Problem #1

Review the Jacobi identities from homework #1; we’ll be using them! Remember, the Jacobians are determinants of derivatives, so the properties of determinants in the math notes can be used for proofs. Prove the following additional property:
\[ \frac{\partial (x,y,z,\ldots)}{\partial (u,v,w,\ldots)} = 1 / \frac{\partial (u,v,w,\ldots)}{\partial (x,y,z,\ldots)} \]. This is the correct way to transform variables and then calculate the “inverse” derivatives. IF YOU USE properties of determinants in your proof, at least illustrate the truth of that/those properties with an example 2x2 matrix (you can put in numbers for matrix elements to illustrate, but not ‘trivial’ ones like the identity matrix, please!)

Solutions

For simplicity, look at the case of the 2x2 Jacobian
\[
\begin{align*}
\frac{\partial (x,y)}{\partial (u,v)} &= \begin{vmatrix} \frac{\partial x}{\partial u} & \frac{\partial x}{\partial v} \\ \frac{\partial y}{\partial u} & \frac{\partial y}{\partial v} \end{vmatrix} \\
\frac{\partial (u,v)}{\partial (x,y)} &= \begin{vmatrix} \frac{\partial u}{\partial x} & \frac{\partial u}{\partial y} \\ \frac{\partial v}{\partial x} & \frac{\partial v}{\partial y} \end{vmatrix}
\end{align*}
\]

Recall HWK1-Q1

\[
\begin{vmatrix} \frac{\partial (x,y)}{\partial (u,v)} & \frac{\partial (x,y)}{\partial (u,v)} \\ \frac{\partial (u,v)}{\partial (x,y)} & \frac{\partial (u,v)}{\partial (x,y)} \end{vmatrix} = \begin{vmatrix} \frac{\partial x}{\partial u} & \frac{\partial x}{\partial v} \\ \frac{\partial y}{\partial u} & \frac{\partial y}{\partial v} \end{vmatrix} \begin{vmatrix} \frac{\partial u}{\partial x} & \frac{\partial u}{\partial y} \\ \frac{\partial v}{\partial x} & \frac{\partial v}{\partial y} \end{vmatrix} = \begin{vmatrix} 1 & 0 \\ 0 & 1 \end{vmatrix} = \det(I)
\]

\[
\frac{\partial (x,y)}{\partial (u,v)} = \frac{1}{\frac{\partial (u,v)}{\partial (x,y)}} \quad \text{and so on for higher order determinants.}
\]

Problem #2

A gas expands quasi-statically in a molecular beam, so dq = TdS = 0 and n = const. Using Jacobi determinants and Maxwell relations, transform the appropriate derivative of
temperature with respect to pressure to show that $dT = \alpha VT/(nC_p)\ dP$. Compute the
coefficient for a monatomic ideal gas, and integrate the result to obtain $T/T_0$ as a function
of $P/P_0$.

**Solutions**

$$dT = \left(\frac{\partial T}{\partial P}\right)_S dP$$

$$\left(\frac{\partial T}{\partial P}\right)_S = \frac{\partial(T,S)}{\partial(P,S)} \cdot \frac{\partial(P,T)}{\partial(P,S)} = -\frac{\partial(S,T)}{\partial(P,T)} \cdot \frac{1}{\partial(T,P)} = -\left(\frac{\partial S}{\partial P}\right)_T$$

$$\left(\frac{\partial V}{\partial T}\right)_P = \frac{\alpha V}{nc_P} \Rightarrow dT = \frac{\alpha VT}{nc_P} dP$$

For ideal monatomic gas,

$$\alpha = \frac{1}{T} = \frac{nR}{PV}, C_p = C_v + R = \frac{5}{2}R \Rightarrow \frac{dT}{T} = \frac{2}{5} \frac{dP}{P} \text{ or } \left(\frac{T}{T_0}\right) = \left(\frac{P}{P_0}\right)^2$$

**Problem #3**

We’ll do phase transitions in lecture instead of heat engines. However, look at the
summary sheet and the chapter on thermodynamic processes, and think about the idea of
how much energy can be extracted as $SdT$ (heat flow), and how much energy can be
extracted from all the other terms ($-PdV+mdN+$... = work flow).

Using the reversible work theorem on the summary sheet, proving that the best possible
efficiency $E$ of a refrigerator is given by the relation. [Hint: see chapter on thermo
processes for answer!]

$$\frac{\partial q}{\partial w} = E = \frac{T_{sys}}{T_{hs} - T_{sys}}$$

The hatches through $dq$ and $dw$ are reminders used in many books that these are energy
flows, not differentials of state functions. The efficiency $E$ is defined as the ratio of the
heat pumped from cooler refrigerator (the system ‘sys’) to hotter room (the heat sink
‘hs’), divided by the work required to do so. Note that the efficiency goes to 0 if you try
to cool things to 0K, and it approaches $\infty$ only if your refrigerator is no cooler than your
room!
Solutions

