

Advanced Statistical Physics II – Problem Sheet 1

Problem 1 – Thermodynamic Potentials and State Variables

a) (2P) Convince yourself that a generic function $f(u, v)$ fulfills the relations:

$$\left(\frac{\partial f}{\partial u}\right)_v \left(\frac{\partial u}{\partial f}\right)_v = 1 \quad \text{and} \quad \left(\frac{\partial f}{\partial u}\right)_v \left(\frac{\partial u}{\partial v}\right)_f \left(\frac{\partial v}{\partial f}\right)_u = -1 \quad (1)$$

In the following, a thermodynamic system with a constant particle number is considered:

b) (1P) Using the results from subtask a), express the isochoric pressure change with temperature

$$\left(\frac{\partial p}{\partial T}\right)_V \quad (2)$$

by the response functions

$$\alpha = \frac{1}{V} \left(\frac{\partial V}{\partial T}\right)_p, \quad \kappa_T = -\frac{1}{V} \left(\frac{\partial V}{\partial p}\right)_T. \quad (3)$$

What is the total differential of $p(T, V)$?

c) (1P) Derive the differential forms of the caloric equations of state $U(T, V)$ and $U(T, p)$. Express the appearing partial derivatives by standard response functions.

d) (1P) Find the following Maxwell relation

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial p}{\partial T}\right)_V \quad (4)$$

and then derive the relation

$$-p + T \left(\frac{\partial p}{\partial T}\right)_V = \left(\frac{\partial U}{\partial V}\right)_T. \quad (5)$$

Hint: V and T are the natural variables of the free energy F .

e) (1P) Show that the functional determinant

$$\frac{\partial(T, S)}{\partial(p, V)} = \begin{vmatrix} \left(\frac{\partial T}{\partial p}\right)_V & \left(\frac{\partial T}{\partial V}\right)_p \\ \left(\frac{\partial S}{\partial p}\right)_V & \left(\frac{\partial S}{\partial V}\right)_p \end{vmatrix} = 1. \quad (6)$$

Hint: You can use the identity $\frac{\partial(T, S)}{\partial(p, V)} = \frac{\partial(T, S)}{\partial(A, B)} \frac{\partial(A, B)}{\partial(p, V)}$, where A and B are any state variables.

Problem 2 – Phase Transition and Clausius-Clapeyron (CC) Equation

A one component system at the interface of two phases (solid and liquid) is considered.

a) (2P) Derive the relationship between the slope of the phase limit curve $P_0(T)$ and the entropy change ΔS and volume change ΔV from the equilibrium condition of the two phases

$$\mu_1(P_0(T), T) = \mu_2(P_0(T), T). \quad (7)$$

b) (2P) Show that the latent heat $\Delta Q_{\text{lat}} = T\Delta S$ for going from a high-temperature to a low-temperature phase is always positive. Which consequence does this have for the sign of the volume change ΔV at the phase transition?

c) (2P) Calculate the heat capacity c_{coex} of a gas along its melting curve. To what extent does it differ from the heat capacity c_p at constant pressure?

Problem 3 – Black-body radiation

For a black-body radiator there is $U = u(T)V$ and $p = \frac{1}{3}u(T)$, where $u(T)$ is the energy density.

a) (5P) Calculate $u(T)$.

b) (3P) Calculate $S(T, V)$, the free energy F and the Gibbs free energy G .