Radial Distribution Functions of Entanglements in Primitive Chain Network Simulations

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Although the entanglement network among polymers has been widely investigated, the spatial distribution of entanglement nodes has been rarely discussed. In this study, we obtained the radial distribution functions (RDFs) for the entanglement nodes from the snapshots of multi-chain slip-link simulations. The model employed in this study is the primitive chain network (PCN) model, which has been validated to reproduce the entangled polymer dynamics semi-quantitatively. The statistics of captured entanglement networks were compared to those reported for the primitive path network extracted by the CReTA procedure from the full-atomistic molecular model of a polyethylene melt. In the range of distance longer than the average strand length, the network structure from PCN does not show any structural correlation, and the intra-chain correlation is close to that for Gaussian chains with non-interacting slip-links. These features are consistent with the CReTA network and the conventional assumptions made for single-chain models. Meanwhile, in the short-range, the structural correlation in PCN is much weaker than that in CReTA. This discrepancy is because the short-range structure in PCN is realized as a result of imposed fluctuations, whereas it is determined by the minimization of the primitive path in CReTA.

Key Words: Viscoelasticity / Entangled polymers / Polymer dynamics / Molecular simulations

1. INTRODUCTION

In analogous to rubber elasticity, the plateau modulus $G_0$ of entangled polymers is related to the number density of entanglement between polymers $v$, often translated into the entanglement molecular weight $M_1$[7]. For the single-chain models like the tube model, $M_e$ is considered as the segment size that characterizes the motional constraint of the test chain[8-10]. Specifically, $M_e$ is used as a parameter to determine the tube segment number per chain $Z$ from the molecular weight $M$ by the relation $Z = M/M_e$. The unit of time is defined from the Rouse time of the segment with the molecular weight of $M_e$. The theories based on this framework have achieved remarkable success in reproducing the rheology of entangled polymers[11, 12].

Because of the stochastic process for the creation of entanglement between polymers, $M_e$ and $Z$ must have distributions as reported by lots of studies[13-20]. Naively, each entanglement emerges randomly along the test chain with a Poisson process. For this case, the number distribution of monomers between consecutive entanglements exhibits a single exponential decay[13, 14]. In contrast, Tzoumanekas and Theodorou[15] reported a non-monotonic distribution function with a peak followed by an exponential-like decay. They explained this behavior by considering a blocking event in addition to the emergence of entanglement. Greco[16] argued that finite-size effects must be considered because the entanglement segment accommodates a limited number of monomers. His distribution function thus derived is similar to that reported by Tzoumanekas and Theodorou. Uneyama and Masubuchi[20] proposed another functional form according to the repulsive nature between neighboring entanglements.

Because the entanglement structure is hardly observed experimentally, the theoretical predictions for the distributions have been evaluated by molecular simulations. Among different proposed methodologies[16, 21-24], the contour-length minimization method[16, 22, 25] allows us to specify every single entanglement point dispersed in the system. Tzoumanekas and Theodorou[16] developed such a computation code, the so-called CReTA, to report the statistics of entanglements. The network statistics along the chain are consistent with the theories mentioned in the previous paragraph. The difference
among the theories falls within the statistical error for the simulations.

Besides, Tzoumanekas and Theodorou\cite{16} reported the radial distribution function (RDF) of entanglements. To the best of our knowledge, RDF of entanglement has not been reported from the other methods. Nevertheless, the RDF from CReTA corresponds to an ideal gas for the range longer than the average subchain length, showing no specific structural correlation between entanglements. Meanwhile, in the short-range, RDF shows a strong pair-correlation for which the mechanism is unknown. One may argue that RDF can be calculated from the entanglement statistics along the chain and the pair-correlation function of the Kuhn segments. But such calculation is not straightforward if the binary nature of entanglement is explicitly considered for multi-chain systems. Tzoumanekas and Theodorou\cite{16} speculated that the directional correlations between entanglement segments and the polydispersity of the segment length play some roles for the short-range correlation.

However, we note that the short-range structure seen in their RDF is affected by their methodology. In the CReTA scheme, non-Gaussianity is inevitably introduced to the primitive paths. In the equilibrated melt, the full-atomic chain is fairly represented by a Gaussian chain in the length scale above the persistent length. The CReTA extracts the entanglement network from such a snapshot by shrinking and thinning the chains. During this process, each entanglement point moves from the original position of the atom. This perturbation does not disturb the chain statistics above the entanglement mesh size because the crossing between segments is prohibited, and the chain ends are pinned at their original position. But the procedure affects the short-range structure below the entanglement mesh.

