

Problem 5.12. Functions encountered in physics are generally well enough behaved that their mixed partial derivatives do not depend on which derivative is taken first. Therefore, for instance,

$$\frac{\partial}{\partial V} \left(\frac{\partial U}{\partial S} \right) = \frac{\partial}{\partial S} \left(\frac{\partial U}{\partial V} \right),$$

where each $\partial/\partial V$ is taken with S fixed, each $\partial/\partial S$ is taken with V fixed, and N is always held fixed. From the thermodynamic identity (for U) you can evaluate the partial derivatives in parentheses to obtain

$$\left(\frac{\partial T}{\partial V} \right)_S = - \left(\frac{\partial P}{\partial S} \right)_V,$$

a nontrivial identity called a **Maxwell relation**. Go through the derivation of this relation step by step. Then derive an analogous Maxwell relation from each of

the other three thermodynamic identities discussed in the text (for H , F , and G). Hold N fixed in all the partial derivatives; other Maxwell relations *can* be derived by considering partial derivatives with respect to N , but after you've done four of them the novelty begins to wear off. For applications of these Maxwell relations, see the next four problems.

Maxwell Relations (Problem 5.12)

Assume $U = U(S, N, V)$ is well behaved so
$$\frac{\partial}{\partial V} \left(\frac{\partial U}{\partial S} \right) = \frac{\partial}{\partial S} \left(\frac{\partial U}{\partial V} \right)$$
 order doesn't matter
(assume $N = \text{fixed}$)

Then use

$$dU = TdS - pdV + \cancel{\mu dN} \quad \begin{matrix} \nearrow \text{ignore as} \\ dN = 0 \end{matrix}$$

$$\left(\frac{\partial U}{\partial S} \right)_{V, N} = T \quad \left(\frac{\partial U}{\partial V} \right)_{S, N} = -p$$

$$\text{Then } \left(\frac{\partial T}{\partial V} \right)_{S, N} = - \left(\frac{\partial p}{\partial S} \right)_{V, N}$$

Similar results (all assuming $N = \text{constant}$)

$$\left(\frac{\partial T}{\partial V} \right)_S = - \left(\frac{\partial p}{\partial S} \right)_V$$

$$\left(\frac{\partial T}{\partial p} \right)_S = \left(\frac{\partial V}{\partial S} \right)_p$$

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

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

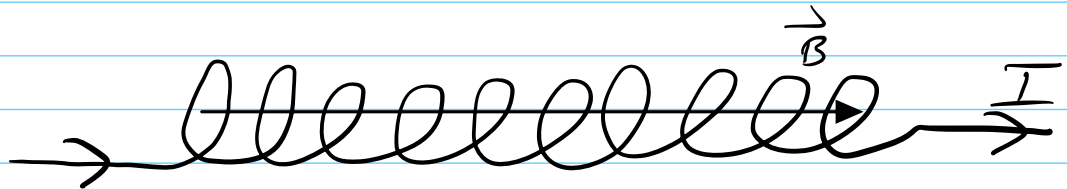
"Maxwell's Relations"

applications: Problem 5.13, 5.14, 5.15, 5.16

These ultimately derive from the idea that
knowing $S \rightarrow$ knowing T and V ,

and they are all related by the first law.

These results can also be generalized to other sorts of work, e.g. magnetic work



Problem 5.17 shows

$$G_m = U - TS - \mu_0 \vec{H} M$$

$$\mu_0 = 4\pi \times 10^{-7} \text{ N/A}^2$$

$\vec{M}$ = total magnetic moment of the sample

$$\vec{H} \equiv \frac{1}{\mu_0} \vec{B} - \frac{\vec{M}}{V}$$

$$(\text{or } \vec{B} = \mu_0 \vec{H} + \mu_0 \frac{\vec{M}}{V}) \quad \text{More: Phys 432.}$$

Changing M takes work!