Thermal Physics II – Problem Sheet 4

Part I: Questions

1. Describe the setup of a canonical ensemble.
2. What is the appropriate thermodynamic potential for a system with heat contact to a large reservoir? State its definition.
3. What condition must the thermodynamic potential hold if a system, that is described by the canonical ensemble, is in equilibrium?
4. How is the temperature defined for a system that is in heat contact with a large reservoir? How is the internal energy defined if the total energy fluctuate all the time under these conditions?

Part II: Problems

1. Partition Function and Internal Energy

By starting from the definition of the Helmholtz free energy and the connection between statistical description and thermodynamics in the canonical ensemble, that is $F = -k_B T \ln Z$, show that the relation

$$U = -\frac{\partial \ln Z}{\partial \beta}$$

holds for the internal energy.

2. Maxwell Relation

Proof the following Maxwell relations:

$$\left(\frac{\partial T}{\partial p}\right)_{S,N} = \left(\frac{\partial V}{\partial S}\right)_{p,N} \qquad \text{and} \qquad -\left(\frac{\partial S}{\partial p}\right)_{T,N} = \left(\frac{\partial V}{\partial T}\right)_{p,N} ,$$

where the first one comes from the Enthalpy/Gibbs energy $H = U + pV$ being a thermodynamic potential (for certain variables) and the second one follows from the Gibbs free energy $G = U - TS + pV$.

3. Probability to Find a Given State

Consider a system in thermodynamic equilibrium in contact with a heat bath at temperature T. In that case, the energy of the system fluctuates. Show that the probability to find the system in a state with energy E, that is $p(E)$, can be expressed as

$$p(E) = \exp(-\beta E + \beta F) ,$$

where F is, of course, the Helmholtz free energy.