The question that arises at this point is how to evaluate the RDF of CReTA. We recall that the term entanglement was originally introduced for the dynamics of concentrated polymeric liquids with high molecular weights. For such liquids, the polymer dynamics is retarded from the Rouse prediction, and the viscoelasticity exhibits the plateau behavior following the Rouse relaxation before the terminal relaxation. Even though we can obtain the characteristic molecular weight from the plateau modulus according to the rubber theory, the relation is unknown between the retarded polymer dynamics and the entwined structure among polymer chains seen in the snapshot of molecular simulations as argued by Bisbee \textit{et al.}\cite{24}.

A possible approach to this problem is the comparison of RDF with that observed for a network model, which is constructed to reproduce the entangled polymer dynamics. A few coarse-grained models have been proposed in which the motion of polymers is calculated as the kinetics of a temporal network\cite{11, 12, 26-30}. The network structure in these models is not based on the entwined structure of real polymers, but it is realized as a result of the dynamics. If the network model represents real polymers, the network structure coincides with that extracted from the entwined polymers. In fact, the entanglement statistics along each chain, such as the distributions of $M_e$ and $Z_e$ are in reasonable agreement between CReTA and one of the network models as reported earlier\cite{18}. But the RDF has never been examined.

In this study, we obtained RDF of entanglement points for the multi-chain slip-link model, the so-called primitive chain network (PCN) model\cite{26}. We confirmed that the statistics along the chain are consistent with the earlier studies mentioned above, as reported previously\cite{18, 20}. The RDF exhibits no spatial correlation in the long-range, being entirely consistent with the CReTA\cite{16}. In contrast, the short-range correlation is much weaker than CReTA. Our results imply that the strong short-range correlation reported for the atomistic simulations is not due to the intrinsic nature of the entanglement network but model-dependent. Details are shown below.

\section{2. MODEL AND SIMULATIONS}

In the PCN model, an entangled polymer melt is replaced by a network consisting of nodes, strands, and dangling ends. Each polymer chain corresponds to a path connecting two dangling ends via several nodes and strands. From each node, four strands diverge according to the binary assumption of entanglement. The diverging strands are bundled by a slip-link, which allows the chain to slide along its contour, restricting the perpendicular motion. The state variables of the system are the position of the nodes and the dangling ends $\{R\}$, the number of Kuhn segments on each strand and dangling segment $\{n\}$, and the number of dangling and network strands for each chain $\{Z\}$. The time development of $\{R\}$ obeys a Langevin-type kinetic equation. The force balance is considered among the drag force, the tension acting on each segment, the osmotic force suppressing the density fluctuations, and the thermal random force. The change of $\{n\}$ with time corresponds to the chain sliding, and it is described by the change rate equation, in which the same force balance with $\{R\}$ is considered along the chain. The slip-link is removed when the chain slides off. Vice versa, a new slip-link is created on the dangling end, which protrudes from the
anchored node beyond a certain threshold due to the chain sliding. For simplicity, we employed the original scheme for the creation and destruction of the slip-links\(^\text{18}\). Namely, we set an allowed window for the Kuhn segment number on each dangling end as \(0.5 \leq n / \langle n \rangle \leq 1.5\), where \(\langle n \rangle\) is the average number of Kuhn segments on the single strand. If \(n\) exceeds the upper or lower threshold, the creation or destruction scheme is triggered. See the previous publications for further details\(^{26, 31-34}\).

We simulated linear monodisperse polymer melts with various molecular weights and densities. We mainly employ the average segment number per chain of \(\langle Z \rangle = 33\) and the segment density at \(C = 5.5\). The melt with these parameters corresponds to the full atomistic simulation\(^{16}\) for a polyethylene melt with the number of carbon atoms per chain of 1,000, as shown later. Our units of length, energy, and time are the average segment length \(\langle a \rangle\), the thermal energy \(kT\), and the diffusion time of the single segment \(\tau = \zeta \langle n \rangle \langle a \rangle^2 / 6kT\), respectively. Here, \(\zeta\) is the friction of the Kuhn segment. Periodic boundary conditions were utilized for the cubic simulation box with the box dimension of \(16^3\), which is sufficiently large to accommodate the examined chains, as shown in Fig. 1.

