

Advanced Statistical Physics II – Problem Sheet 2

Problem 1 – Computing thermodynamic potentials

For an one component system we know the isothermal compressibility κ_T , the thermal expansion coefficient α and the heat capacity at constant volume C_V . These are given by

$$\kappa_T = \frac{2}{p}, \quad \alpha = \frac{3}{T}, \quad \frac{C_V}{N} = \frac{3\sigma T^2}{2p}, \quad (1)$$

where σ is a numerical constant. With the assumption that the entropy is zero at zero temperature, $S(T=0) = 0$, we want to compute the internal energy $U(S, V)$ up to a constant U_0 .

- (3P) Use the first two equations and calculate $V(T, p)$. You will be left with a constant prefactor c that does not depend on T and p .
- (2P) Using your result in a) show that the free energy is of the form $F(T, V) = f_1(T, V) + f_2(T)$. Determine $f_1(T, V)$.
- (2P) Using your result in b) compute C_V . Compare to the given function for this quantity to obtain the constant c . What can you say about $f_2(T)$ now?
- (1P) With the help of $S(T=0) = 0$ argue that $f_2(T) = U_0$ is a constant.
- (2P) Compute the internal energy $U(S, V)$.

Problem 2 – Thermodynamics of macromolecular deformation

For a rubber band of length z the following relation between temperature T , pulling force F in z -direction and length z is given by

$$z = z_0 + \frac{\alpha F}{T}, \quad \alpha, z_0 > 0. \quad (2)$$

Further, it is known that in order to heat the rubber band at fixed length z the constant heat capacity $C_z > 0$ is needed, which is independent of temperature T .

- (3P) Show that the internal energy U is independent of z .
Hint: In this scenario the internal energy is given by $dU = TdS + Fdz$. Why? Reformulate $U(S, z)$ as $U(T, z)$ and remember that S is a total differential $\frac{\partial^2 S}{\partial z \partial T} = \frac{\partial^2 S}{\partial T \partial z}$.
- (1P) Show that the heat capacity at constant z is not a function of z or T .

- (3P) Derive the heat capacity at constant pulling force F

$$C_F = \left(\frac{\Delta Q}{\Delta T} \right)_F \quad (3)$$

Hint: First, derive an expression for $dS(T, F)$

- (3P) The rubber band is pulled from z_1 to $z_2 > z_1$. Derive an expression for $\left(\frac{\partial T}{\partial z} \right)_S$. Does the temperature increase or decrease?