Relaxation of Rouse Modes for Unentangled Polymers Obtained by Molecular Simulations

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Although the Rouse model has been widely used to describe unentangled polymer dynamics, there are some experimental and simulation results, in which the local chain dynamics is not fully consistent with the Rouse predictions. In this study, molecular simulations by a few different molecular models were conducted to reveal the effects of inter-molecular interactions on the relaxation of Rouse modes. Kremer-Grest bead-spring simulations exhibited that the second and third Rouse modes relaxations deviate from the Rouse prediction even though the first Rouse mode relaxation is fairly consistent with the Rouse behavior. A similar deviation was observed for full-atomistic simulations of polybutadiene and polyisoprene. For dissipative particle dynamics simulations, the magnitude of deviation was much smaller. Additional Kremer-Grest simulations with various molecular weights and full-atomistic simulations without excluded volume interactions suggest that the chain rigidity and the hard-core inter-beads interactions are attributable to the deviation through short-time relaxations induced by inter-beads collisions.

Key Words: Atomistic simulations / Bead-spring simulations / Dissipative particle dynamics simulations / Rouse model / Unentangled polymers

1. INTRODUCTION

The Rouse model has been established for the description of polymer dynamics in unentangled concentrated polymeric liquids. For instance, Onogi et al. have reported that linear viscoelasticity of polystyrene melts with narrow molecular weight distributions is semi-quantitatively compatible with the Rouse prediction given that the molecular weight is lower than the onset of entanglement. Brueggeman et al. have reported similar results for several polymers in concentrated solutions. Pearson et al. measured the self-diffusion coefficient for hydrogenated polybutadiene melts in addition to the zero shear viscosity to report that the molecular weight dependence of these measures follows the Rouse prediction. Imanishi et al. have performed dielectric measurements for polyisoprene melts to report that the molecular weight dependence of dielectric relaxation time is consistent with the Rouse theory for unentangled melts. Richter et al. have shown that the dynamic structure factor for poly(ethylene-1-butene) copolymer melts obtained from neutron spin echo experiments can be described by the Rouse theory, as long as the molecular weight is smaller than the critical value for the onset of entanglement. Kremer and Grest have reported that the melts of bead-spring chains show the Rouse dynamics for the short chains. Similar results have been reported for atomistic molecular dynamics simulations for polyethylene as well.

However, a few experimental and simulation data have revealed that the polymer dynamics is not fully compatible with the Rouse theory for the local dynamics. Paul et al. have conducted atomistic molecular simulations and neutron spin echo experiments for polyethylene melts to measure the intermediate dynamic structure factor. For the wave numbers smaller than the reciprocal chain dimension, the obtained results are fairly consistent with the Rouse model as examined earlier. However, for the larger wave numbers, the results apparently deviate from the Rouse prediction. Watanabe et al. have intensively measured the dielectric relaxation for a series of dipole-inverted polyisoprene solutions to report that the eigenfunction is not compatible with the Rouse description and deviates from the sinusoidal function. Kaznessis et al. have reported similar results for bead-spring simulations.

For the discrepancies between data and Rouse predictions, there are a few possible explanations. Harnau et al. concluded that the deviation is due to the chain rigidity (CR) from the atomistic molecular simulations for polyethylenes.
for which the molecular weight is larger than that used by Paul et al.\textsuperscript{11}. A similar discussion has been made for bead-spring chains by Bulacu and van der Giessen\textsuperscript{19}. Other possible mechanisms are the excluded volume interactions (EVI) and the hydrodynamic interactions (HI). The former affects the dynamics under the global incompressibility, whereas the latter induces long-range motional coupling between segments. Note that HI in this study means the momentum conservation and not the interaction generated by the solvent flow, which does not exist in melts. For these interactions, the screening concept has been established\textsuperscript{20-22}. However, their effects on the internal relaxation modes of polymer chains in melts have not frequently been discussed. Actually, the Markovian assumption employed in the Rouse model may not be fully consistent with the local chain dynamics, if the system has EVI and HI.

