EP 2827: Thermodynamics

Homework Set 4*

March 13, 2019

1. Show that the following Pfaffian form (of *three* variables x, y, z) does not admit an integrating factor:

$$đF = x\,dy + k\,dz$$

where k is a constant. (Hint: Refer to the note on exact and inexact differentials posted on the website)

3 points

Solution

The condition for integrability of a differential form,

$$đF = \sum_{i=1}^{n} Y_i\,dx_i$$

is,

$$Y_i\left(\frac{\partial Y_j}{\partial x_k} - \frac{\partial Y_k}{\partial x_j}\right) + Y_j\left(\frac{\partial Y_k}{\partial x_i} - \frac{\partial Y_i}{\partial x_k}\right) + Y_k\left(\frac{\partial Y_i}{\partial x_j} - \frac{\partial Y_j}{\partial x_i}\right) = 0 \forall i \neq j \neq k. \tag{1}$$

In the case at hand, $n = 3$, $x_1 = x$, $x_2 = y$ and $x_3 = z$ and,

$$Y_1 = 0,\ Y_2 = x,\ Y_3 = k.$$

For $i = 1, j = 2, k = 3$, we evaluate the quantity in the lhs of the integrability equation,

$$\begin{aligned} &Y_1\left(\frac{\partial Y_2}{\partial x_3} - \frac{\partial Y_3}{\partial x_2}\right) + Y_2\left(\frac{\partial Y_3}{\partial x_1} - \frac{\partial Y_1}{\partial x_3}\right) + Y_3\left(\frac{\partial Y_1}{\partial x_2} - \frac{\partial Y_2}{\partial x_1}\right) \\ &\quad = 0\left(\frac{\partial x}{\partial z} - \frac{\partial k}{\partial y}\right) + x\left(\frac{\partial k}{\partial x} - \frac{\partial (0)}{\partial z}\right) + k\left(\frac{\partial (0)}{\partial y} - \frac{\partial x}{\partial x}\right) = -k \neq 0. \end{aligned}$$

Thus the integrability condition is not satisfied and the given Pfaffian does not admit an integrating factor.

*Due in class on Friday March 8th, 2019

2.

Starting from the principle of increase of entropy of the universe, show that during an isothermal process i.e. one in which a system remains in contact with a single reservoir at temperature say T throughout , the work done by the system is,

$$W_T \leq -\Delta F,$$

where $\Delta F \equiv F_{final} - F_{initial}$ is the change in Helmholtz potential; the equality holds when the process is reversible. In addition if the process is occurring at constant external pressure, say P, the non-expansion work or *non-PdV* work performed by the system satisfies,

$$\overline{W}_{T,P} \leq -\Delta G,$$

where $\Delta G \equiv G_{final} - G_{initial}$, is the change in the Gibbs potential; the equality holding when the process is reversible. These inequalities justify the nomenclature of the thermodynamic potentials F, G is "*free energy*", i.e. the part of the internal energy which can be made free/available by a system to be converted into mechanical energy (work) i.e. the amount of work that can be extracted from the system.

$(2 + 2 = 4$ points)

Solution: The principle of increase of entropy of the universe i.e. the combined entropy of the system, call it S and the entropy of surroundings, call it $S_{surroundings}$

$$\Delta S + \Delta S_{surroundings} \geq 0$$

Now during an isothermal process i.e. one in which a system remains in contact with a single reservoir at temperature say T throughout, the surroundings/reservoir undergoes a reversible isothermal process in which let's say it dumps some amount of heat, Q into the system. Then,

$$\Delta S_{surroundings} = -\frac{Q}{T}$$

Thus we have,

$$\Delta S - \frac{Q}{T} \geq 0,$$

or,

$$T\Delta S - Q \geq 0.$$

Then using the first law we can write, $Q = \Delta U + W_T$, where W_T is the work done ***by the system isothermally*** and thus we get,

$$T\Delta S - \Delta U - W_T \geq 0,$$

or,

$$\begin{aligned} W_T &\leq T\Delta S - \Delta U \\ &\leq \Delta(TS - U) \\ &\leq -\Delta F. \end{aligned} \tag{2}$$

where in going from the first and second step we used the constancy of T to write, $T\Delta S = \Delta(TS)$, and in going from the second to third we have used the definition of the Helmholtz potential, $F \equiv U - TS$. Hence the first part of the problem is proved.

