Statistical Mechanics (MP461) Assignment 2

Please hand in your solutions no later than Monday, November 3, 15:05 pm.
If you have questions about this assignment, please ask your lecturer,
Joost Slingerland, (`joost-at-thphys-dot-nuim-dot-ie`), Office 1.7D, Theoretical Physics

Please hand in Ex. 2.2 below and Ex. 3.25 from Schroeder's book.
Other recommended exercises from the book (not for handing in) are 3.33 and 3.34.
Ex. 2.1 below asks for derivations of some important identities used in Ex. 2.2. The identities are given in part **b**. A solution is overleaf, so you don't have to hand this in.

Ex. 2.1 Identities for partial derivatives

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. 2.2: 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

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

c. Now derive the following identities,

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

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. 2.1**, show that the two equations in part **c.** above are equivalent.

Answers to Ex. 2.1

Please note that the derivations below are by no means the only way to get the right answers.

a. $dC = \left(\frac{\partial C}{\partial A}\right)_B dA + \left(\frac{\partial C}{\partial B}\right)_A dB$.
You can get this by taking $dC = C(A+dA, B+dB) - C(A,B)$ and doing first order Taylor expansion around the point (A,B) on $C(A+dA, B+dB)$.

b. - For a process with constant C, we have $dC = 0$ and hence, from part a., $\left(\frac{\partial C}{\partial A}\right)_B dA + \left(\frac{\partial C}{\partial B}\right)_A dB = 0$. Dividing by dB, we get $\left(\frac{\partial C}{\partial A}\right)_B \frac{dA}{dB} + \left(\frac{\partial C}{\partial B}\right)_A = 0$. In the limit where dA and dB are both small (and C remains constant), we have $\frac{dA}{dB} \to \left(\frac{\partial A}{\partial B}\right)_C$. This proves the first identity.
- In any infinitesimal process where C is constant, we have that dA is determined by dB and vice versa, and we have $\frac{dA}{dB} \to \left(\frac{\partial A}{\partial B}\right)_C$ and $\frac{dB}{dA} \to \left(\frac{\partial B}{\partial A}\right)_C$ as dA and dB both go to zero. Clearly in any process, $1 = \frac{dA}{dB}\frac{dB}{dA}$ and taking the limit of small dA and dB at constant C, we find the second identity.
- The third identity follows from the first and second. Starting from the first identity, bring $\left(\frac{\partial C}{\partial B}\right)_A$ to the right hand side and multiply both sides by $\left(\frac{\partial B}{\partial C}\right)_A$. Using the second identity (with the variables renamed), we see that the right hand side becomes -1 and the third identity is proved:

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