From notes chapter 5

\[ dS = dS_{sys} + dS_{hs} = \frac{dQ_{sys}}{T_{sys}} - \frac{dQ_{hs}}{T_{hs}} = 0 \]

\[ W = dQ_{sys} - dQ_{hs} = dQ_{sys} \left( 1 - \frac{T_{sys}}{T_{hs}} \right) = dQ_{sys} \left( \frac{T_{hs} - T_{sys}}{T_{hs}} \right) \]

The engine efficiency

\[ \frac{dQ_{sys}}{W} = \left( \frac{T_{hs}}{T_{hs} - T_{sys}} \right) \]

Problem #4

In class, we showed that \( 0 < C_V < C_p \), but we made use of the canonical partition function from statistical mechanics to prove the first part. Now prove \( C_V > 0 \) using thermodynamic relations only. Start by proving that \( \partial^2 U / \partial S^2 = (\partial T / \partial S)V > 0 \). Then use that to prove in one simple step that \( C_V > 0 \) because \( T > 0 \). [Tip: feel free to consult the stat mech lecture notes, chapter 7, but make sure you explain every step in your own solution.]

Solutions

Note from the lecture, the eigenvalues of the second derivative matrix of the internal energy are

\[ \lambda = \frac{U_{ss} + U_{vv}}{2} \pm \frac{1}{2} \sqrt{(U_{ss} - U_{vv})^2 + 4U_{sv}^2} \]

If \( U_{ss} < 0 \), then

\[ \Rightarrow (U_{ss} + U_{vv})^2 < (U_{ss} - U_{vv})^2 + 4U_{sv}^2 \] and \( \lambda < 0 \)

However, if even just one eigenvalue is less then zero, we cannot be at a minimum in energy and thus not in equilibrium. Therefore, \( U_{ss} \) must be greater than zero. Then,

\[ U_{ss} = \left( \frac{\partial T}{\partial S} \right)_V = \frac{T}{nC_V} > 0 \]

\( T > 0, n > 0 \Rightarrow C_V > 0 \)

Problem #5
Instead of Legendre transforming $U = U(S,V,n)$ to $U[S]=A(T,V,n)$, start with $S(U,V,n)$, and go through an analogous derivation to derive $S[U]=f(T,V,n)$ and its differential $dS[U]$? Legendre transforms of the entropy are important in statistical mechanics and are called Massieu functions. $S[U]=f(T,V,n)$ is the entropy analog of the Helmholtz free energy $A(T,V,n)$.

**Solutions**

$$S = \frac{U}{T} + \frac{PV}{T} - \frac{\mu N}{T} \quad \therefore S[U] = S - \left( \frac{\partial S}{\partial U} \right)_{V,n} U = \frac{PV}{T} - \frac{\mu N}{T}$$

$$dS[U] = \frac{PdV}{T} - \frac{\mu dN}{T} - P\frac{V-\mu N}{T^2}dT$$

**Problem #6**

A binary mixture (e.g. benzene and cyclohexane) has a free energy given by

$$G(T,P,n_1,n_2) = n_1 f_1(T,P) + n_2 f_2(T,P) + n_1RT\ln \chi_1 + n_2RT\ln \chi_2 + wnR\chi_1\chi_2$$

Show that above the temperature $T_c=w/2$, phase separation no longer occurs because the stability criterion $d^2G$ has only one minimum as a function of $\chi_1$, whereas below that critical temperature, there are two local minima. (Hint: $\chi_1 = 1-\chi_2$, so there is only one independent variable to consider.)

**Solutions**

$$\left( \frac{\partial^2 G}{\partial N^2_2} \right)_T = \left( \frac{\partial^2 g}{\partial N^2_2} \right)_T = 0$$

Let $g = G/n$. Stability requires that separation first occurs.

$$\frac{\partial^2 g}{\partial N_1^2} = \frac{\partial}{\partial N} \left( \frac{\partial g}{\partial \chi_1} \frac{\partial \chi_1}{\partial N} \right) = \frac{\partial^2 g}{\partial \chi_1^2} \frac{\partial \chi_1}{\partial N} + \frac{\partial g}{\partial \chi_1} \frac{\partial^2 \chi_1}{\partial N^2}$$

$$\frac{\partial g}{\partial \chi_1} = 0 \quad \therefore \quad \left( \frac{\partial^2 g}{\partial N^2} \right)_T = 0 \Rightarrow \left( \frac{\partial^2 g}{\partial \chi_1^2} \right)_T = 0$$

but we already know that $\frac{\partial g}{\partial \chi_1} = 0$ at the critical point,

$$\frac{\partial^2 g}{\partial \chi_1^2} = RT \left( \frac{1}{\chi_1} + \frac{1}{\chi_2} \right) - 2Rw = 0 \Rightarrow T = 2w \left( \frac{1}{\chi_1} + \frac{1}{\chi_2} \right)^{-1} = 2w \chi_1(1-\chi_1)$$
This function describes the set of all possible temperatures at the onset of unmixing. The maximum of this function therefore yields the highest value of \( T \) at which separation can occur at all.

\[
\frac{dT}{d\chi_1} = 1 - 2\chi_1 = 0 \Rightarrow \chi_1 = \chi_2 = \frac{1}{2} \Rightarrow T = 2w\left(\frac{1}{2}\right)^2 = \frac{w}{2}
\]

Above this point in \( T \), \( G \) has no quadratic local minimum (it still has a fourth order one).