For the next part we divide the work into two parts, namely the expansion work or "PdV" work done by the system and the non-expansion work done by the system, lets say chemical or electrical or magnetic work, $\overline{W}_T$ (also done isothermally). Thus,

$$W_T = \int PdV + \overline{W}_T.$$

Substituting this in the LHS of (2) and then simplifying, we obtain

$$\overline{W}_T \leq -\Delta F - \int P dV$$

Now if the pressure remains constant, one can write, $\int PdV = P\int dV = P\Delta V = \Delta(PV)$. Thus for constant pressure (and constant temperature) processes, one has,

$$\begin{aligned}\overline{W}_T &\leq -\Delta F - \Delta(PV)\\ &\leq -\Delta(F+PV)\\ &\leq -\Delta G.\end{aligned}$$

Here in going from the second to the third step we have used the definition of the Gibbs function, $G = U - TS + PV = F + PV$. Thus we have established that the maximal amount of ***non-expansion*** work that can be extracted out of the system under isothermal and isobaric conditions is equal to the change in the Gibbs function of the system.

3.

Taking P and V as independent variables, derive a third "TdS" equation, namely,

$$TdS = \frac{C_V\kappa}{\beta}dP + \frac{C_P}{\beta V}dV.$$

(4 points)

Solution

Taking P and V as independent variables, i.e. $S = S(P,V)$, the differential of entropy

$$dS = \left(\frac{\partial S}{\partial P}\right)_V dP + \left(\frac{\partial S}{\partial V}\right)_P dV$$

and multiplying both sides by T,

$$TdS = T\left(\frac{\partial S}{\partial P}\right)_V dP + T\left(\frac{\partial S}{\partial V}\right)_P dV. \tag{3}$$

Temporarily we revert to S as a function of V,T and we have,

$$\frac{\partial S}{\partial P} = \frac{\partial S}{\partial V}\frac{\partial V}{\partial P} + \frac{\partial S}{\partial T}\frac{\partial T}{\partial P}$$

so at constant volume,

$$\left(\frac{\partial S}{\partial P}\right)_V = \left(\frac{\partial S}{\partial T}\right)_V \left(\frac{\partial T}{\partial P}\right)_V$$

and similarly reverting temporarily to S being a function of P,T we obtain,

$$\left(\frac{\partial S}{\partial V}\right)_P = \left(\frac{\partial S}{\partial T}\right)_P \left(\frac{\partial T}{\partial V}\right)_P.$$

Substituting these back in the intermediate form of the third "TdS" equation, we get,

$$TdS = T\left(\frac{\partial S}{\partial T}\right)_V \left(\frac{\partial T}{\partial P}\right)_V dP + T\left(\frac{\partial S}{\partial T}\right)_P \left(\frac{\partial T}{\partial V}\right)_P dV.$$

Next we substitute the following,

$$T\left(\frac{\partial S}{\partial T}\right)_V = \left(\frac{TdS}{dT}\right)_V = C_V,$$

$$T\left(\frac{\partial S}{\partial T}\right)_P = \left(\frac{TdS}{dT}\right)_P = C_P,$$

$$\left(\frac{\partial T}{\partial P}\right)_V = \frac{-1}{\left(\frac{\partial P}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P} = \frac{-\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T}{\frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P} = \frac{\kappa}{\beta},$$

$$\left(\frac{\partial T}{\partial V}\right)_P = \frac{\frac{1}{V}}{\frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P} = \frac{1}{\beta V},$$

and obtain the final form of the third "TdS" equation,

$$TdS = \frac{C_V \kappa}{\beta} dP + \frac{C_P}{\beta V} dV. \tag{4}$$

4.