In this paper, we discuss the effects of CR, EVI, and HI on the Rouse modes for unentangled polymer melt from the results of molecular simulations. We mainly performed Kremer-Grest\textsuperscript{10} bead-spring simulations (KG simulations) and dissipative particle dynamics simulations\textsuperscript{23} (DPD simulations). A few full-atomic molecular dynamics simulations (FA simulations) were also conducted for comparison. We assume that all the effects mentioned above are naturally considered in the FA simulations, as long as the inter-atomic interactions reasonably mimic the van der Waals interactions and the momentum conservation is attained in the numerical integration scheme. On the other hand, HI is not reproduced in KG simulations because of its Langevin thermostat whereas EVI and CR are neglected in DPD simulations due to the soft-core interaction. The obtained trajectory of the segments was converted to the Rouse modes, and the time auto-correlation functions of Rouse modes were compared to the Rouse prediction. For the obtained Rouse mode relaxations, all the simulation results were fairly consistent with the Rouse prediction for the first Rouse mode that corresponds to the global chain motion. However, for the higher modes, small deviations were observed, and the magnitude of deviation depends on the implemented interactions. Indeed, EVI was found to be relevant for the deviation compared to HI. The effects of CR seem not to be essential for the chains examined. Details are shown below.

2. MODEL AND SIMULATIONS

KG simulations were conducted with the standard parameters reported in the original study by Kremer and Grest\textsuperscript{10}. For this model the units of length, energy and time are chosen as the bead diameter $\sigma_{KG}$, thermal energy $k_B T$ and the standard time for Lennard-Jones (LJ) fluids $\tau_{KG} = \sqrt{\frac{\sigma_{KG}^2 m_{KG}}{\varepsilon}}$, where $m_{KG}$ and $\varepsilon$ are the bead-mass and the energy factor for the LJ interaction employed as the inter-beads interaction. The parameters were set as follows. The attractive part of LJ interaction was eliminated with the cut-off length $R_{c, KG} = 2^{1/6}$. FENE potential was employed for the chain connectivity with the spring constant $k_{KG} = 30$ and the maximum length $R_{m, KG} = 1.5$. For the Langevin thermostat, the friction coefficient was $\zeta_{KG} = 0.5$. The number of chains was fixed at 150, and the number of beads per chain was varied as 7, 15, 30, 60 and 120. After the local equilibration of randomly generated initial configurations, global equilibration via NVT simulations was made for a sufficiently long time. For the equilibrated system thus obtained, the data were acquired in additional NVT simulations, for which the simulation time was at least 10 times larger than the longest relaxation time of each system.

DPD simulations were carried out with the following parameters, for which unit of length, energy and time are chosen as the cutoff radius of the DPD potential $r_{c, DPD}$, thermal energy $k_B T$, and the DPD time $\tau_{DPD} = r_{c, DPD} \sqrt{m_{DPD}/k_B T}$. $m_{DPD}$ is the bead-mass. The repulsion parameter was $\sigma_{DPD} = 25$, the bead density $\rho_{DPD} = 3$, the spring constant $k_{DPD} = 4$, the noise amplitude for the DPD thermostat was $\sigma_{DPD} = 3$. The number of chains was fixed at 150 whereas the number of beads per chain was 30, 60, 90 and 120. For a randomly generated initial configuration, the dynamics was calculated for a sufficiently long time with NVT ensemble attained by the DPD thermostat with the parameters mentioned above.

FA simulations were performed for polybutadiene (PB) melts and a polyisoprene (PI) melt. For PB, the number of repeating units examined was 20 and 40, whereas it was 20 for PI. The set of interaction parameters used was DREIDING. As the initial configuration, 60 polymer chains were dispersed in a simulation box with a low concentration at 0.05 g/cm$^3$, for which the polymers were well-separated from each other. After sufficient equilibration of the internal structure by NVE molecular dynamics calculations, the simulation boxes were compressed by NPT calculation with Berendsen method at the pressure of 0.1 MPa and the temperature of 400 K. For the obtained systems, NVE calculations were made for further relaxation of inter-molecular structures, followed by another Berendsen calculations. Finally, long-time NPT calculations by Andersen barostat and Nose-Hoover thermostat were performed for data acquisition at the pressure of 0.1 MPa and the temperature of 400 K. The numerical integrations were attained by velocity 
Verlet method with the integration time-step at 1.0 fs. For the discussion on the effect of chain rigidity, FA simulations without the excluded volume interactions (yet with the bending and torsional forces) were additionally performed under NVT ensemble attained by Kemer-Grest thermostat.