After sufficient equilibration, we evaluated the RDF of the system following the study by Tzoumanekas and Theodorou\(^{16}\). They decomposed the total RDF according to common polymer chains in the subjected pair of entanglements. We recall that four polymer chains are involved in a pair of entanglements because each entanglement consists of two polymer chains due to the binary assumption. RDF-0 stands for the pair-correlation calculated for the pair of entanglements, for which all the four involved chains are different. RDF-1 is obtained between the entanglements that share one polymer chain, whereas the other two chains are different. RDF-2 is for the entanglements formed by two like chains, including self-entanglements created within single chains. For a schematic representation of these RDFs, see Fig. 11 in Ref. 16. During the equilibrium calculation, the stress fluctuation was recorded, and converted to the linear relaxation modulus \(G(t)\) via the Green-Kubo formula.

3. RESULTS

3.1 Entanglement statistics along the chain

Before comparing RDF, let us confirm the consistency of PCN with CReTA\(^{16}\) for the distribution functions along the chain contour. Fig. 2 shows the distributions for the number of Kuhn segments on each strand \(P(n)\) and the strand...
number per chain \( P(Z) \). In the top panel, as mentioned in the introduction, \( P(n) \) does not exhibit single exponential decay, but it shows a peak, implying the repulsive nature between consecutive entanglements\(^{16,17,20}\). There is a spike at a short-range for PCN due to the cut-off employed for numerical convenience. Apart from this artifact, the PCN result reasonably coincides with that for CReTA, except the range \( n \geq 4 \), for which the statistics for CReTA seem insufficient. Indeed, the full-atomistic system has only 8 chains, and the simulation box dimension is 4.4\( \langle a \rangle \). The bottom panel shows \( P(Z) \), which is close to a Gaussian distribution. The segment density for PCN does not affect these distribution functions. Details for these distribution functions have been reported earlier\(^{18,20}\).

3.2 RDF compared with CReTA

Figure 3 shows the obtained RDFs for the PCN simulations with \( (Z) = 33 \) and \( C = 5.5 \) in comparison to those for CReTA of polyethylene, for which \( (a) = 14\AA\)\(^{16}\). The total RDF (shown in black) indicates no specific structural correlation in the distance longer than the average segment length \( (r/(a) \geq 1.0) \). The main contribution to the total RDF in this range comes from RDF-0 (blue). The contributions from the other RDFs are relatively small since these RDFs decay being consistent with the intra-chain pair-correlation. All RDFs from PCN are in reasonable agreement with those from CReTA in this range.

In contrast, in the short-range \( (r/(a) < 1.0) \), RDFs for PCN largely deviate from those for CReTA. The total RDF shows a correlation hole, which indicates a repulsion between entanglements at \( r/(a) \sim 1.0 \) for PCN, but it locates at \( r/(a) \sim 0.5 \) for CReTA. This discrepancy in the location of the correlation hall is mainly due to the difference of RDF-0, which is significantly larger for PCN than that for CReTA in the short-range. RDF-1 and RDF-2 for PCN are also more extensive than those for CReTA. These results mean that the overlap between different chains is suppressed in CReTA.

3.3 RDF for various segment densities

To see the effect of chain overlapping on RDFs, we conducted PCN simulations with various segment densities, and the obtained RDFs are shown in Fig. 4. The total RDF (top panel) reflects these RDFs, and it approaches that of an ideal gas as the segment density increases. The second panel shows that, with decreasing the value of \( C \), RDF-0 decreases because the interpenetration between different chains is reduced. Vice versa, RDF-1 and RDF-2 (two panels from the bottom) increase with decreasing \( C \), demonstrating the relative growth of intra-chain correlation. This density dependence of RDF is reasonable since the PCN is designed to simulate the entangled dynamics of phantom chains.

