

# Statistical Physics: Example Sheet 4

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**1i.** By examining variations in  $E$ ,  $F$ ,  $H$  and  $G$ , derive the four different Maxwell relations for the partial derivatives of  $S$ ,  $P$ ,  $T$  and  $V$ .

**ii.** Obtain the partial derivative identity

$$\left. \frac{\partial S}{\partial T} \right|_p = \left. \frac{\partial S}{\partial T} \right|_V + \left. \frac{\partial S}{\partial V} \right|_T \left. \frac{\partial V}{\partial T} \right|_p$$

**iii.** Obtain the partial derivative identity

$$\left. \frac{\partial p}{\partial T} \right|_V \left. \frac{\partial T}{\partial V} \right|_p \left. \frac{\partial V}{\partial p} \right|_T = -1$$

**2.** Consider a gas with a fixed number of molecules. Two experimentally accessible quantities are  $C_V$ , the heat capacity at fixed volume and  $C_p$ , the heat capacity at fixed pressure, defined as

$$C_V = T \left. \frac{\partial S}{\partial T} \right|_V, \quad C_p = T \left. \frac{\partial S}{\partial T} \right|_p$$

Using the results of the previous question, show that:

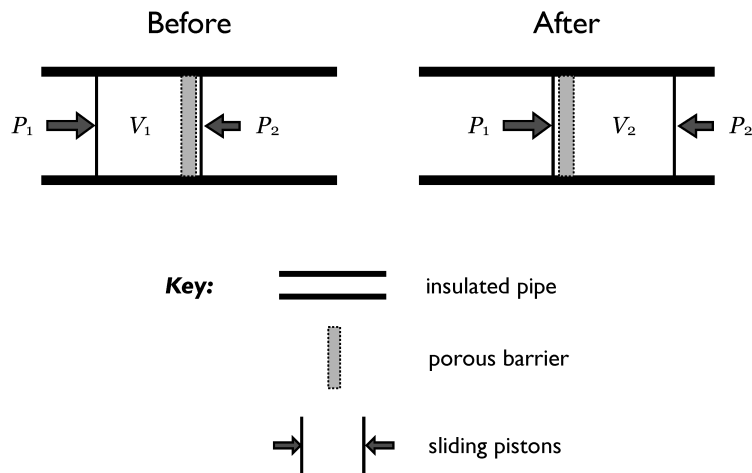
- i.**  $C_p - C_V = T \left. \frac{\partial V}{\partial T} \right|_p \left. \frac{\partial p}{\partial T} \right|_V = -T \left. \frac{\partial V}{\partial T} \right|_p^2 \left. \frac{\partial p}{\partial V} \right|_T$
- ii.**  $\left. \frac{\partial E}{\partial V} \right|_T = T \left. \frac{\partial p}{\partial T} \right|_V - p$
- iii.**  $\left. \frac{\partial E}{\partial p} \right|_T = -T \left. \frac{\partial V}{\partial T} \right|_p - p \left. \frac{\partial V}{\partial p} \right|_T$
- iv.**  $\left. \frac{\partial C_V}{\partial V} \right|_T = T \left. \frac{\partial^2 p}{\partial T^2} \right|_V$
- v.**  $\left. \frac{\partial C_p}{\partial p} \right|_T = -T \left. \frac{\partial^2 V}{\partial T^2} \right|_p$

3. Consider a classical ideal gas with equation of state  $pV = Nk_B T$  and constant heat capacity  $C_V = Nk_B \alpha$  for some  $\alpha$ . Use the results above to show that  $C_p = Nk_B(\alpha+1)$ , and that the entropy is

$$S = Nk_B \log \left( \frac{V}{N} \right) + Nk_B \alpha \log T + \text{const.}$$

Deduce that, for an adiabatic process (with  $dS = 0$ ),  $VT^\alpha$  is constant and, equivalently,  $pV^\gamma$  is constant, where  $\gamma = C_p/C_V$ .

