Mathematical Tripos Part II Christopher Thomas

STATISTICAL PHYSICS Examples 4 Lent 2024

1. (a) By considering dE, dF, dG and dH, obtain four different Maxwell relations for the partial derivatives of S, p, T and V.

   (b) Obtain the partial derivative identity
$$\left(\frac{\partial S}{\partial T}\right)_V = \left(\frac{\partial S}{\partial T}\right)_p + \left(\frac{\partial S}{\partial p}\right)_T \left(\frac{\partial p}{\partial T}\right)_V .$$

   (c) Obtain the partial derivative identity
$$\left(\frac{\partial p}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_p \left(\frac{\partial T}{\partial p}\right)_V = -1 .$$

   [Hint: Consider the analogue of the identity in part (b) with S replaced by V.]

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
$$C_V = T\left(\frac{\partial S}{\partial T}\right)_V \quad , \quad C_p = T\left(\frac{\partial S}{\partial T}\right)_p$$
   Using the results of the previous question, show that:

   (a) $$C_p - C_V = T\left(\frac{\partial V}{\partial T}\right)_p \left(\frac{\partial p}{\partial T}\right)_V = -T\left(\frac{\partial V}{\partial T}\right)_p^2 \left(\frac{\partial p}{\partial V}\right)_T$$

   (b) $$\left(\frac{\partial E}{\partial V}\right)_T = T\left(\frac{\partial p}{\partial T}\right)_V - p$$

   (c) $$\left(\frac{\partial E}{\partial p}\right)_T = -T\left(\frac{\partial V}{\partial T}\right)_p - p\left(\frac{\partial V}{\partial p}\right)_T$$

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

   (e) $$\left(\frac{\partial C_p}{\partial p}\right)_T = -T\left(\frac{\partial^2 V}{\partial T^2}\right)_p$$

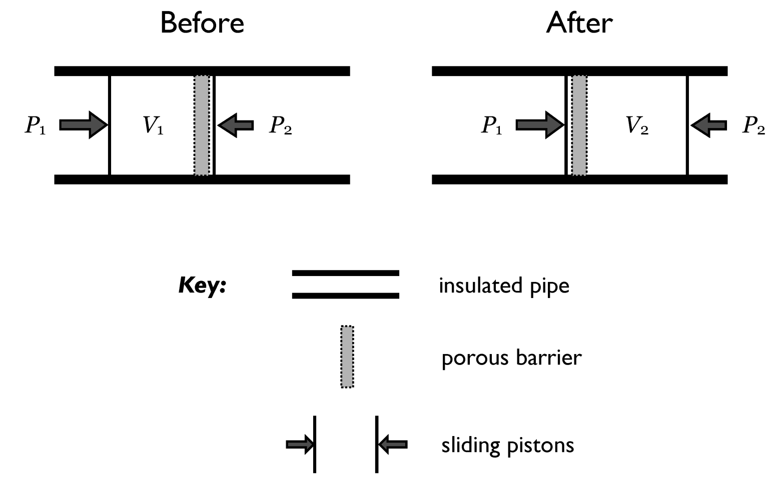
3. Consider a classical ideal gas with equation of state $pV = Nk_BT$ and constant heat capacity $C_V = Nk_B\,\alpha$ for some α. Use the results above to show that $C_p = Nk_B(\alpha+1)$, and that the entropy is
$$S = Nk_B \ln(V/N) \; + \; Nk_B\,\alpha \ln T \; + \; \text{const}\,.$$
   Deduce that, for a reversible adiabatic process (with S constant), VT^α is constant and, equivalently, pV^γ is constant, where $\gamma = C_p/C_V$.

4. Show that the entropy of a Van der Waals gas can be written as

$$S = Nk_B \ln\left(\frac{V}{N} - b\right) + Nk_B f(T)\,,$$

where $f(T)$ is some function of temperature. Find F, the free energy of the gas. Determine S and F more explicitly in the case that C_V is a constant.

5. 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 quasi-statically. 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.



(a) Show that enthalpy, $H = E + pV$, is conserved.

(b) Find the Joule-Thomson coefficient $\mu_{\rm JT} \equiv \left(\frac{\partial T}{\partial p}\right)_H$ 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].

(c) What is $\mu_{\rm JT}$ for an ideal gas?

(d) If we wish to use the Joule-Thomson process to cool a real (non-ideal) gas, what must the sign of $\mu_{\rm JT}$ be?

(e) Derive $\mu_{\rm JT}$ 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?

6. 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.

7. The Dieterici equation of state for a gas is

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

where $v = V/N$. Find the critical point and compute the ratio $p_c v_c / k_B T_c$. Calculate the critical exponents β, δ and γ.

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

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

(a) How many ground states does the system have at $T = 0$?

(b) 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

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

(c) 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 theory 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 $\vec{m} = (m, 0)$.]

9. 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 stable equilibrium 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.

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