As the models examined in this study have been used for simulations of real polymers, there must be compatibility between different models. Indeed, attempts to determine the scaling factors for temporal and spatial measures have been made, mainly focusing on the onset of entanglement \(^{10,24,25}\). Kremer and Grest \(^{10}\) have reported the entanglement molecular weight for their model as ca. 35 beads. This value is smaller than that reported in the recent studies \(^{26-28}\). Nevertheless, owing to the experimentally determined values for the entanglement molecular weight \(^{29}\), a direct comparison between atomistic and KG models can be made for specific chemistries. In a rough comparison in such a way, one bead in KG model carries a few repeating units for polybutadiene\(^{10}\). For DPD model, however, this strategy does not work because the original DPD does not exhibit entangled polymer dynamics \(^{30}\). A possible option would be the comparison of chain conformation, which is not perfectly Gaussian for KG and even DPD. According to the results on the mean square internal distances reported by Auhl \ et al. \(^{31}\) and Langeloth et al. \(^{32}\), one DPD bead roughly corresponds to two KG beads. From the molecular weight dependence of square end-to-end distance, the Kuhn length estimated in our simulations is 1.1 \(\sigma_{KG}\), 0.95 \(r_{SP}\), and 13 Å for KG, DPD and full-atomistic polybutadiene. For polybutadiene it roughly corresponds to 4 repeating units. Note that further detailed analysis is necessary for a rigorous comparison, which is out of the scope of this study.

For all the simulations, the simulation code COGNAC90 included in OCTA \(^{33}\) was used. The simulations were performed in our computer cluster mainly equipped with Intel Xeon E5-2690 2.60 GHz. For KG and DPD simulations, the results from four different initial configurations were averaged, whereas single simulation run was made for FA simulations.

### 3. RESULTS

Hereafter, the auto-correlation function of Rouse modes is in focus. The Rouse modes \(\mathbf{X}_p(t)\) are obtained from the simulation trajectories by the following equation \(^{34}\).

\[
\mathbf{X}_p(t) = \frac{1}{N} \sum_{i=1}^{N} \mathbf{r}_i(t) \cos \left( \frac{2\pi}{N-1} (i-1) \right) - \frac{1}{2N} \left( \mathbf{r}_1(t) + \mathbf{r}_N(t) \right)
\]  

Here, \(N\) is the total number of atoms or beads along the main chain, and \(\mathbf{r}_i(t)\) is the position of \(i\)-th atom or bead. \(p\) is the mode index. For \(\mathbf{X}_p(t)\), the auto-correlation function can be defined as follows.

\[
C_p(\tau) = \frac{\langle \mathbf{X}_p(t) \cdot \mathbf{X}_p(0) \rangle}{\langle \mathbf{X}_p(0) \cdot \mathbf{X}_p(0) \rangle}
\]  

Here, \(\langle \cdots \rangle\) means the ensemble average for the time origin. By definition, \(C_p(\tau)\) for large \(p\) corresponds to the internal local chain dynamics. For the Rouse model, \(C_p(\tau)\) is written as

\[
C_p(\tau) = \exp \left( -\frac{\tau}{\tau_1} \right)
\]

Here, \(\tau_1\) is the longest relaxation time for \(p = 1\). It has been confirmed in our analysis that \(C_p(\tau)\) for freely jointed bead-spring chain without EVI, HI and CR coincides with the Rouse prediction within a numerical error, which is much smaller than the deviations discussed below.

It is fair to note that, as mentioned above, Watanabe et al. \(^{14-16}\) and Kaznessis et al. \(^{17}\) have revealed that the eigenfunction deviates from the sinusoidal function. In this respect, the Rouse mode analysis attempted in this study is different from the normal mode analysis. In other words, the Rouse modes may not be orthogonal with each other. However, since the exact form of eigenfunction has been unknown, we use eq 1 to discuss the relaxation behavior assuming that the eigenfunction is not significantly different from the sinusoidal function, and the Rouse modes are orthogonal. Indeed, the earlier results \(^{17}\) have shown that for \(p < 4\) the eigenfunction is fairly close to the sinusoidal function. It has also been noted that Bulacu and van der Giessen \(^{19}\) have utilized the sinusoidal eigenfunction to discuss the effect of chain stiffness on the normal modes for bead-spring simulations even for larger values of \(p\). Hirao et al. \(^{35}\) have obtained the exact eigenfunction numerically using the variational method \(^{36}\) for single Kremer-Grest chain floating in vacuum to report that the obtained function is virtually identical to sinusoidal function for \(p \leq 4\). Hagita et al. \(^{37}\) have applied the variational method to obtain the relaxation time for normal modes for polymer melts simulated via dynamic Monte Carlo. They mentioned that the eigenfunction is close to sinusoidal function for \(p \leq 2\).

