

# Supporting Information for “Disentanglement of Two Single Polymer Chains: Contacts and Knots”

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## Monte Carlo Sampling

In order to sample the phase space of long chains efficiently, we utilized the Pruned-Enriched Rosenbluth Method (PERM) first described by Grassberger,<sup>1</sup> which corresponds to a stochastic chain-growth scheme. Each configuration  $\{\mathbf{R}_n\}$  of length  $N$  ( $n = 1, \dots, N$ ) is reweighted by its Rosenbluth weight

$$W_N = \prod_{n=1}^N w_n, \quad (1)$$

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where the individual, monomeric weights  $w_n$  are given by the Boltzmann factors of  $k$  random trial directions:

$$w_n = \sum_{m=1}^k \exp \left( -\frac{u(\mathbf{R}_1, \dots, \mathbf{R}_n^{(m)})}{k_B T} \right) \quad (2)$$

Here,  $u(\mathbf{R}_1, \dots, \mathbf{R}_n^{(m)})$  contains the energetic interaction of the trial move  $m$  for monomer  $n$  with all previously grown monomers  $1, \dots, n-1$ . Out of the  $k$  trial directions, one is chosen with probability  $p_m \propto \exp(-u(\mathbf{R}_1, \dots, \mathbf{R}_n^{(m)})/(k_B T))$ . After having generated a set of  $M$  chains of length  $n$ , the average of any thermodynamic quantity  $A$  may then be evaluated as

$$\langle A \rangle = \frac{\sum_{i=1}^M A_i W_{N,i}}{\sum_{i=1}^M W_{N,i}}. \quad (3)$$

What sets the PERM algorithm apart from simple Rosenbluth sampling is that it suppresses the fluctuations of the  $W_{N,i}$ , which become especially severe in the limit of long chains, via population control. To this end, we calculated the ratio  $r$  of the current weight  $W_{N,i}$  and the average weight during each growth step, i.e.  $r = W_{N,i}/\langle W_N \rangle$ , as proposed by Prellberg *et al.*<sup>2</sup> If  $r > 1$ ,  $\lfloor r \rfloor + 1$  copies of the current configuration are created with probability  $p = r - \lfloor r \rfloor$  (with  $\lfloor r \rfloor$  being the closest integer value smaller than  $r$ ), or, alternatively,  $\lfloor r \rfloor$  copies are made with  $1 - p$ . This is done in a depth-first implementation, so that several configurations branch off from a single parent structure. On the other hand, if  $r < 1$ , the current branch is stopped with probability  $p = 1 - r$ . In either case, one sets  $W_{N,i} \leftarrow \langle W_N \rangle$ . All structural quantities were computed on the fly (see ref 3).

To increase the performance of our code, we employed a neighbor-list scheme as described elsewhere,<sup>3</sup> which makes the energy calculation (roughly) independent of chain size. In the remaining steps during which the neighbor list for a given monomer  $n$  is constructed, we additionally exploited the chain connectivity in the following way: If one considers two remote monomers  $n$  and  $m$  ( $n > m$ ) separated by  $r_{nm} \gg r_{\text{cut}}$  ( $r_{\text{cut}}$  being the cutoff radius of the Lennard-Jones potential), one can skip the next  $m' = \lfloor (r_{nm} - r_{\text{cut}})/b_{\text{max}} \rfloor$  monomers (i.e.  $m+1, \dots, m+m'$ ) in the energy evaluation, where  $b_{\text{max}} = 1.4\sigma$  is an arbitrary upper limit for the bond length (note that our choice of  $b_{\text{max}}$  involves a thermal activation of about  $100k_B T$ ). In this manner, the original

computational cost (complexity of  $\mathcal{O}(N)$  at each step  $n$  due to the fact that all interactions with the previously grown monomers have to be calculated, giving rise to a total complexity of  $\mathcal{O}(N^2)$ ) is drastically reduced. This algorithm – in combination with neighbor lists – has also been used in the MD simulations.

## Determination of the $\Theta$ -Temperature

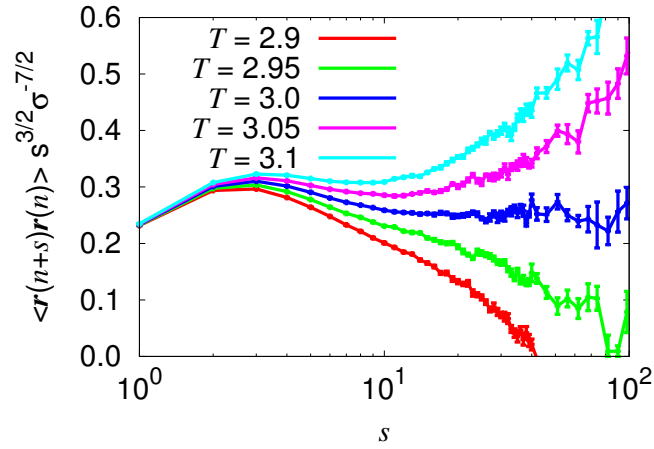


Figure 1: Bond-vector autocorrelation function  $\langle \mathbf{r}(n+s) \cdot \mathbf{r}(n) \rangle$  between two bond vectors  $n$  and  $m$  separated by  $s = |n - m|$  other monomers.