From the two "TdS" equations covered in class, derive the "*heat capacity equations*",

$$C_P - C_V = \frac{T\beta^2 V}{\kappa}.$$

$$\frac{C_P}{C_V} = \frac{\kappa_T}{\kappa_S}.$$

where κ_T, κ_S are the isothermal and adiabatic (isentropic) compressibility respectively. From the first heat capacity equation, show that for water at $4°C$, $C_P = C_V$.

$(3 + 3 + 1 = 7$ points)

Solution

The first two TdS equations are,

$$TdS = C_V dT + T\left(\frac{\partial T}{\partial P}\right)_V dV$$

$$TdS = C_P dT - T\left(\frac{\partial V}{\partial T}\right)_P dP.$$

and subtracting the two equations we get,

$$C_P dT - T\left(\frac{\partial V}{\partial T}\right)_P dP = C_V dT + T\left(\frac{\partial T}{\partial P}\right)_V dV,$$

rearranging which we get,

$$C_P - C_V = T\left(\frac{\partial V}{\partial T}\right)_P \frac{dP}{dT} + T\left(\frac{\partial T}{\partial P}\right)_V \frac{dV}{dT}$$

Now for constant volume processes this equation turns into,

$$C_P - C_V = T\left(\frac{\partial V}{\partial T}\right)_P \left(\frac{\partial P}{\partial T}\right)_V. \tag{5}$$

Next, using the lemma,

$$\left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial T}{\partial V}\right)_P \left(\frac{\partial V}{\partial P}\right)_T = -1$$

we get,

$$\left(\frac{\partial P}{\partial T}\right)_V = \frac{\left(\frac{\partial V}{\partial T}\right)_P}{-\left(\frac{\partial V}{\partial P}\right)_T} = \frac{\frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P}{-\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T} = \frac{\beta}{\kappa}. \tag{6}$$

Substituting (6) in (5) we obtain,

$$C_P - C_V = T \underbrace{\left(\frac{\partial V}{\partial T}\right)_P}_{=\beta V} \left(\frac{\beta}{\kappa}\right) = \frac{T\beta^2 V}{\kappa}.$$

Next starting from the 3rd TdS equation (4), we have for an isentropic process

$$0 = \frac{C_V \kappa_T}{\beta} dP_S + \frac{C_P}{\beta V} dV_S,$$

where the subscript S denotes isentropic. Rearranging this we have,

$$\begin{aligned} \frac{C_P}{C_V} &= -\kappa_T V \frac{dP_S}{dV_S} \\ &= \frac{\kappa}{-\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_S} \\ &= \frac{\kappa}{\kappa_S}. \end{aligned}$$

For water at $4°C$, the density is maximum i.e. for a fixed amount/mass the volume has a minima as a function of temperature,

$$\left(\frac{\partial V}{\partial T}\right)_P = 0.$$

So inserting this in (5) we obtain

$$C_P - C_V = 0.$$

5.

Using the results from the preceding exercise, show that

$$\kappa_T - \kappa_S = \frac{T\beta^2 V}{C_P}$$

(3 points)

Solution:

The third "TdS" equation, for a (reversible) adiabatic process i.e. when $dS = 0$ becomes,

$$\frac{C_p}{\beta V} dP + \frac{C_V \kappa}{\beta} dV = 0,$$

rearranging which gives,

$$\frac{C_P}{C_V} = \frac{\kappa}{-\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_S} = \frac{\kappa}{\kappa_S}.$$

Thus,

$$\kappa_S = \frac{\kappa}{\gamma}.$$

Next we take the difference,

$$\begin{aligned} \kappa - \kappa_S &= \kappa\left(\frac{\gamma - 1}{\gamma}\right) \\ &= \kappa\frac{C_P - C_V}{C_P}. \end{aligned}$$

Using the *heat capacity equation*,

$$C_P - C_V = \frac{T\beta^2 V}{\kappa},$$

we get,

$$\kappa - \kappa_S = \frac{T\beta^2 V}{C_P}.$$

6.

