Thermodynamics (MP460) Assignment 6

Please hand in your solutions no later than Thursday, November 14, 10:05 am. Late assignments will not be accepted. If you have questions about this assignment, please ask your lecturer, Joost Slingerland, (`joost-at-thphys-dot-nuim-dot-ie`), Office 1.7D, Mathematical Physics

Ex. 6.1

Ex. 6.1 is exercise 1 on page 75 of the book by Fermi.

Ex. 3.3 reprinted (no need to hand in)

In this exercise, you will derive a number of identities for derivatives which are very useful in thermodynamic calculations. Let A, B and C be three thermodynamic variables related by a single equation of state, so that we can choose two of the variables as the independent variables and then the other will be a function of the first two. For example, we can choose A and B to be independent and then $C = C(A, B)$ is a function of A and B, but we could also choose A and C or B and C as the independent variables. The canonical example would have A, B and C equal to the pressure, temperature and volume of a gas, but the equations below will work for any triple of quantities.

a. We take A and B as independent quantities. In some process, these are varied by infinitesimal amounts dA and dB. Write an equation for dC in terms of dA, dB and derivatives of $C(A, B)$.

b. Derive the following three identities

$$\begin{aligned}
\left(\frac{\partial C}{\partial A}\right)_B \left(\frac{\partial A}{\partial B}\right)_C + \left(\frac{\partial C}{\partial B}\right)_A &= 0 \\
\left(\frac{\partial A}{\partial B}\right)_C \left(\frac{\partial B}{\partial A}\right)_C &= 1 \\
\left(\frac{\partial A}{\partial B}\right)_C \left(\frac{\partial B}{\partial C}\right)_A \left(\frac{\partial C}{\partial A}\right)_B &= -1
\end{aligned}$$

Hint: *One way to do this is to use the result of part* ***a.*** *for the case of a process in which C is constant.*

Ex. 6.2: Entropy for a (p, V, T)-system

Consider a fluid with pressure p, volume V and temperature T. We will be interested in the entropy S of this fluid and its relation to the first and second law.

a. Write the first law of thermodynamics in differential form, for independent variables p and V. Show that

$$\begin{aligned}
\left(\frac{\partial S}{\partial p}\right)_V &= \frac{1}{T}\left(\frac{\partial U}{\partial p}\right)_V \\
\left(\frac{\partial S}{\partial V}\right)_p &= \frac{1}{T}\left(\frac{\partial U}{\partial V}\right)_p + \frac{p}{T}
\end{aligned}$$

b. Similarly, show that

$$\left(\frac{\partial S}{\partial p}\right)_T = \frac{1}{T}\left(\frac{\partial U}{\partial p}\right)_T + \frac{p}{T}\left(\frac{\partial V}{\partial p}\right)_T$$
$$\left(\frac{\partial S}{\partial T}\right)_p = \frac{1}{T}\left(\frac{\partial U}{\partial T}\right)_p + \frac{p}{T}\left(\frac{\partial V}{\partial T}\right)_p$$

c. Now derive the following identities,

$$\left(\frac{\partial U}{\partial p}\right)_T = -p\left(\frac{\partial V}{\partial p}\right)_T - T\left(\frac{\partial V}{\partial T}\right)_p$$
$$\left(\frac{\partial T}{\partial V}\right)_p\left(\frac{\partial U}{\partial p}\right)_V = \left(\frac{\partial T}{\partial p}\right)_V\left(\frac{\partial U}{\partial V}\right)_p + p\left(\frac{\partial T}{\partial p}\right)_V - T.$$

d. Show that

$$\left(\frac{\partial U}{\partial p}\right)_T = \left(\frac{\partial U}{\partial p}\right)_V + \left(\frac{\partial U}{\partial V}\right)_p\left(\frac{\partial V}{\partial p}\right)_T$$

e. Using the identities in part **d.** and in **Ex. 3.3**, show that the two equations in part **c.** above are equivalent.