In addition, rearranging the equation above relating \( T \) and \( \chi_1 \),

\[
2w\chi_1^2 - 2w\chi_1 + T = 0 \Rightarrow \chi_1 = \frac{1}{2} \pm \frac{1}{2w}\sqrt{w^2 - 2wT}
\]

\( T > w/2 \Rightarrow \) no real roots (one phase)

\( T = w/2 \Rightarrow \) one real root (critical point)

\( T < w/2 \Rightarrow \) two real roots (two phases)

Another possible solution

Rewrite \( G \) in terms of \( \chi_1 \).

\[
G(T,P,\chi_1,\chi_2) = n\chi_1 f_1(T,P) + n\chi_2 f_2(T,P) + n\chi_1 RT \ln \chi_1 + n\chi_2 RT \ln \chi_2 + wn\chi_1\chi_2
\]

\[
= n\chi_1 f_1(T,P) + n(1 - \chi_1) f_2(T,P) + n\chi_1 RT \ln \chi_1 + n(1 - \chi_1) RT \ln(1 - \chi_1) + wn\chi_1(1 - \chi_1)
\]

A local minimum in \( G-\chi_1 \) curve has to satisfy

\[
\frac{\partial G}{\partial \chi_1} = 0 \quad \text{---- (1)}
\]

\[
\left( \frac{\partial^2 G}{\partial \chi_1^2} \right) > 0 \quad \text{----(2)}
\]
For the sake of convenience, use G/n instead of G

\[
\frac{\partial^2 (G/n)}{\partial \chi_i^2} = RT \left( \frac{1}{\chi_1} + \frac{1}{\chi_2} \right) - 2Rw > 0
\]

Therefore

\[ T > 2w\chi_1(1 - \chi_1) \]

The right side function is constrained to maximize at w/2. If T exceeds w/2, then \[ \frac{\partial^2 (G/n)}{\partial \chi_i^2} > 0 \] will always be satisfied for any solution of \[ \frac{\partial G}{\partial \chi_i} = 0 \]

There will be no maximum that can separate minima along the G-\chi 1 curve, therefore no phase separation. On the other hand, if T<w/2, possible solutions of (1) can satisfy \[ \frac{\partial^2 G}{\partial \chi_i^2} < 0 \]
to create local maximum that separate the minima.

**Problem #7**

Consider two substances (e.g. A=methanol and B=water) whose vapor and liquid are in equilibrium (a distillation).

a. According to Gibb’s rule, how many degrees of freedom f does the coexistence region have? Is it a line, like the P(T) for one substance and two phases?

b. The coexistence region at pressure P=1 atm is shown in gray as a function of T and mole fraction of A.

For example, if you start at ‘start’ and heat up, you have all liquid at first, then liquid and vapor coexist over a temperature range in the gray zone, then only vapor exists if you raise T even higher. For our case, the upper and lower bounding curves are \[ T = T_B - (T_B - T_A)c_A^2 \] and \[ T = T_B - (T_B - T_A)c_A(2 - c_A) \], where \( T_B \) is the boiling point of B, \( T_A \) is the boiling point of A, and \( T_B > T_A \).

Show that in a distillation of 50:50 liquid A and B by mole fraction, the composition of the vapor initially is \( c_A = (3/4)^{1/2} \). Is the vapor enriched or depleted in A compared to the liquid?

c. If the pressure were raised to 2 atmospheres, how would the coexistence region shift? Sketch both the ‘old’ 1 atm and the ‘new’ 2 atm coexistence regions on the same T,c_A diagram.
Solutions

(a) Gibbs’ phase rule: \( f = C - P + 2 = 2 - 2 + 2 = 2 \). It is not a line but a 2D region.

(b) Find the temperature at which \( \chi_A = 0.5 \) intersects the lower curve.

\[
T = T_0 - (T_0 - T_1) \cdot \frac{1}{2} \cdot \frac{3}{2} = \frac{1}{4} T_0 + \frac{3}{4} T_1
\]

If you continue to heat gently (as you would in a distillation), this is also the temperature at which both gases will be pulled off (corresponding to a horizontal movement on the graph), so now find the value of \( \chi_A \) when component B boils at this same temperature.

\[
T = \frac{1}{4} T_0 + \frac{3}{4} T_1 = T_0 - (T_0 - T_1) \chi_A^2 \Rightarrow \chi_A = \left( \frac{3(T_1 - T_0)}{4(T_1 - T_0)} \right)^{\frac{1}{2}} = \frac{\sqrt{3}}{2}
\]

Because \( \sqrt{3}/2 = 0.86 > 0.5 \), component A is enriched in the vapor phase.

(c) The boiling point of A and B will increase at elevated pressure. The coexistence region will shift up. We will draw them at different planes along the pressure axis (P).