3.1: Statistical Ensembles

Concept of an Ensemble

Probability densities in phase space cannot be computed by considering only a single system at a single instant in time. Such a system will be in some random microstate, but what we need is the statistics of such microstates. This problem was solved by Gibbs, who considered ensembles that consist of a very large number of identical systems in possibly different microstates. The microstates for a system with M molecules with f degrees of freedom each are points in $2fM$-dimensional phase space. If we have information on the probability density assigned to such points, we can use probability theory to compute thermodynamical state functions.

Ergodicity

Instead of considering a large ensemble of systems at the same time (ensemble average), we could also consider a long trajectory of a single system in phase space. The single system will go through different microstates and if we observe it for a sufficiently long time, we might expect that it visits all accessible points in phase space with a frequency that corresponds to the associated probability density. This idea is the basis of analyzing MD trajectories in terms of thermodynamic state functions. The ensemble average $\langle A \rangle$ is replaced by the time average $\overline{A}$. We assume

$$\langle A \rangle = \overline{A}\,. \tag{3.1.1}$$

Systems where this assumption holds are called *ergodic* systems.

Often, experiments are performed on a large ensemble of identical systems. An example is a spectroscopic experiment on a dilute solution of chromophores: Each chromophore can be considered as an individual system and their number may be of the order of 10^{10} or higher. In some cases an equivalent experiment can be performed on a single chromophore, but such single-molecule experiments require many repetitions and measure a time-average. The results of ensemble and single-molecule experiments are equivalent if the system is ergodic and the measurement time in the single-molecule experiment is sufficiently long.

Whether or not a system is ergodic depends on kinetic accessibility of the whole thermodynamically accessible phase space. We shall see later that thermodynamic accessibility is related to temperature and to the energy assigned to points in phase space. Points are accessible if their energy is not too much higher than the energy minimum in phase space. Whether a single dynamic system visits all these points at the same given temperature- and what time it needs to sample phase space- depends on energy barriers. In MD simulations sampling problems are often encountered, where molecular conformations that are thermodynamically accessible are not accessed within reasonable simulation times. A multitude of techniques exists for alleviating such sampling problems, none of them perfect. In general, time-average methods, be they computational or experimental, should be interpreted only with care in terms of thermodynamics. In this lecture course we focus on ensemble-average methods, which suffer from a loss in dynamic information, but get the thermodynamic state functions right.