Figure 1 shows \(C_p(\tau)\) for KG simulations with various chain length for \(p = 1, 2\) and 3. The longest relaxation time \(\tau_1\) was determined by the fitting of \(C_p(\tau)\) to the single exponential decay and summarized in Table I. For all the chain length examined, \(C_p(\tau)\) is close to the Rouse prediction, including
the relaxation time for each mode, as earlier reported\textsuperscript{34}. However, a deviation of $C_p(\tau)$ from the Rouse prediction is apparently observed for the second and third Rouse modes. Indeed, the calculated $C_2(\tau)$ and $C_3(\tau)$ are smaller than that of the Rouse curve (solid line). For clarity, in Fig. 2 the ratio of the calculated $C_p(\tau)$ to the Rouse prediction $C_{R_p}(\tau)$ is shown.

Owing to CR, the short chains with $N \leq 30$ the magnitude of deviation decreases with increasing the chain length. Conversely, for the long chains with $N \geq 30$, the magnitude of deviation increases with increasing chain length, probably owing to the entanglement\textsuperscript{38}, although the chain length dependence of the longest relaxation time shown in Table I fairly exhibits the power-law dependence with the power-law exponent of around 2, as observed earlier\textsuperscript{34}.

Figures 3 and 4 show the results of DPD simulations. The longest relaxation times are summarized in Table II. Irrespective to the chain length, the DPD results are closer to the Rouse prediction than the KG results even for large $p$ values. In particular, in the short time range, the KG results are apparently smaller than the Rouse prediction, but such a tendency is not apparent for the DPD results, as clarified in Fig. 4. The results demonstrate that HI implemented in DPD does not disturb the Rouse dynamics even for the internal modes. The deviation observed in the long-time region shows an upturn in almost all the cases examined. This behavior is also seen for the KG results, and it might suggest a common slow relaxation mechanism or just an artifact in the estimation of the longest relaxation time. Nevertheless, the long-time behavior is not systematic with respect to the chain length, and further analysis is difficult due to the poor statistics.

Now let us turn our attention to the full-atomistic simulations. Figures 5 and 6 show the results for polyisoprene and polybutadiene melts. The longest relaxation time was 3.0 ns

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### Table I Longest relaxation time for KG simulations

| $N$ | $\tau_1^*$  |
|-----|-------------|
| 7   | 9.6$\times 10^1$ |
| 15  | 5.1$\times 10^2$ |
| 30  | 2.2$\times 10^3$ |
| 60  | 1.1$\times 10^4$ |
| 120 | 6.3$\times 10^5$ |

*$\tau_1$ is normalized with respect to the standard Lennard-Jones unit.

### Table II Longest relaxation time for DPD simulations

| $N$ | $\tau_1^*$  |
|-----|-------------|
| 30  | 1.1$\times 10^2$ |
| 60  | 4.2$\times 10^2$ |
| 90  | 9.7$\times 10^2$ |
| 120 | 1.7$\times 10^3$ |

*$\tau_1$ is normalized with respect to the standard DPD unit time.
Fig. 3 Rouse mode relaxations for DPD simulations at the mode index $p = 1, 2$ and 3 from top to bottom. The results for various chain lengths are plotted as indicated in the figure. Black solid curve shows the Rouse prediction.

Fig. 4 Rouse mode relaxation for DPD simulations divided by the Rouse prediction at the mode index $p = 1, 2$ and 3 from top to bottom. The results for various chain lengths are plotted as indicated in the figure. Horizontal broken curve shows the Rouse prediction.