A hydrostatic system has the properties that $\left(\frac{\partial U}{\partial V}\right)_T$ and $\left(\frac{\partial H}{\partial P}\right)_T = 0$. Show that the equation of state must be $T = A\,P\,V$ where A is some constant. (Hint: Use the internal energy and enthalpy equations). (5 points)

Solution:

Combining the first law with the first TdS equation, we have the so called *internal energy* equation

$$\begin{aligned} dU &= TdS - PdV \\ &= C_V dT + \left[T\left(\frac{\partial P}{\partial T}\right)_V - P\right] dV. \end{aligned}$$

This implies,

$$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V - P. \tag{7}$$

Similarly using the second law with the second TdS equation, we have an equation for enthalpy form,

$$\begin{aligned} dH &= TdS + VdP \\ &= C_P dT + \left[V - T\left(\frac{\partial V}{\partial T}\right)_P\right] dP. \end{aligned}$$

This implies,

$$\left(\frac{\partial H}{\partial P}\right)_T = V - T\left(\frac{\partial V}{\partial T}\right)_P. \tag{8}$$

In the present case, both $\left(\frac{\partial U}{\partial V}\right)_T = 0$ and $\left(\frac{\partial H}{\partial P}\right)_T = 0$ so we have,

$$\left(\frac{\partial P}{\partial T}\right)_V = \frac{P}{T}, \quad \left(\frac{\partial V}{\partial T}\right)_P = \frac{V}{T}$$

or,

$$\left(\frac{\partial T}{\partial P}\right)_V = \frac{T}{P} \quad \left(\frac{\partial T}{\partial V}\right)_P = \frac{T}{V}.$$

Taking T as a function of P, V, we can write,

$$\begin{aligned} dT &= \left(\frac{\partial T}{\partial P}\right)_V dP + \left(\frac{\partial T}{\partial V}\right)_P dV \\ &= \frac{T}{P} dP + \frac{T}{V} dV, \\ \implies \frac{dT}{T} &= \frac{dP}{P} + \frac{dV}{V} \\ \implies d \ln \left(\frac{T}{PV}\right) &= 0 \\ \implies T &= APV. \end{aligned}$$

A is a constant of integration.

7.

Recall the *Joule free expansion* experiment, where a gas was confined on one side of a partitioned cylinder while the other side was empty, and then the partition was suddenly removed/ broken so that the gas free streamed and filled out the entire cylinder. Using the energy and enthalpy equations, show that the *Joule coefficient*, $\eta \equiv \left(\frac{\partial T}{\partial V}\right)_U$ is given by,

$$\eta = -\frac{1}{C_V}\left(\frac{\beta T}{\kappa} - P\right).$$

Also recall the *Joule-Thomson throttling* experiment, where a gas was again confined on one side of a partitioned cylinder, but this time the partition was porous and the gas was pushed into the other side thru the porous partition (plug) with a different yet constant pressures on both sides of the partition. A measure of how the temperature drops as a result of this is given by the *Joule-Thomson coefficient*, $\mu \equiv \left(\frac{\partial T}{\partial P}\right)_H$. Show that,

$$\mu = \frac{V}{C_p}\left(\beta T - 1\right).$$

(4 + 4 = 8 points)

Solution:

One consider the state variables, U, V, T. Out of these only two are independent. Hence we have the equation,

$$\left(\frac{\partial T}{\partial V}\right)_U \left(\frac{\partial V}{\partial U}\right)_T \left(\frac{\partial U}{\partial T}\right)_V = -1$$

or,

$$\left(\frac{\partial T}{\partial V}\right)_U = -\frac{\left(\frac{\partial U}{\partial V}\right)_T}{\left(\frac{\partial U}{\partial T}\right)_V}$$

