Spring Semester (2016)
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Homework #3: Thermodynamics & Statistical Mechanics: Basic principles (III)   Due: April 12, 2016

1: Derive the four Maxwell's relations:

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

2: Prove in isothermal expansion pressure always decreases, i.e.,

$$\left(\frac{\partial P}{\partial V}\right)_T < 0.$$

3: Prove for heat capacities at constant pressure, C_p and at constant volume C_v:

$$C_p > C_v, \quad C_v > 0 \quad \text{hence} \quad C_p > 0.$$

4: Prove in adiabatic expansion the temperature of the body falls or rises depending on the sign of the thermal expansion coefficient, $\alpha_p = V^{-1}(\partial V/\partial T)_P$.

5: Prove that adiabatic compressibility is always smaller in absolute value than isothermal compressibility.

6: *Measuring absolute temperature using an arbitrary body whose equation of state is not known* a priori: Assume T is the absolute temperature that we need to measure, τ is the arbitrary scale by an arbitrary calibrated "thermometer". Then prove that we have for the one-to-one function $T(\tau)$:

$$\frac{d\log T(\tau)}{d\tau} = -\frac{(\partial V/\partial \tau)_P}{(\bar{\partial} Q/\partial P)_\tau}$$

in which $\bar{\partial}$ is the incomplete partial. **Hint:** Start with the following relation (in which all the quantities refer to the body in question):

$$\left(\frac{\bar{\partial} Q}{\partial P}\right)_T = T\left(\frac{\partial S}{\partial P}\right)_T = -T\left(\frac{\partial V}{\partial T}\right)_P$$

i) Interpret this result.
ii) T is determined to within a constant. Why? What is its meaning ?

7: Derive Liouville's equation governing the probability density function of a *closed* Hamiltonian system in phase space. Can this equation describe the relaxing time-evolution of the probability density function to its equilibrium value? Justify your answer. Explain how relaxation to equilibrium state is achieved in real systems, which cannot mostly be assumed as closed.