

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:

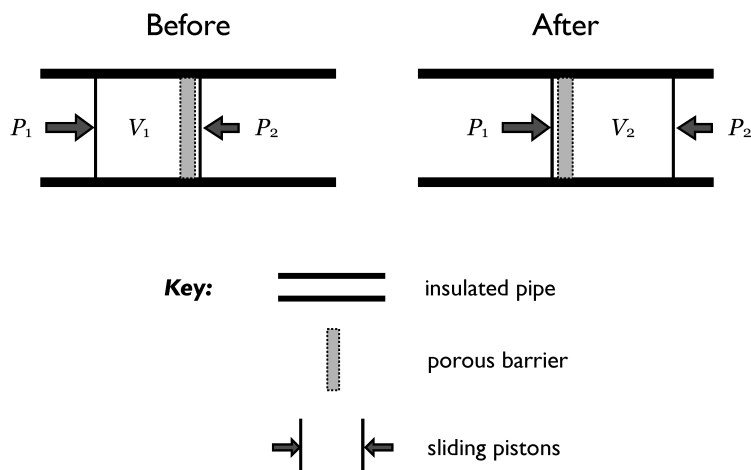
- i.** $C_p - C_V = T \left. \frac{\partial V}{\partial T} \right|_p \left. \frac{\partial p}{\partial T} \right|_V = -T \left. \frac{\partial V}{\partial T} \right|_p^2 \left. \frac{\partial p}{\partial V} \right|_T$
- ii.** $\left. \frac{\partial E}{\partial V} \right|_T = T \left. \frac{\partial p}{\partial T} \right|_V - p$
- 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 $pV = NkT$ and constant heat capacity $C_V = Nk\alpha$ for some α . Use the results above to show that $C_p = Nk(\alpha + 1)$, and that the entropy is

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

Deduce that, for a reversible adiabatic process (with $dS = 0$), VT^α is constant and, equivalently, pV^γ 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 μ_{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 μ_{JT} be?
- v. Derive μ_{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. In this question we will determine the critical exponent β for the van der Waals equation of state. Starting from the law of corresponding states

$$\bar{p} = \frac{8\bar{T}}{3\bar{v} - 1} - \frac{3}{\bar{v}^2}$$

let $\bar{T} = 1 + t$ and $\bar{v} = 1 + \phi$ where t and ϕ are small. Expand in ϕ to show that

$$\bar{p} = 1 - \frac{3}{2}\phi^3 + \mathcal{O}(\phi^4) + t [4 - 6\phi + \mathcal{O}(\phi^2)]$$

Now, at fixed small t , let $\phi_l(t)$ and $\phi_g(t)$ be the values of ϕ corresponding to the liquid and gas phases respectively. The Maxwell construction gives

$$0 = \int_l^g \bar{v} d\bar{p} = \int_l^g (1 + \phi) d\bar{p} = \int_l^g \phi d\bar{p}$$

where the integral is evaluated along an isotherm and we used $\bar{p}_l(t) = \bar{p}_g(t)$ in the final step. Now change integration variable from \bar{p} to ϕ and evaluate the integral to leading order to show that either $\phi_l(t) = -\phi_g(t)$ or $\phi_l(t)^2 + \phi_g(t)^2 + 8t/3 = 0$. Finally use $\bar{p}_l(t) = \bar{p}_g(t)$ to exclude the latter case, and in the former case to deduce that $\phi_g(t) \propto (-t)^{1/2}$ and hence

$$\bar{v}_g - \bar{v}_l \propto (T_c - T)^{1/2}$$

7. The Dieterici equation of state for a gas is

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

where $v = V/N$. Find the critical point and compute the ratio $p_c v_c / kT_c$. 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 $\sigma_i \in \{1, 2, \dots, q\}$. 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 have 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 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 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.