From the internal energy equation in the last problem,

$$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V - P, \quad \left(\frac{\partial U}{\partial T}\right)_V = C_V.$$

Using these,

$$\eta = \left(\frac{\partial T}{\partial V}\right)_U = -\frac{T\left(\frac{\partial P}{\partial T}\right)_V - P}{C_V} = -\frac{1}{C_V}\left(\frac{\beta T}{\kappa} - P\right),$$

where in going from the penultimate to the last step we substituted:

$$\left(\frac{\partial P}{\partial T}\right)_V = \frac{-1}{\left(\frac{\partial T}{\partial V}\right)_P \left(\frac{\partial V}{\partial P}\right)_T} = \frac{\frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P}{-\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T} = \frac{\beta}{\kappa}.$$

Similarly, to compute the Joule-Thomson coefficient we start with the identity involving (derivatives) of H, P, T,

$$\left(\frac{\partial T}{\partial P}\right)_H = \frac{-1}{\left(\frac{\partial P}{\partial H}\right)_T \left(\frac{\partial H}{\partial T}\right)_P} = -\frac{\left(\frac{\partial H}{\partial P}\right)_T}{\left(\frac{\partial H}{\partial T}\right)_P} = \frac{T\left(\frac{\partial V}{\partial T}\right)_P - V}{C_P} = \frac{V}{C_P}\left(T\beta - 1\right).$$

where in the final step we have used one of the so called "enthalpy equations" $\left(\frac{\partial H}{\partial P}\right)_T = V - T\left(\frac{\partial V}{\partial T}\right)_P$ from the last problem.

8.

Derive the relations,

$$\left(\frac{\partial C_V}{\partial V}\right)_T = T\left(\frac{\partial^2 P}{\partial T^2}\right)_V,$$

and,

$$\left(\frac{\partial C_P}{\partial P}\right)_T = -T\left(\frac{\partial^2 V}{\partial T^2}\right)_P.$$

$(3 + 3 = 6$ points)

Solution:

From the first TdS equation,

$$\left(\frac{\partial S}{\partial T}\right)_V = \frac{C_V}{T}, \left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$$

Since the derivatives in the mixed second derivative can be taken in any order,

$$\begin{aligned}
\left(\frac{\partial}{\partial V}\left(\frac{\partial S}{\partial T}\right)_V\right)_T &= \left(\frac{\partial}{\partial T}\left(\frac{\partial S}{\partial V}\right)_T\right)_V \\
\implies \left(\frac{\partial}{\partial V}\left(\frac{C_V}{T}\right)\right)_T &= \left(\frac{\partial}{\partial T}\left(\frac{\partial P}{\partial T}\right)_V\right)_V \\
\implies \left(\frac{\partial C_V}{\partial V}\right)_T &= T\left(\frac{\partial^2 P}{\partial T^2}\right)_V.
\end{aligned}$$

Similarly from the second TdS equation

$$\left(\frac{\partial S}{\partial T}\right)_P = \frac{C_P}{T}, \left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P.$$

Equating the (mixed) second derivatives in either order,

$$\begin{aligned}
\left(\frac{\partial}{\partial P}\left(\frac{\partial S}{\partial T}\right)_P\right)_T &= \left(\frac{\partial}{\partial T}\left(\frac{\partial S}{\partial P}\right)_T\right)_P \\
\implies \left(\frac{\partial}{\partial P}\left(\frac{C_P}{T}\right)\right)_T &= -\left(\frac{\partial}{\partial T}\left(\frac{\partial V}{\partial T}\right)_P\right)_V \\
\implies \left(\frac{\partial C_P}{\partial V}\right)_T &= -T\left(\frac{\partial^2 V}{\partial T^2}\right)_P .
\end{aligned}$$