) \ln(N - n_1 - n_2 - n_3)] + N \] (15)

and the definitions \( p_i = n_i/N \),

\[ S = -N k_B [p_1 \ln(p_1) + p_2 \ln(p_2) + p_3 \ln(p_3) + (1 - p_1 - p_2 - p_3) \ln(1 - p_1 - p_2 - p_3)] \] (16)

2. (8 points)
(i) From the fundamental thermodynamic relation show that at equilibrium \( p_1 = p_2 \), \( T_1 = T_2 \), \( \mu_1 = \mu_2 \).

**Solution.** Consider two systems, systems 1 and 2, characterized by their entropy, volume and number of particles, \((S_1, V_1, N_1)\) and \((S_2, V_2, N_2)\) respectively. The two systems are at equilibrium with each other, and are in contact and can exchange both energy and particles, their volumes may also change provided the total volume is fixed. In the thermodynamic limit, the combined system has internal energy \( U = U_1 + U_2 \), entropy \( S = S_1 + S_2 \), volume \( V = V_1 + V_2 \), and number of particles \( N = N_1 + N_2 \). The combined system is isolated, and is at equilibrium. We then have,

\[ dU_1 = dE_1 = T_1 dS_1 - P_1 dV_1 + \mu_1 dN_1, \quad \text{and} \quad dU_2 = dE_2 = T_2 dS_2 - P_2 dV_2 + \mu_2 dN_2 \] (17)

In the combined system \( E, S, V, N \) are fixed, so we can write,

\[ dU_2 = dE_2 = T_2 dS_2 - P_2 dV_2 + \mu_2 dN_2 = d(E - E_1) = T_2 d(S - S_1) - P_2 d(V - V_1) + \mu_2 d(N - N_1) \] (18)

which reduces to

\[ -dE_1 = -(T_2 dS_1 - P_2 dV_1 + \mu_2 dN_1) \] (19)
Comparing the first of Eq. (26) with Eq. (28) we find the equilibrium conditions,

\[ T_1 = T_2; \quad P_1 = P_2; \quad \mu_1 = \mu_2 \]  

(20)

(ii) Starting with the Gibbs form of the entropy and using the expression for the Boltzmann weight in the grand canonical ensemble, show that the Grand potential \( \Phi_G = -PV = -k_B T \ln(\Xi) \), where \( \Xi \) is the grand canonical partition function.

**Solution.** Using the Boltzmann probability in the grand canonical ensemble \( p_i = \exp[-\beta(\epsilon_i - \mu N_i)]/\Xi \), we have,

\[ S = -k_B \sum_i p_i \left[ \frac{(\epsilon_i - \mu N_i)}{k_B T} - \ln(\Xi) \right] = \frac{U - \mu N}{T} + k_B \ln(\Xi) \quad \text{so} \quad U - TS - \mu N = -k_B T \ln(\Xi) \]  

(21)

The Grand Potential \( \Phi_G = U - TS - \mu N \), so the relation between the grand potential and the grand partition function is,

\[ \Phi_G = U - TS - \mu N = -k_B T \ln(\Xi). \]  

(22)

Now if we use the relation \( U = TS + PV + \mu N \), we find \( \Phi_G = -PV = -k_B T \ln(\Xi) \).

3. (14 points)

(i) (3 points) Derive the Maxwell relation,

\[ \left( \frac{\partial S}{\partial V} \right)_T = \left( \frac{\partial P}{\partial T} \right)_V \]  

(23)

**Solution**

The independent variables are \( T, V \) (assuming \( N \) is fixed and does not play a role in the analysis), so we use the Helmholtz energy,

\[ F = U - TS; \quad dF = dU - d(TS) = -SdT - PdV = \left( \frac{\partial F}{\partial T} \right)_V dT + \left( \frac{\partial F}{\partial V} \right)_T dV \]  

(24)

The Maxwell relation is then,

\[ \left( \frac{\partial^2 F}{\partial V \partial T} \right) = \left( \frac{\partial^2 F}{\partial T \partial V} \right); \quad \text{so} \quad \left( \frac{\partial S}{\partial V} \right)_T = \left( \frac{\partial P}{\partial T} \right)_V \]  

(25)

(ii) (3 points) Using Eq. (5) or otherwise, show that,

\[ \left( \frac{\partial U}{\partial V} \right)_T = -P + T \left( \frac{\partial S}{\partial V} \right)_T \]  

(26)

**Solution** Using Eq. (5), with \( A = U, x = V, z = T, y = S \)

\[ \left( \frac{\partial U}{\partial V} \right)_T = \left( \frac{\partial U}{\partial V} \right)_S + \left( \frac{\partial U}{\partial S} \right)_V \left( \frac{\partial S}{\partial V} \right)_T = -P + T \left( \frac{\partial S}{\partial V} \right)_T \]  

(27)

This result can also be found by taking the fundamental thermodynamic relation,

\[ dU = TdS - PdV; \quad \text{divide by} \ dV; \quad \frac{dU}{dV} = \frac{TdS}{dV} - P \rightarrow \left( \frac{\partial U}{\partial V} \right)_T = T \left( \frac{\partial S}{\partial V} \right)_T - P \]  

(28)

(iii) (4 points) From EM theory we have the result that in a cavity the radiation pressure is one third the energy density, \( P = U/3V = u/3 \), where \( u = U/V \) is the energy density. Using (i) and (ii) show that,

\[ u = \frac{1}{3} \left[ T \frac{du}{dT} - u \right]. \]  

(29)

where \( u \) is independent of \( V \).

**Solution** Using the fact that \( U = uV \), with \( u \) independent of the volume, and the Maxwell relation (i) in (ii) yields,

\[ u = -P + T \left( \frac{\partial P}{\partial T} \right)_V \]  

(30)
using \( P = u/3 \) in this equation yields Eq. (29)

(iii) (4 points) Solve this equation to obtain Stefan’s law relating \( u \) and \( T \) for EM waves in a cavity.

**Solution.** This equation reduces to,

\[
4 \frac{dT}{T} = \frac{du}{u} \quad \text{which gives} \quad 4\ln(T) = \ln(u) + c
\]

so that \( u = AT^4 \), which is Stefan’s law and \( A \) is an integration constant.