

Advanced Statistical Physics II – Problem Sheet 1

Problem 1 – Integrating Factor

Recall that a differential

$$df(\vec{x}) = a_1(\vec{x})dx_1 + a_2(\vec{x})dx_2 + \cdots + a_n(\vec{x})dx_n \quad (1)$$

is called *exact* if it can be integrated, i.e. if there exists a scalar potential $f(\vec{x})$ such that $a_i(\vec{x}) = \partial f / \partial x_i$ for $i = 1, \dots, n$.

(a) (2P) Consider the following expression

$$\Delta Q(U, V, N) = dU + \frac{U}{V}dV + \frac{U}{N}dN \quad (2)$$

Convince yourself that it is *not* an exact differential (and that Q thus cannot define a thermodynamic potential) by showing that the curl of the vector field $(1, U/V, U/N)$ is non-zero.

(b) (2P) Given a non-exact differential $\Delta g(\vec{x})$, we might be able to find a function $c(\vec{x})$ such that $c(\vec{x})\Delta g(\vec{x})$ becomes an exact differential. Such a function c is called *integrating factor*. Verify for our particular example that the entropy is a potential function by showing that for

$$T = \left(\frac{U^2}{aVN} \right)^{1/3} \quad (3)$$

$dS = \Delta Q/T$ is an exact differential.

(c) (1P) Integrate dS to find the entropy S .

Problem 2 – Legendre Transform

(a) (2P) Compute the Helmholtz free energy $F(T, V, N)$ from the internal energy

$$U(S, V, N) = \frac{S^3}{27aVN} \quad (4)$$

(b) (1P) Do the back-transform

Problem 3 – Gibbs-Duhem Equation

(3P) Consider the thermodynamic potential $J(S, P, \mu)$. By using extensive/intensive arguments find an expression for J and use it to derive the Gibbs-Duhem equation:

$$SdT - VdP + Nd\mu = 0 \quad (5)$$

Problem 4 – Differential form of $U(T, V, N)$

The aim of this exercise is to derive the differential form of the caloric equation of state mentioned in the lecture:

$$dU = C_V dT + \left(\frac{\alpha T}{\kappa_T} - P \right) dV + \left(\frac{U}{N} - \frac{V}{N} \left[\frac{\alpha T}{\kappa_T} - P \right] \right) dN \quad (6)$$

Intermediate steps:

(a) (3P) Show that

$$\left. \frac{\partial U}{\partial V} \right|_{T,N} = T \left. \frac{\partial P}{\partial T} \right|_{V,N} - P \quad (7)$$

Hint: Consider the differential of $S(U, V, N) - U/T$ and derive the appropriate Maxwell relation.

(b) (3P) Show that $\partial P / \partial T|_{V,N} = \alpha / \kappa_T$ by using the thermal equation of state $V(T, P, N)$.

(c) (3P) $\partial U / \partial N|_{T,V}$ can be obtained by noting that the caloric equation of state may be written as

$$U(T, V, N) = Nu(T, V/N) \quad (8)$$

For this exercise, recall the definition of the following material constants:

$$C_V = \left. \frac{\partial U}{\partial T} \right|_{V,N}, \quad \alpha = \frac{1}{V} \left. \frac{\partial V(T, P, N)}{\partial T} \right|_{P,N}, \quad \kappa_T = -\frac{1}{V} \left. \frac{\partial V(T, P, N)}{\partial P} \right|_{T,N} \quad (9)$$