With the CReTA results shown by symbol, RDFs obtained for PCN at \( C = 5.5 \) (blue) are in good agreement in the long-range, as shown in Fig. 3. To be fair, we note that this segment density in PCN is not consistent with the simulation condition for the corresponding full atomistic simulation. The atomistic system contains 8 chains, and the average number of entanglement segments per chain is \( (Z) = 33 \) as shown in Fig. 2. For the atomistic simulation, the box dimension is 4.4\( \langle a \rangle \), which gives the segment density of ca. 3. In this respect, we should compare the PCN result for \( C = 2.6 \) or 3.5 to CReTA, but RDFs for these \( C \) values are discrepant from the atomistic system. Meanwhile, the entanglement density obtained experimentally is larger than \( C = 5.5 \). Lin\(^3\) reported the number of entanglement strands per cubed tube diameter \( n_t \) for various polymers, and the value for polyethylene is \( n_t = 17.7 \). This value is obtained for the entanglement segment concerning Graesslay’s definition for \( M_e \)\(^{1,1,10}\). Namely, this number density is for the entanglement segment that carries the entanglement molecular weight defined as \( M_e = (4/5)\rho RT / G_0^N \). Here, \( \rho = 0.802 \text{ g/cm}^3 \) is the polymer density, \( G_0^N = 0.27 \text{ GPa} \) is the plateau modulus, \( T = 373 \text{ K} \) is the temperature, and \( M_e = 737 \) is thus obtained. According to this \( M_e^0 \) value, the number of entanglement segments per chain for PE1000 is \( Z^0 = 19 \), which is much smaller than our employed value \( (Z) = 33 \). This discrepancy is due to the fluctuations around entanglements considered in PCN\(^7\), 18, 35-37).
From the value of \( n_t \) and the ratio of \( Z^G / Z = 0.57 \), the \( C \) value concerning Lin’s data is calculated as \( C = 7.4 \) (\( = 17.7 \times 0.57^{3/2} \)). The difference of \( C \) values for CReTA and Lin’s data is due to several reasons, including the difference in \( \rho \) and the experimental evaluation of \( G^0_R \). Nevertheless, \( C = 5.5 \) for PCN is within a reasonable range of uncertainty, and we consider it a fitting parameter.

Concerning RDF-1, the decay is consistent with that expected for a Gaussian chain in the long-range, as discussed later. However, in the short-range, the simulation results deviate from this Gaussian behavior. For CReTA, RDF-1 exhibits an upward deviation. Tzoumanekas and Theodorou\(^{16}\) suggested that this steep decay of RDF-1 is related to the intrinsic nature of the entanglement network, in which the strand length is polydispersed, and each entanglement node is stochastically formed by a binary contact. In contrast, RDF-1 becomes flat for PCN, reflecting the lack of detailed structure due to the employed coarse-graining. This comparison between CReTA and PCN connotes that the strong pair-correlation in CReTA is not due to the intrinsic nature of the entanglement network but due to the network structure in the length scale smaller than the entanglement mesh.

### 3.4 Viscoelastic relaxation for various segment densities

As seen in Fig. 4, the segment density affects the structure of the entanglement network. As the density decreases, the amount of intra-chain entanglement increases because the overlapping between chains is suppressed. In PCN simulations, the intra-chain entanglement does not sustain the orientational memory because of the imposed fluctuations at the entanglement. In this respect, the relaxation of the system is accelerated by an increase in intra-chain entanglement. We examine this argument in Fig. 5, where the viscoelastic relaxation \( G(t) \) is shown for various segment densities. In harmony with the discussion above, we see that \( G(t) \) for large \( C \) values relax slower than that for small \( C \). This result implies that the effect of \( C \) must be carefully considered. But unfortunately, \( G(t) \) is not available for the discussed full-atomistic system, and we cannot evaluate our result for this case.

According to the earlier studies\(^2, 3, 38-40\), the entanglement density is similar for various polymer melts. In this respect, the effect of \( C \) on rheology may be concealed in the modeling of melt rheology. For instance, for the PCN simulations performed in the earlier studies, \( C \) value has been fixed at 10, with which the simulation results are in semi-quantitative agreement with experiments for \( G(t) \) and other rheological properties. A possible direction for further investigation would be the cases for stiff polymers and non-\( \Theta \) solutions, but those systems are out of scope for the present study.

### 3.5 RDF for various molecular weights

One may argue that the RDFs depend on the molecular weight because the magnitude of chain overlapping varies...
not only due to the density but also by the chain dimension. Figure 6 shows the RDFs for various \(Z\) from PCN simulations at \(C = 5.5\). Due to the chain dimension, the decay of RDF-1 becomes longer with increasing \(Z\). Because the extended chain suppresses the interpenetration between different chains, RDF-0 decreases with increasing \(Z\). RDF-2 increases with increasing \(Z\), demonstrating the rise in self-entanglements, but only slightly. Nevertheless, the \(Z\) dependence seen in different RDFs compensates for each other, and the total RDF is insensitive to the molecular weight.