4. This question describes the Joule-Thomson process (also known as the Joule-Kelvin process). The figure shows a thermally insulated pipe which has a porous barrier separating two halves of the pipe. A gas of volume  $V_1$ , initially on the left-hand side of the pipe, is forced by a piston to go through the porous barrier using a constant pressure  $p_1$ . Assume the process can be treated quasistatically. As a result the gas flows to the right-hand side, resisted by another piston which applies a constant pressure  $p_2$  ( $p_2 < p_1$ ). Eventually all of the gas occupies a volume  $V_2$  on the right-hand side.



- i. Show that enthalpy,  $H = E + PV$ , is conserved.
- ii. Find the Joule-Thomson coefficient  $\mu_{JT} \equiv \left( \frac{\partial T}{\partial p} \right)_H$  in terms of  $T$ ,  $V$ , the heat capacity at constant pressure  $C_p$ , and the volume coefficient of expansion  $\alpha \equiv \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_p$ . (Hint: You will need to use a Maxwell relation).
- iii. What is  $\mu_{JT}$  for an ideal gas?
- iv. If we wish to use the Joule-Thomson process to cool a real (non-ideal) gas, what must the sign of  $\mu_{JT}$  be?
- v. Derive  $\mu_{JT}$  for a gas obeying the van der Waals equation of state to leading order in the density  $N/V$ . For what values of temperature  $T$  can the gas be cooled?

5. A (non-ideal) gas has constant heat capacities  $C_V$  and  $C_p$ . Using the results of Question 2, show that its equation of state can be written as

$$(C_p - C_V)T = (p + a)(V + b)$$

where  $a$  and  $b$  are constants. Show also that  $E$  is of the form  $E = C_V T + f(V)$ , find  $f(V)$  and calculate the entropy as a function of  $V$  and  $T$ .

6. The Dieterici equation of state for a gas is

$$p = \frac{k_B T}{v - b} \exp\left(-\frac{a}{k_B T v}\right)$$

Find the critical point and compute the ratio  $p_c v_c / k_B T_c$ . Calculate the critical exponents  $\beta$ ,  $\delta$  and  $\gamma$ .

7. The  $q$ -state Potts model is a generalisation of the Ising model. At each lattice site lives a variable  $\sigma_i \in \{1, 2, \dots, q\}$ . The Hamiltonian is given by the sum over nearest neighbours

$$H_{\text{Potts}} = -\frac{3J}{2} \sum_{\langle ij \rangle} \delta_{\sigma_i \sigma_j}$$

How many ground states does the system at  $T = 0$ ?

Show that the 3-state Potts model is equivalent to the Hamiltonian

$$H = -J \sum_{\langle ij \rangle} \vec{s}_i \cdot \vec{s}_j$$

where  $\vec{s}_i$  take values in the set

$$\vec{s}_i \in \left\{ \begin{pmatrix} 1 \\ 0 \end{pmatrix}, \begin{pmatrix} -1/2 \\ \sqrt{3}/2 \end{pmatrix}, \begin{pmatrix} -1/2 \\ -\sqrt{3}/2 \end{pmatrix} \right\}$$

By developing a mean field theory for  $H$  determine the self-consistency requirement for the magnetisation  $\vec{m} = \langle \vec{s}_i \rangle$ . Compute the mean field free energy and show that the system undergoes a first order phase transition even in the absence of an external field.

[Hint: This calculation will be simpler if you argue that you can focus on magnetisation vectors of the form  $\vec{m} = (m, 0)$ .]

8. Consider the free energy

$$F = a(T)m^2 + b(T)m^4 + c(T)m^6$$

where  $b(T) < 0$  and, for stability,  $c(T) > 0$  for all  $T$ . Sketch the possible behaviours of the free energy as  $a(T)$  varies and, in each case, identify the ground state and metastable states. Show that the system undergoes a first order phase transition at some temperature  $T_c$ . Determine the value  $a(T_c)$  and the discontinuity in  $m$  at the transition.