In order to determine the  $\Theta$ -point, we use the predictions by Shirvanyants *et al.*<sup>4</sup> for the bond-vector autocorrelation function  $\langle \mathbf{r}(n+s) \cdot \mathbf{r}(n) \rangle$  between two distinct bonds separated by  $s$  other bonds. This is due to the fact that this quantity has been proven to be highly sensitive to a zero or non-zero second virial coefficient. In particular, at  $T = \Theta$ , one has<sup>4</sup>  $\langle \mathbf{r}(n+s) \cdot \mathbf{r}(n) \rangle \propto s^{-3/2}$ . Figure 1 shows  $\langle \mathbf{r}(n+s) \cdot \mathbf{r}(n) \rangle s^{3/2}$  for a chain of length  $N = 10000$  monomers at various temperatures around  $\Theta$ . While for small  $s$  the curves are dominated by the details of the chain chemistry (i.e. the local packing of the beads in case of our simulation model), the expected power law  $\langle \mathbf{r}(n+s) \cdot \mathbf{r}(n) \rangle \propto s^{-3/2}$  emerges for larger  $s$  at  $T = \Theta \approx 3.0$ .

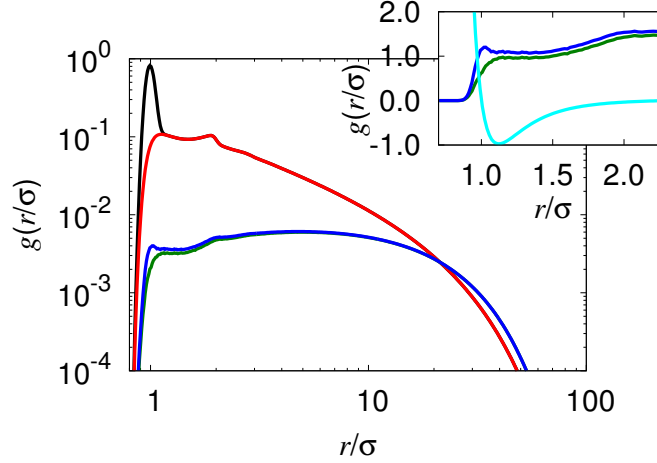


Figure 2: Pair correlation functions for various types of monomer pairs: all monomer pairs (black curve), all monomer pairs without nearest neighbors (red), monomer pairs between distinct halves (blue) and monomer pairs between distinct halves without the two central monomers (green). The inset shows the short-distance regime in combination with the nonbonded interaction potential, *i. e.* the Lennard-Jones potential (cyan).

## Pair Correlation Function

Figure 2 shows the pair correlation function  $g(r)$  for all monomer pairs and for monomer pairs from distinct halves. For the latter, the pair arising from the trivial, central bond has been neglected. The inset shows the regime of short distances in combination with the monomeric interaction potential (Lennard-Jones potential).

## Separation Criterion in the MD Simulations

The time  $\tau$  for a given configuration to disentangle is measured as follows: After each MD step we compute the centers of mass  $\mathbf{R}_{c1}$  and  $\mathbf{R}_{c2}$  for both half-chains and  $\mathbf{d}_c = \mathbf{R}_{c2} - \mathbf{R}_{c1}$ . Then, we project the monomer positions onto the unit vector  $\hat{\mathbf{d}}_c$ . If all projections of the first half are lower than any projection of the second half, the two subchains are regarded as disentangled, since they can then be separated by a plane orthogonal to  $\mathbf{d}_c$ . This criterion is illustrated in Figure 3 via snapshots of three successive stages in the MD simulations. The graphs in the lower half show the smoothed monomer densities projected onto this coordinate at each stage.

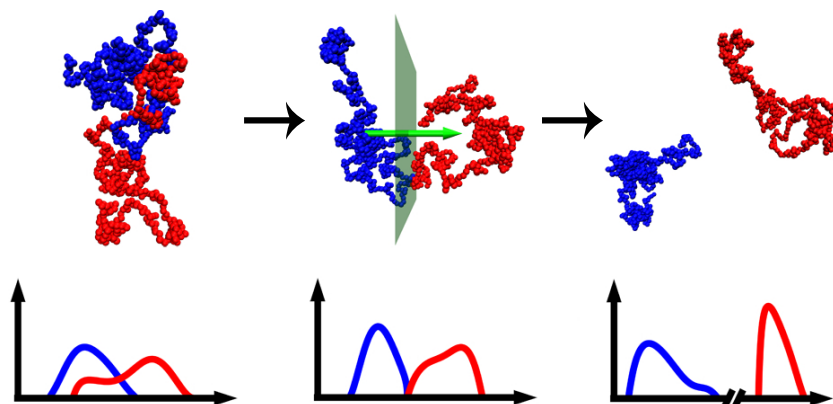


Figure 3: Snapshots of the disentanglement process in the MD simulations: entangled starting configuration (left), disentanglement and loss of topological constraints (center) and ultimate separation (right). Two subchains are considered as disentangled if both halves can be separated by a plane (green square in the central snapshot) perpendicular to the vector connecting their respective centers of mass (green arrow). The graphs show the smoothed monomer densities projected onto this coordinate at each stage. All snapshots have been created with VMD.<sup>5</sup>

## References

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