4. DISCUSSION

4.1 RDF-1 for a Gaussian chain with slip-links

In this section, we describe RDF-1 from the Gaussian chain statistics and the entanglement statistics along the chain to analyze the results from PCN and CReTA. Let us consider a single Gaussian chain, on which some slip-links are randomly distributed. If the slip-links do not interact with each other, the number of Kuhn segments between consecutive slip-links \(n\) obeys the following probability distribution.

\[
P(n) = \frac{1}{N_0} \exp \left( -\frac{n}{N_0} \right) \tag{1}
\]

Here, \(N_0\) is a parameter, and \(\langle n \rangle = \int nP(n)dn = N_0\). For a subchain having \(n\) segments, the probability distribution of the end-to-end vector \(Q\) is given as the Gaussian distribution.

\[
P(Q|n) = \left( \frac{3}{2\pi m b^2} \right)^{3/2} \exp \left( -\frac{3Q^2}{2n b^2} \right) \tag{2}
\]

Here, \(b\) is the length of the single Kuhn segment. From eqs 1 and 2, the distribution for \(Q\) is obtained as

\[
P(Q) = \int_0^\infty dn P(Q|n)P(n) = \frac{3}{2\pi \rho N_0 b^2} \exp \left[ -\frac{6}{(N_0 b^2)} \right] \tag{3}
\]

The RDF-1 can be given by \(P(Q)\) as

\[
g_1(r) = \frac{1}{\rho} P(Q)|_{r=0} = \frac{3}{2\pi \rho N_0 b^2} \exp \left[ -\frac{6}{(N_0 b^2)} \right] \tag{4}
\]

Here, \(\rho\) is the number density of the slip-links. For convenience, we simplify eq (4) by employing the dimensionless length \(\tilde{r} = r/(|Q|)\), where \(|Q| = 2(N_0 b^2/6)^{1/2}\) from eq 3. The simplified form is given as

\[
g_1(\tilde{r}) = \frac{1}{8\pi \tilde{r}^2} \exp \left[ -2\tilde{r}^2 \right] \tag{5}
\]

Here, \(\tilde{\rho} = \rho (|Q|)^2\). Eq 5 is shown in comparison to the results from PCN and CReTA in Fig. 7, in which the decay in the long-range at \(r > 0.4\) is consistent with the data. To be fair, we note that the parameters \(|Q|\) and \(\tilde{\rho}\) are artificially chosen for the fitting.

Meanwhile, RDF-1 in the short-range do not coincide with each other. Because RDF-1 is determined from \(P(n)\) and \(P(Q|n)\), the discrepancy is due to these distributions. For instance, \(P(n)\) for PCN is different from eq 1 due to the repulsive interaction between slip-links as discussed earlier. According to that \(P(n)\), RDF-1 for PCN is expected to be a constant at \(r = 0\) as seen in Fig. 7.

One may argue that \(P(n)\) given by eq (1) is inconsistent with the results shown in Fig. 1. We note that \(P(n)\) in Fig. 1 is for the chains after the primitive path analysis, in which we pull the chains with fixing the position of slip-links and the chain ends to minimize the total potential energy given as

\[
U = \sum_r \frac{Z}{2} k \frac{Q_i^2}{n_i} \tag{6}
\]

Here, \(Z\) is the number of primitive path segments and \(k\) is the spring constant. Let us minimize \(U\) with respect to \(n_i\) under the constraint of \(\sum_i n_i = N\), where \(N\) is the total number of Kuhn segments on the test chain. The result is expressed as follows with the Lagrange multiplier \(\lambda^2\).
\[ \frac{Q^2}{n_0^2} = \lambda^2 \]  

This \( \lambda \) is given as

\[ \lambda = \frac{1}{N} \sum_{i=1}^{Z} |Q_i| \approx \frac{1}{N} \frac{N}{N_0} \langle |Q| \rangle = \left( \frac{2b^2}{3N_0} \right)^{\frac{1}{2}} \]  

Here, we obtain \( \lambda \) by approximating \( Z \sim N/N_0 \) and \( |Q_i| \sim \langle |Q| \rangle \).

