Solution to Homework 2
MAE 216: Statistical Thermodynamics
University of California, Davis, Winter Quarter 2014

1 Ideal Gas and Maxwell’s Relations (10 points)

1.a Starting from \( dU = T \, dS - P \, dV \), show that the equation of state \( PV = mRT \) in fact implies that \( U \) can only depend on \( T \).

In general, \( U(T, V, P) \). However, due to the equation of state \( PV = mRT \), only two of the three variables \( T, V \) and \( P \) are independent. Without loss of generality, we choose \( U(T, V) = U(T, V, \frac{mRT}{V}) \). All other thermodynamic functions thus also depend on \( T \) and \( V \) alone, e.g., \( S(T, V) \).

We now calculate the total derivative of \( S(T, V) \)

\[
dS = \frac{\partial S}{\partial T} \bigg|_V dT + \frac{\partial S}{\partial V} \bigg|_T dV
\]

which we then use to calculate the total derivative of \( U(T, V) \)

\[
dU = T \, dS - P \, dV = T \, \frac{\partial S}{\partial T} \bigg|_V dT + T \, \frac{\partial S}{\partial V} \bigg|_T dV - P \, dV = T \, \frac{\partial S}{\partial T} \bigg|_V dT + \left( T \, \frac{\partial S}{\partial V} \bigg|_T - P \right) dV . \tag{2}
\]

By equating the cross derivatives of the Helmholtz free energy \( F(T, V) = U(T, V) - TS(T, V) \), we obtain one of Maxwell’s relations (see lecture notes)

\[
\frac{\partial P}{\partial T} \bigg|_V = \frac{\partial S}{\partial V} \bigg|_T \tag{3}
\]

which can may be used in equation (2)

\[
dU = T \, \frac{\partial S}{\partial T} \bigg|_V dT + \left( T \, \frac{\partial P}{\partial T} \bigg|_V - P \right) dV . \tag{4}
\]

From the equation of state, we have

\[
P = \frac{mRT}{V} \quad \Rightarrow \quad T \frac{\partial P}{\partial T} \bigg|_V = \frac{mR}{V} = P \tag{5}
\]

which gives

\[
dU = T \, \frac{\partial S}{\partial T} \bigg|_V dT + (P - P) \, dV \quad \Rightarrow \quad dU = T \, \frac{\partial S}{\partial T} \bigg|_V dT . \tag{6}
\]

Hence, \( U \) can only depend on \( T \).
1. b Now consider a Carnot Cycle using an ideal gas as the working substance with internal energy $U = \frac{3}{2}Nk_BT$ (where $k$ is a constant). Using the fact that $dU = \delta Q - P \, dV$, show that the adiabatic portions of the cycle must obey the relation $PV^\gamma = \text{constant}$ and solve for the value of $\gamma$.

By definition of an adiabatic process, $\delta Q = 0$ and thus $dU = -P \, dV$. Using the equation of state $PV = mRT = Nk_BT$, the internal energy becomes $U = \frac{3}{2}PV$. Considering $U(P,V)$ as a function of $P$ and $V$ alone, its total derivative gives

$$dU = \left( \frac{\partial}{\partial V} \frac{3}{2}PV \right)_{P} \, dV + \left( \frac{\partial}{\partial P} \frac{3}{2}PV \right)_{V} \, dP = \frac{3}{2}(P \, dV + V \, dP) \ .$$ (7)

Equating to $dU = -P \, dV$, we obtain

$$\frac{3}{2}(P \, dV + V \, dP) = -P \, dV \Rightarrow \frac{dP}{P} = -\frac{5}{3} \frac{dV}{V} \ .$$ (8)

Integrating both sides from state $(P_0, V_0)$ to state $(P_1, V_1)$, we obtain

$$\int_{P_0}^{P_1} \frac{dP}{P} = -\frac{5}{3} \int_{V_0}^{V_1} \frac{dV}{V} \Rightarrow \ln P_1 - \ln P_0 = \frac{5}{3} (\ln V_0 - \ln V_1) \Rightarrow \ln \frac{P_1}{P_0} = \ln \left( \frac{V_0}{V_1} \right)^{5/3} \ .$$ (9)

Exponentiating both sides and rearranging the terms gives

$$P_0 V_0^{5/3} = P_1 V_1^{5/3} \ ,$$ (10)

which implies that $PV^\gamma$ with $\gamma = 5/3$ is constant during the adiabatic process.

2 Hard core gas (5 points)

A first correction for the ideal gas behaviour is to account for the fact that each gas molecule has some volume, which we denote here by $b$. To correct for the excluded volume introduced by each particle, we arrive at the modified equation of state, $P(V - Nb) = mRT$.

*Using a similar approach to problem 1 above, show that the heat capacity at constant volume, $C_V$, can only be a function of $T$. *

As in problem 1.a, we can express $U$ as a function of $T$ and $V$ alone (this time $U(T,V) = U(T,V,\frac{mRT}{V-Nb})$) and equations (1)–(4) can be obtained in the same way. Equation 5 becomes

$$P = \frac{mRT}{V-Nb} \Rightarrow T \frac{\partial P}{\partial T} \bigg|_V = T \frac{mR}{V-Nb} = P$$ (11)

which leaves equation (6) unaffected. Hence, once again, $U$ is a function of $T$ alone. As a consequence,

$$C_V = \frac{\partial U}{\partial T} \bigg|_V = \frac{dU}{dT}$$ (12)

is also a function of $T$ alone.