Fig. 5 Rouse mode relaxation for FA simulations at the mode index $p = 1, 2$ and 3 from top to bottom. The results for different chemistries and chain length are plotted as indicated in the figure. Black solid curve shows the Rouse prediction.

Fig. 6 Rouse mode relaxations for FA simulations divided by the Rouse prediction at the mode index $p = 1, 2$ and 3 from top to bottom. The results for different chemistries and chain length are plotted as indicated in the figure. Horizontal broken curve shows the Rouse prediction.
and 14 ns for polybutadienes containing the repeating units of 20 and 40, and 9.5 ns for polyisoprene. As expected, the FA result is in fair agreement for $p = 1$. Even for the higher modes, the Rouse prediction roughly captures the simulation results. However, the results deviate from the Rouse prediction, as apparently shown for the higher modes in Fig. 6. The behavior is similar to that observed for KG model (see Fig. 2), for which $C_p(\tau)$ is lower than the Rouse prediction in the short time range. The upturn behavior in the long-time range is also similar to KG and DPD results, though further analysis is difficult due to poor statistics. Concerning the effect of molecular weight, the results for PB with different molecular weights do not exhibit that the long chain is closer to the Rouse prediction than the short chain. Namely, the short PB shows better agreement with Rouse than the long PB.

For further investigation on the effect of CR, FA simulations without Lennard-Jones interactions were performed for polybutadiene. The absence of the interaction attains the simulation without EVI and HI, yet with CR. The results compared with the FA simulations with EVI and HI are shown in Fig. 7. The chains without EVI and HI are close to the Rouse prediction for the long chain. On the other hand, very interestingly, for the short chain $C_p(\tau)$ is larger than the Rouse prediction for $p = 2$ and 3. These results mean that the effect of CR appears in the opposite direction to the effect of EVI. Namely, EVI suppresses $C_p(\tau)$ (as seen in Figs. 1 and 2) whereas CR gains $C_p(\tau)$. The larger $C_p(\tau)$ than the Rouse prediction for the short chain would be due to the relative mobility between chain ends and chain center. For a rigid chain, the chain center dynamics is relatively suppressed by the bending and torsion potentials, and the retardation from the chain end motion would be further significant than that for Rouse chain. In such a case, $C_p(\tau)$ for higher modes shows slower relaxation than the Rouse prediction.

### 4. DISCUSSION

It so appears that for the Rouse mode relaxations, FA and KG deviate from, and DPD is close to, the Rouse prediction. The magnitude of deviation for FA and KG is apparently larger than that for DPD.

The main reason for the deviation would be attributable to CR. Actually, DPD utilizes linear springs and no EVI, whereas FENE and EVI are implemented for FA and KG. The molecular weight dependence for KG calculations shown in Figs. 1 and 2 supports this idea, which is also consistent with the earlier results$^{12}$. For instance, for the KG model, Auhl et al.$^{31}$ have shown that the internal chain statistics is not Gaussian below the bead number of 100.

However, on the basis that CR is of importance, the hard-core inter-beads potential contributes the deviation from the Rouse prediction, at least partly. It is worth noting that, even for DPD simulations, a similar non-Gaussian nature of internal chain statistics has been reported, up to the bead number of ca. 75$^{32}$, owing to the repulsive inter-beads interaction. Further, the results shown in Fig. 7 for the skeleton chains that only have CR exhibit the deviation from Rouse in the opposite direction to FA and KG. These results suggest another mechanism rather than CR. As shown in Figs. 2 and 6, the deviation appears for FA and KG as intensified short time relaxations. Such relaxations would be attributable to the collisions between hard-core particles, and they disallow straightforward replacement by the Gaussian random force. Indeed, Sukumaran and Likhtman$^{39}$ have shown that a random force with a colored noise (rather than the white noise) is necessary to reproduce the dynamics of KG model by their Rouse-like single chain model. This view is consistent with the eigenfunction that is distorted from the sinusoidal shape, in a sense that CR is not directly attributable to the distorted eigenfunction.

For the local dynamics mentioned above, one may argue the effects of numerical integration scheme that includes thermostat and barostat. The results presented here for FA...
simulations are generated by Nose-Hoover thermostat\(^{40}\) and Andersen barostat\(^{41}\), for which the relaxation time of temperature and pressure is sufficiently shorter than that discussed for the chain dynamics. However, the results certainly depend on the choice of thermostat and barostat. For instance, because momentum is not conserved for the Langevin thermostat, FA simulations with a similar thermostat may generate different results. But such calculations are out of the scope of this paper.

