Thermal Physics II – Solutions for Problem Sheet 7

1. Relation of Thermodynamics and Statistics

- The left hand side is easy to show as $\Omega_{gr} = -pV$. The pressure is an intensive quantity and the volume is of course extemsive. Thus, the product must be extensive (linearly increasing with N and V).

- On the right hand side, we have $k_B T \ln Z_{gr}$. As T is an intensive quantity, $\ln Z_{gr}$ must be extensive.

- We consider the grand partition function in the form

$$Z_{gr} = z^N Z_{can},$$

 where both the fugacity, $z = \exp(\beta\mu)$ nor the canonical partition function Z_{can} are intensive as they do not depend on particle number explicitly.

- For the logarithm of the grand partition function, we find

$$\ln Z_{gr} = \ln\left(z^N Z_{can}\right) = N\left[\ln z + \ln Z_{can}\right]$$

 which, due to the prefactor N, is clearly extensive. The functions in the brackets do not explicitly depend on N.

2. Relation of Thermodynamics and Statistics

- We start with the definition of the grand partition function

$$Z_{gr} = \sum_{E,N} \exp[-\beta(E - \mu N)] \ .$$

- Now we transform the derivative of this function with respect to μ

$$
\begin{aligned}
\frac{\partial}{\partial \mu} Z_{gr} &= \beta \sum_{E,N} N \exp[-\beta(E - \mu N)] \\
&= \beta Z_{gr} \sum_{E,N} N \ Z_{gr}^{-1} \exp[-\beta(E - \mu N)] \\
&= \beta Z_{gr} \sum_{E,N} N \ P(E,N) \\
&= \beta Z_{gr} \langle N \rangle \,,
\end{aligned}
$$

  where the probabilities to find the system in the state (E, N) was introduced and then used to generate the average particle number $\langle N \rangle$

- By easy re-arrangements, this becomes

$$\langle N \rangle = k_B T \ Z_{gr}^{-1}(T, V, \mu) \ \frac{\partial Z_{gr}(T, V, \mu)}{\partial \beta} \ .$$

3. Gibbs-Duhem Relation

- We start with the internal energy $U = U(S, V, N_i, N_j, ...)$

- Now we make the system a-times larger and obtain a new internal energy
  $U' = aU = U(aS, aV, aN_i, aN_j, ...)$.

- Thus U is a homogeneous function and Euler's theorem can be applied

$$
U = S \left(\frac{\partial U}{\partial S} \right)_{V,N_i,N_j,...} + V \left(\frac{\partial U}{\partial V} \right)_{S,N_i,N_j,...}
$$
$$
+ \sum_{k=i,j,...} N_k \left(\frac{\partial U}{\partial N_k} \right)_{S,V,N_i \neq N_k} .
$$

- The partial derivatives are well-known from the fact that U is a exact differential. Thus, we have

$$
U = ST - Vp + \sum_{k=i,j,...} N_k \mu_k .
$$

- Now we apply the definition of the Gibbs free energy $G = U - TS + pV$ and find

$$
G = \sum_{k=i,j,...} \mu_k N_k \qquad \text{or for one component} \qquad G = \mu N .
$$

This is the Gibbs-Duhem relation that states that the chemical potential is the Gibbs free energy per particle.

4. More Maxwell- Relations

- It should be clear by now how to do this ...