From eqs 7 and 8, we have

\[ n_1 = \left( \frac{3N_0}{2b^2} \right)^{\frac{1}{2}} |Q| \]  

\( P(n) \) for the primitive path with the minimized total potential energy can be derived from eqs 3 and 9 as

\[ P(n) = \int dQ \delta \left( n - \left( \frac{3N_0}{2b^2} \right)^{\frac{1}{2}} |Q| \right) P(Q) = \frac{4n}{N_0} \exp \left( -\frac{2n}{N_0} \right) \]  

By employing the dimensionless Kuhn segment number \( \bar{n} = n/N_0 \), we have the following simplified form.

\[ P(\bar{n}) = 4\bar{n} \exp(-2\bar{n}) \]  

Eq 11 is shown in Fig. 8 in comparison to the results from PCN and CReTA, demonstrating good agreement without any fitting parameters in the range \( n \geq 0.3 \). This result is consistent with RDF-1 shown in Fig. 7. Note that we have proposed \( P(n) \) with considering the interaction between slip-links to describe \( P(n) \) in PCN\(^{20}\). The approximated form is written as

\[ P(n) = \frac{25}{6} \left( \frac{10n^3}{\pi N_0^2} \right)^{1/2} \exp \left( -\frac{5n}{2N_0} \right) \]  

Figure 8 demonstrates that eqs 11 and 12 are indistinguishable in the large \( n \) regime, whereas in the small \( n \) regime, eq 12 predicts a steep increase in comparison to eq 11 and the data. This result implies that the small \( n \) data strongly reflect the interaction between slip-links. Nevertheless, further discussion is difficult because the data in this \( n \) range are not in good statistics due to the inevitable numerical cut-off.

4.2 Short-range correlation

It so appears that RDFs of PCN agree with those reported by CReTA in the range longer than the average network mesh size. Namely, there exists no specific structural correlation in the total RDF, the intra-chain entanglements distribute close to that for single Gaussian chain with non-interacting slip-links, and the entanglements on different chains permeate to maintain the uniform density of entanglements. These behaviors are consistent with the conventional idea in the coarse-grained models. For instance, in the single-chain slip-link and tube models, the statistics of the primitive paths are assumed to be Gaussian, like those of the polymers in the melt.

In contrast, the short-range correlation in PCN is much
weaker than that in CReTA. In what follows, let us discuss this short-range discrepancy from the fundamental difference between CReTA and PCN.

Because CReTA extracts the network by minimizing the primitive path length, it gives information on the entanglement network as a local stable structure without fluctuation. In the original melt structure, the atoms are dispersed in an incompressible state. The CReTA process relocates their position by dragging at the entanglement kinks with thinning the chain. Such relocation separates the entanglements on different chains, as seen in the short-range repulsion of RDF-0 (see Fig. 3, blue circle), and the CReTA relocation also tightens up the knots on the same chain to induce attraction, as seen in RDF-1 and 2 (Fig. 3, red and yellow circles).

In PCN, the number of segments and their positions fluctuate over time, and the fluctuations affect the network statistics. The effect of fluctuation depends on the details of the model, such as various interactions, and it is significant below the network mesh. For instance, Okuda et al.\textsuperscript{19} reported the total RDF for a modified PCN model, in which they employed a pair-wise soft-core interaction between the entanglement segments. Their RDF exhibits a short-range repulsion as the segment overlap is suppressed in comparison to the present case. This discrepancy demonstrates that the RDFs in PCN exhibit the overlap between segments induced by the incorporated fluctuations.

**CONCLUSIONS**

The RDFs of entanglement networks were investigated for snapshots in PCN simulations. For the range longer than the average strand length, there is no specific structural correlation like an ideal gas, and the distribution of intra-chain entanglements is close to that of Gaussian chains with non-interacting slip-links. These features are consistent with the results reported for the primitive path extracted by the CReTA method from the full-atomistic simulation of polyethylene. In contrast, the short-range RDFs are different because the structure below the entanglement mesh size is realized as a result of imposed fluctuations in PCN, whereas it is determined by the minimization of the primitive path in CReTA.

Further investigation is necessary for the spatial distribution of entanglements. As mentioned above, the short-range structure seems strongly dependent on the details of the construction methodology of entanglement networks. In this respect, RDF from the other primitive path methods is worth examined since it has never been reported except CReTA. The study for coarse-grained models is also required since the short-range structure is sensitive to the fluctuations imposed on the network nodes. Although PCN has been established to describe the entangled polymer dynamics, the model is not based on a systematic coarse graining. Comparison to other multi-chain models like slip-spring models\textsuperscript{27,28} is required to validate the presented results. Another interesting direction is to observe the entanglement network in various molecular simulations, including the standard bead-spring model with varying inter-beads interactions. The effects of flows and deformations on the network statistics are worth discussing as well. Studies toward such directions are ongoing, and the results will be published elsewhere.

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