Supramolecular bond forming / breaking moves: microscopic reversibility

The acceptance criterion for the bond forming / breaking moves is illustrated following standard simulation textbooks [1, 2, 3, 4] and earlier works [5, 6, 7, 8, 9, 10, 11], in the Fig. 1. Panel A shows the configuration before attempting to create a bond between segment 0 and one of the three potential bonding partners 1, 2, and 3 (i.e. here \( N_n = 3 \)) within the sphere of radius \( d_b \). Denoting as \( m \) the state where the bond 0 \(-\) 2 does not exist (Fig. 1A) and \( n \) where it has been formed (Fig. 1B), we require the transition probabilities to obey the condition of detailed balance.

\[
P_m P_{m \rightarrow n} = P_n P_{n \rightarrow m}
\]  

(1)

where \( P_m \) and \( P_n \) are the equilibrium probabilities of observing the states \( m \) and \( n \), while \( P_{m \rightarrow n} \) and \( P_{n \rightarrow m} \) denote the probabilities of making a transition from the state \( m \) to state \( n \) and from state \( n \) to \( m \), respectively. These transition probabilities take the form

\[
P_{m \rightarrow n} = a_{m \rightarrow n} P_{\text{acc}}^{m \rightarrow n}
\]  

(2)

where \( a_{m \rightarrow n} \) is probability, with which a transition \( m \rightarrow n \) is proposed in the course of the Monte-Carlo simulation. \( P_{\text{acc}}^{m \rightarrow n} \) denotes the probability of accepting this bond-forming attempt (see Eqs. (7) and (8) of the main text). Similarly, \( a_{n \rightarrow m} \) and \( P_{\text{acc}}^{n \rightarrow m} \) are the corresponding probabilities for the bond-breaking transition, \( n \rightarrow m \).

In the bond-forming move, \( m \rightarrow n \), one of the \( N_n \) potential bonding partners is chosen with a probability, which is proportional to the Boltzmann weight of the bonded interaction, i.e., the probability to propose the move, \( m \rightarrow n \), equals:

Figure 1: A) A sketch showing the configuration, \( m \), before attempting the formation of the 0 \(-\) 2 bond (red dashed line). The sphere containing the potential bonding partners is indicated by a dashed orange circle with radius, \( d_b \). In this specific configuration, the potential bonding partners of segment, 0, are numbered 1, 2, and 3, i.e., \( N_n = 3 \), and the number of monomers bonded to segment 0 is \( N_c = 1 \). B) A sketch of the configuration, \( n \), before attempting to break the bond and reverse the move of A. The number of potential bonding partners of segment 0 within the sphere of radius, \( d_b \), is \( \tilde{N}_n = N_n - 1 = 2 \) while the number of bonded neighbours is \( \tilde{N}_c = N_c + 1 = 2 \).
\[ a_{m \rightarrow n} = \frac{w_{01}}{w_{01} + w_{02} + w_{03}} \]  

(3)

where \( w_{0j} \) stands for the Boltzmann factor \( \exp \left[ -\frac{3}{2} b^2 (r_{0} - r_{j})^2 \right] \) of the bonded interaction. In the specific example, the number of segments bonded to 0 is \( N_c = 1 \).

In the bond-breaking attempt, one of the bonds, which is connected to segment 0, is randomly selected. Thus, the probability to propose the reverse, bond-breaking move, \( n \rightarrow m \), is:

\[ a_{nm} = \frac{1}{N_c} = \frac{1}{N_c + 1} \]  

(4)

where \( \tilde{N}_c = N_c + 1 = 2 \) denotes the number of bonded neighbours of segment 0 in Fig. 1B.

In order to fulfill detailed balance, we compute \( Z_{\text{bond}} = w_{01} + w_{02} + w_{03} \), exactly as in the bond-formation move by summing the Boltzmann factors of all segments, \( \tilde{N}_n = N_n - 1 \), that are available for bonding, 0 − 1 and 0 − 3, and, additionally, the bond, 0 − 2, which is to be broken.

Following Eq. (7) and Eq. (8) of the main text, we use the acceptance probabilities,

\[ P_{\text{acc}}^{m \rightarrow n} = \min \left[ 1, \frac{Z_{\text{bond}}}{N_c + 1} \exp \left( -\frac{E_b}{k_B T} \right) \right] \]  

(5)

and

\[ P_{\text{acc}}^{n \rightarrow m} = \min \left[ 1, \frac{\tilde{N}_c}{\tilde{N}_c - 1} \exp \left( \frac{E_b}{k_B T} \right) \right] = \min \left[ 1, \frac{N_c + 1}{Z_{\text{bond}}} \exp \left( \frac{E_b}{k_B T} \right) \right] \]  

(6)

Using the identity \( x = \frac{\min(1,x)}{\min(1,1/x)} \), we find

\[ \frac{P_{m,n}}{P_{n,m}} = w_{02} \exp \left[ -\frac{E_b}{k_B T} \right] \]  

(7)

Since the right hand side equals the ratio,

\[ \frac{P_n}{P_m} = \exp \left( -\frac{3}{2 k_B T} (r_2 - r_0)^2 - \frac{E_b}{k_B T} \right) \]  

(8)

of the equilibrium weights of the two states, the choice of acceptance probability satisfies detailed balance, Eq. (1).

References


[3] D. Frenkel and B. Smit, Understanding Molecular Simulation,


