2.1: Lattice Models

Lattice Models

Lattice models provide a minimalist, or coarse-grained, framework for describing the translational, rotational, and conformational degrees of freedom of molecules, and are particularly useful for problems in which entropy of mixing, configurational entropy, or excluded volume are key variables. The lattice forms a basis for enumerating different configurations of the system, or microstates. Each of these microstates may have a different energy, which is then used to calculate a partition function.

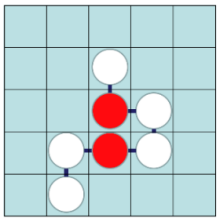
$$Q = \sum_i e^{-E_i/k_BT} \tag{2.1.1}$$

The thermodynamic quantities then emerge from

$$F = -k_BT \ln Q$$
$$S = -k_B \sum_i P_i \ln P_i$$
$$U = \sum_i P_i E_i$$

and other internal variables (X) can be statistically described from

$$\langle X \rangle = \sum_{i=1}^{N} P_i X_i \quad P_i\left(E_i\right) = \frac{e^{-E_i/k_BT}}{Q}$$



We will typically work with a macroscopic volume broken into cells, typically of a molecular size, which we can fill with the fundamental building blocks in our problem (atoms, molecules, functional groups) subject to certain constraints. In this section we will concern ourselves with the mixing of rigid particles, i.e., translational degrees of freedom. More generally, lattice models can include translational, rotational, and conformational degrees of freedom of molecules.