# 3.4: Grand Canonical Ensemble

For the description of an open system in the thermodynamical sense, i.e., a system that can exchange not only heat, but also matter with its environment, we need to replace particle number $N$ with another constant of motion. If we would fail to introduce a new constant of motion, we would end up with a system that is not at equilibrium and thus cannot be fully described by time-independent state functions. If we assume that the system is in chemical as well as thermal equilibrium with its environment, the new constant of motion is the chemical potential $\mu$, or more precisely, a vector $\vec{\mu}$ of the chemical potentials $\mu_k$ of all components.

**Concept 3.4.1: Grand Canonical Ensemble**

An ensemble with constant chemical potential $\mu_k$ of all components, and constant volume $V$ that is at thermal equilibrium with a heat bath at constant temperature $T$ and in chemical equilibrium with its environment is called a **grand canonical ensemble**. It can be considered as consisting of canonical subensembles with different particle numbers $N$. The grand canonical state energies and partition function contain an additional chemical potential term. With this additional term the results obtained for the canonical ensemble apply to the grand canonical ensemble, too.

The partition function for the grand canonical ensemble is given by

$$Z_{\mathrm{gc}}(\mu, V, T) = \sum_i e^{(\sum_k N_{i,k}\mu_k - \epsilon_i)/k_{\mathrm{B}}T} \,, \tag{3.4.1}$$

whereas the probability distribution over the levels and particle numbers is

$$P_i = \frac{e^{(\sum_k N_{i,k}\mu_k - \epsilon_i)/k_{\mathrm{B}}T}}{Z_{\mathrm{gc}}} \,. \tag{3.4.2}$$

Note that the index range $i$ is much larger than for a canonical ensemble, because each microstate is now characterized by a set of particle numbers $N_{i,k}$, where $k$ runs over the components.

At this point we are in conflict with the notation that is often used in other course. For example, we often define the chemical potential $\mu$ as a *molar* quantity, here it is a molecular quantity. The relation is $\mu_{\mathrm{PCI}} = N_{\mathrm{Av}}\mu_{\mathrm{PCVI}}$ . Using the PC I notation in the current lecture notes would be confusing in other ways, as $\mu$ is generally used in statistical thermodynamics for the molecular chemical potential. A similar remark applies to capital letters for state functions. Capital letters denote either a molecular quantity or a molar quantity. The difference will be clear from the context. We note that in general small letters for state functions (except for pressure $p$) denote extensive quantities and capital letters (except for volume $V$) denote intensive quantities.