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:

$$\left(\frac{\partial f}{\partial u}\right)_{v} \left(\frac{\partial u}{\partial f}\right)_{v} = 1 \quad \text{and} \quad \left(\frac{\partial f}{\partial u}\right)_{v} \left(\frac{\partial u}{\partial v}\right)_{f} \left(\frac{\partial v}{\partial f}\right)_{u} = -1 \tag{1}$$

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

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

by the response functions

$$\alpha = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_p, \qquad \kappa_{\rm T} = -\frac{1}{V} \left(\frac{\partial V}{\partial p} \right)_T. \tag{3}$$

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

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

and then derive the relation

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

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

e) (1P) Show that the functional determinant

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

The internal energy of a system in its natural variables is given by

$$U(S,V) = (\sigma V)^{-m/n} N^{(m-1)/n} \left(\frac{nS}{n+1}\right)^{(n+1)/n}$$
(7)

a) (4P) Calculate U(T, V).

b) (2P) Calculate p(T, V).

c) (3P) Calculate the free energy F, the enthalpy H and the Gibbs free energy G in their natural variables.

d) (4P) Compute the response functions α and κ_T from problem 1 b). Compute also the quotient α/κ_T .

e) (1P) Choose the parameter m such that p in b) is independent of the Volume V. What do you obtain for for the results of a)-c) when additionally choosing n = 3? Which physical system is described by these equations?