Chemistry 223A
Homework assignment # 4
Reading: Callen Chapter 7

A few problems to review our study of Maxwell relations, the connection between second derivatives of the thermodynamic potentials. You will also get to consider heat engines. Each problem is still worth ten points.

1. A photon Carnot engine

A photon gas is Carnot cycle is shown in the figure below. The aim of this problem is to obtain the black-body radiation relation

\[ U(T, V) \propto VT^4 \]  \hspace{1cm} (1)

starting from the equation of state by performing an infinitesimal Carnot cycle on the photon gas.

(a) Find the work done \( W \) in the above cycle in terms of \( dV \) and \( dp \).

(b) Find the heat absorbed \( Q \) in expanding the gas along an isotherm in terms of \( p, dV \), and the derivative of \( U(T, V) \).

(c) Using the efficiency of the Carnot cycle, relate \( W \) and \( Q \) to \( T \) and \( dT \).

(d) Observations indicate that the pressure of a photon gas is \( p = AT^4 \), where \( A \) is a constant. Assume that \( U(T = 0, V) = 0 \) and use this information to obtain \( U(T, V) \).
2. A hard core gas

A gas of particles with an excluded volume interaction (i.e. hard cores) obeys the equation of state

\[ p(V - Nb) = Nk_B T \]  \hspace{1cm} (2)

and has a heat capacity \( C_V \) that is independent of temperature. You may assume that the number of particles \( N \) is fixed throughout this problem.

(a) Find the Maxwell relation involving \( \frac{\partial S}{\partial V} \bigg|_{T,N} \)

(b) By calculating \( dU(T, V) \) show that \( U \) is a function of \( T \) and \( N \) alone.

(c) Show that \( \gamma = \frac{C_P}{C_V} = 1 + Nk_B/C_V \) and is thus independent of \( T \) and \( V \).

(d) By writing \( U = U(p, V) \) or otherwise show that an adiabatic change satisfies the relation

\[ p(V - Nb)\gamma = \text{const.} \]  \hspace{1cm} (3)

3. The Joule-Thompson Process: Callen 6.3-2 and 6.3-3

4. Practice with thermodynamic derivatives: Callen 7.2-2 and 7.2-3

5. Crushing more derivatives! Callen 7.3-3 and 7.3-4

6. Thinking about experiments in terms of derivatives: Callen 7.4-1