Supramolecular bond forming / breaking moves: microscopic reversibility

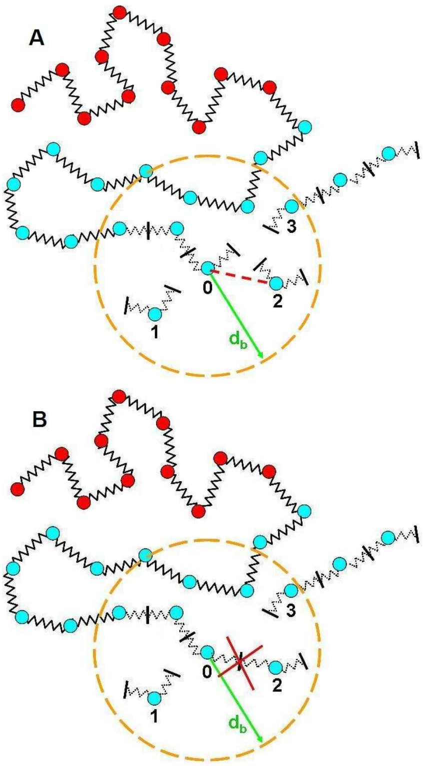

Figure 1: A) A sketch showing the configuration, m, before attempting the formation of the $0-2$ bond (red dashed line). The sphere containing the potential bonding partners is indicated by a dashed orange circle with radius, $d_{\rm b}$. In this specific configuration, the potential bonding partners of segment, 0, are numbered 1, 2, and 3, i.e., $N_{\rm n}=3$, and the number of monomers bonded to segment 0 is $N_{\rm c}=1$. 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, $d_{\rm b}$, is $\tilde{N}_{\rm n}=N_{\rm n}-1=2$ while the number of bonded neighbours is $\tilde{N}_{\rm c}=N_{\rm c}+1=2$.

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 $N_{\rm n}=3$) within the sphere of radius $d_{\rm b}$. 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.

$$P_m P_{m\to n} = P_n P_{n\to m} \tag{1}$$

where P_m and P_n are the equilibrium probabilities of observing the states m and n, while $P_{m\to n}$ and $P_{n\to m}$ 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

$$P_{m\to n} = a_{m\to n} P^{\rm acc}_{m\to n} \tag{2}$$

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

In the bond-forming move, $m\to n$, one of the $N_{\rm n}$ 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, $m\to n$, equals:

$$a_{m\to n} = \frac{w_{01}}{\underbrace{w_{01}+w_{02}+w_{03}}_{Z_{\mathrm{bond}}=\sum_{j=1}^{N_{\mathrm{n}}} w_{0j}}} \tag{3}$$

where w_{0j} stands for the Boltzmann factor $\exp\left[-\frac{3}{2b^2}\left[\mathbf{r}_0-\mathbf{r}_j\right]^2\right]$ of the bonded interaction. In the specific example, the number of segments bonded to 0 is $N_{\mathrm{c}}=1$.

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, $n\to m$, is:

$$a_{\mathrm{nm}} = \frac{1}{\tilde{N}_{\mathrm{c}}} = \frac{1}{N_{\mathrm{c}}+1} \tag{4}$$

where $\tilde{N}_{\mathrm{c}} = N_{\mathrm{c}}+1=2$ denotes the number of bonded neighbours of segment 0 in Fig. 1B.

In order to fulfil detailed balance, we compute $Z_{\mathrm{bond}} = w_{01}+w_{02}+w_{03}$, exactly as in the bond-formation move by summing the Boltzmann factors of all segments, $\tilde{N}_{\mathrm{n}} = N_{\mathrm{n}}-1$, 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,

$$P^{\mathrm{acc}}_{m\to n} = \min\left[1, \frac{Z_{\mathrm{bond}}}{N_{\mathrm{c}}+1}\exp\left[-\frac{E_{\mathrm{b}}}{k_{\mathrm{B}}T}\right]\right] \tag{5}$$

and

$$\begin{aligned} P^{\mathrm{acc}}_{n\to m} &= \min\left[1, \frac{\tilde{N}_{\mathrm{c}}}{Z_{\mathrm{bond}}}\exp\left[\frac{E_{\mathrm{b}}}{k_{\mathrm{B}}T}\right]\right] \\ &= \min\left[1, \frac{N_{\mathrm{c}}+1}{Z_{\mathrm{bond}}}\exp\left[\frac{E_{\mathrm{b}}}{k_{\mathrm{B}}T}\right]\right] \end{aligned} \tag{6}$$

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

$$\frac{P_{\mathrm{m,n}}}{P_{\mathrm{n,m}}} = w_{02}\exp\left[-\frac{E_{\mathrm{b}}}{k_{\mathrm{B}}T}\right] \tag{7}$$

Since the right hand side equals the ratio,

$$\frac{P_n}{P_m} = \exp\left[-\frac{3}{2b^2}(\mathbf{r}_2-\mathbf{r}_0)^2 - \frac{E_{\mathrm{b}}}{k_{\mathrm{B}}T}\right] \tag{8}$$

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

References

[1] K. Binder, *Monte Carlo and Molecular Dynamics Simulations in Polymer Science*, Oxford University Press: New York,1995.

[2] D.N. Theodorou and M. Kotelyanskii, Eds. *Simulation Methods for Polymers*, Marcel Dekker: New York, 2004.

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

[4] M.P. Allen and D.J. Tildesley, *Computer Simulations of Liquids*, Oxford University Press: New York, 1991.

[5] M. Müller and K. Binder, *Macromolecules*, 1995, **28**, 1825.

[6] M. Müller and N.B. Wilding, *Phys. Rev. E*, 1996,**51** 2079.

[7] J.P. Wittmer, A. Milchev, and M.E. Cates, *J. Chem. Phys*, 1998, **109**, 834.

[8] A. Milchev, J.P. Wittmer, and D.P. Landau, *Phys. Rev. E*, 2000, **61**, 2959.

[9] C.C. Huang, H. Xu, F. Crevel, J. Wittmer, and J.P. Ryckaert, *Lect. Notes Phys.*, 2006, **704**, 379.

[10] C.C. Chen and E.E. Dormidontova, *Macromolecules*, 2004, **37**, 3905.

[11] C.C. Chen and E.E. Dormidontova, *Macromolecules*, 2006, **39**, 9528.

Supplementary Material (ESI) for Soft Matter