Statistical and Thermal Physics: Homework 12
Due: 3 March 2020

1 Gibbs free energy and thermodynamic derivatives
a) Starting with $G = E - TS + PV$, express $dG$ in terms of $dT$ and $dP$ and use the result to express $S$ and $V$ in terms of derivatives of $G$ (remember to indicate variables in the parentheses subscripts).
b) Use the second derivative rule to show that
\[
\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P.
\]

2 Enthalpy and thermodynamic variables
a) Express $dH$ in terms of $dP, dS$ and $dN$ and use the result to express $T, V, \mu$ in terms of relevant derivatives of $H$ (remember to indicate variables in the parenthesis subscript).
b) Show that
\[
\left(\frac{\partial T}{\partial P}\right)_{S,N} = \left(\frac{\partial V}{\partial S}\right)_{P,N}
\]
for any system.

3 Enthalpy for an ideal gas
The enthalpy of a system is
\[
H = E + PV.
\]
a) Show that
\[
\left(\frac{\partial H}{\partial P}\right)_T = T\left(\frac{\partial S}{\partial P}\right)_T + V.
\]
b) Use the previous result plus one of the Maxwell relations to show that for an ideal gas
\[
\left(\frac{\partial H}{\partial P}\right)_T = 0.
\]

4 Energy of a van der Waals gas
In general
\[
\left(\frac{\partial E}{\partial T}\right)_V = c_V
\]
and
\[
\left(\frac{\partial E}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V - P.
\]
a) Show that
\[
\left( \frac{\partial c_V}{\partial V} \right)_T = T \frac{\partial^2 P}{\partial T^2}.
\]

b) Starting with the equation of state for a van der Waals gas, show that
\[
\left( \frac{\partial E}{\partial V} \right)_T = \frac{N^2}{V^2} a
\]
and also that
\[
\left( \frac{\partial c_V}{\partial V} \right)_T = 0.
\]

c) Suppose that \( c_V \) is independent of temperature for a van der Waals gas. Use the previous results to determine an expression for the energy of the gas \( E = E(V, T) \) in terms of \( c_V, N, V \) and \( a \).

5 Heat capacities for water

Consider water at standard temperature and pressure (298 K and 1.01 \( \times \) 10^5 Pa). The heat capacity at constant pressure per mole is \( c_P = 73 \text{ J/mol K} \). The (volume) thermal expansion coefficient is \( 207 \times 10^{-6} \text{ K}^{-1} \) and the isothermal compressibility is \( 3.57 \times 10^{-10} \text{ Pa}^{-1} \). Determine the heat capacity at constant volume, \( c_V \), per mole under these conditions. Does it differ by much from \( c_P \)?