2.6 First results from the calculation of the state sum

The canonical partition function for a Hamiltonian which completely separates into subspaces can be written in the form

$$Z_C(T,V,N) = \sum_i \exp(-\beta U_i) = \sum_{[n_\alpha]}^{N} \exp\left(-\beta \sum_\alpha n_\alpha \epsilon_\alpha\right) \quad . \tag{2.40}$$

The equation on the right side must fulfill the restriction

$$N = \sum_\alpha n_\alpha \quad . \tag{2.41}$$

The grand canonical partition function of a Hamiltonian which completely separates into subspaces can be written in the form

$$Z_{GC}(T,V,\mu) = \sum_{N=0}^{\infty} \sum_{[n_\alpha]}^{N} \exp\left(-\beta \sum_\alpha n_\alpha(\epsilon_\alpha - \mu)\right) \quad . \tag{2.42}$$

The big advantage of this partition function is the identity

$$\sum_{N=0}^{\infty} \sum_{[n_\alpha]}^{N} \ldots = \sum_{n_1} \sum_{n_2} \sum_{n_3} \ldots \tag{2.43}$$

i.e. states can be occupied independently and within the partition function an independent sum over independent energy subspaces is performed, leading to a product over subspace sums.
Finally we get

$$\begin{aligned} Z_{GC}(T,V,\mu) &= \prod_\alpha \sum_{n_\alpha} \exp(-\beta n_\alpha(\epsilon_\alpha - \mu)) \\ &= \prod_\alpha (1 - \exp(-\beta(\epsilon_\alpha - \mu))^{-1} \qquad \text{for Bosons} \\ &= \prod_\alpha (1 + \exp(-\beta(\epsilon_\alpha - \mu))^{+1} \qquad \text{for Fermions} \end{aligned} \tag{2.44}$$

Just a reminder:

- All quantum mechanical particles with half value spin are called Fermions (electrons, holes, ...). They obey the Pauli principle, have antisymmetric complete wave functions and each state can only be occupied once.
- All quantum mechanical particles with integer spin are called Bosons (photons, phonons, ...). They obey not the Pauli principle, have symmetric complete wave functions and there is no restriction for the number of particles within one state.

For the grand canonical potential we find

$$\Omega(T,V,\mu) = \pm kT \sum_\alpha \ln\left(1 \mp \exp\left(-\frac{\epsilon_\alpha - \mu}{kT}\right)\right) \tag{2.45}$$

and

$$N = -\frac{\partial \Omega}{\partial \mu} = \mp kT \sum_\alpha \frac{1}{\exp\left(\frac{\epsilon_\alpha - \mu}{kT}\right) \mp 1} \frac{\mp 1}{kT} = \sum_\alpha \frac{1}{\exp\left(\frac{\epsilon_\alpha - \mu}{kT}\right) \mp 1} \quad . \tag{2.46}$$

If $\exp\left(-\frac{\epsilon_\alpha - \mu}{kT}\right) \ll 1$ holds we get

$$\ln\left(1 \mp \exp\left(-\frac{\epsilon_\alpha - \mu}{kT}\right)\right) \approx \mp \exp\left(-\frac{\epsilon_\alpha - \mu}{kT}\right) \quad . \tag{2.47}$$

In this case we find for Fermions as well as for Bosons

$$N = -\frac{\partial \Omega}{\partial \mu} = \mp kT \sum_\alpha \mp \exp\left(-\frac{\epsilon_\alpha - \mu}{kT}\right) \frac{1}{kT} = \sum_\alpha \exp\left(-\frac{\epsilon_\alpha - \mu}{kT}\right) \tag{2.48}$$

This is the so called Boltzmann statistics. As we will see later the above assumption is fulfilled for extremely diluted systems and at high temperatures (classical particles).

- Without much effort we could calculate the Fermi-, Bose- and Boltzmann statistics for the grand canonical ensemble.
- Almost all calculations for solids are performed for the grand canonical ensemble.
- μ, respectively E_F (exactly $E_F = \mu(T = 0)$) are just Lagrange parameter (from a mathematically point of view); they allow to calculate the partition function without any restrictions due to the particle number. From a physical point of view μ is the energy which a particles has when added to the system. Consequently $\Delta\mu$ is a force leading to a particle flow.
- $\Omega = \Omega(T, \mu, V)$; since V is the only extensive parameter in the potential, Ω must be proportional to V. We find:

$$\Omega \propto V \qquad \text{and} \qquad \frac{\partial \Omega}{\partial V} = -p \qquad \text{, leading to} \qquad \Omega = -pV \tag{2.49}$$