Concerning the effect of HI, the effect seems much weaker than that for EVI and CR. Apart from the earlier studies for the screening lengths\(^{20,21}\), which are virtually identical for EVI and HI, Ahlrichs et al.\(^{12}\) have revealed that the screening for HI occurs only beyond a certain crossover time, and in the short time region, the chain shows Zimm dynamics on all length scales. In our DPD simulations, however, such behavior is not seen in the short time range, and thus, the cross-over time seems much shorter than the timescale of our interest.

5. CONCLUSION

In this study, the relaxation of Rouse modes was examined for unentangled polymer melts in different molecular simulation methods that are KG, DPD, and FA. The obtained relaxation behaviors were basically consistent with the Rouse prediction. However, small deviations were observed, and the magnitude of deviation was larger for FA and KG than that for DPD. The deviation seems attributable to the chain rigidity mainly, and short time collision among hard-core particles partly.

The results presented in this study suggest possible difficulties in the strategy of multi-scale modeling of polymers. On the basis of the experimentally established universality for static and dynamic properties of polymers, simulations of polymeric systems are attempted via multi-scale approaches, in which several simulation schemes are combined\(^{43}\). These approaches implicitly assume that the employed simulations are universal, at least for a certain spatial and temporal range. However, as reported recently\(^{25}\), the universality among simulation schemes is still a matter of discussion, even for the global dynamics such as diffusion. The present study suggests that further consideration on simulation details is necessary for coarse-grained models (such as KG and DPD) to attain equivalent local chain dynamics to FA.

Finally, note that the Rouse mode analysis conducted in this study is different from the normal mode analysis as shown earlier\(^{14-17}\). In particular, orthogonality between Rouse modes would give further insights for the deviation of the normal modes from the Rouse modes. Studies toward such a direction are being conducted, and the results will be reported elsewhere.

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REFERENCES

1) Rouse PE, J Chem Phys, 21, 1272 (1953).
2) Ferry JD, “Viscoelastic Properties of Polymers”, 3rd ed. (1980), John Wiley & Sons, Inc.,
3) Watanabe H, Prog Polym Sci, 24, 1253 (1999).
4) Graessley W, “Polymeric Liquids & Networks: Dynamics and Rheology”, (2008), Garland Science, London.
5) Onogi S, Masuda T, Kitagawa K, Macromolecules, 3, 109 (1970).
6) Brueggeman BG, Minnick MG, Schrag JL, Macromolecules, 11, 119 (1978).
7) Pearson DS, Fetters LJ, Graessley WW, Strate GV, von Meerwall E, Macromolecules, 27, 711 (1994).
8) Imanishi Y, Adachi K, Kotaka T, J Chem Phys, 89, 7585 (1988).
9) Richter D, Willner L, Zirkel A, Farago B, Fetters L, Huang J, Macromolecules, 27, 7437 (1994).
10) Kremer K, Grest GS, J Chem Phys, 92, 5057 (1990).
11) Paul W, Yoon DY, Smith GD, J Chem Phys, 103, 1702 (1995).
12) Paul W, Smith GD, Yoon DY, Macromolecules, 30, 7772 (1997).
13) Paul W, Smith GD, Yoon DY, Farago B, Rathgeber S, Zirkel A, Willner L, Richter D, Phys Rev Lett, 80, 2346 (1998).
14) Watanabe H, Urakawa O, Kotaka T, Macromolecules, 26, 5073 (1993).
15) Watanabe H, Urakawa O, Kotaka T, Macromolecules, 27, 3525 (1994).
16) Watanabe H, Yamada H, Urakawa O, Macromolecules, 28, 6443 (1995).
17) Kaznessis YN, Hill DA, Maginn EJ, Macromolecules, 32, 6679 (1999).
18) Harnau L, Winkler RG, Reineker P, Phys Rev Lett, 82, 2408 (1999).
19) Bulaci M, Van Der Giessen E, J Chem Phys, 123, (2005).
20) De Gennes PG, Macromolecules, 9, 594 (1976).
21) Muthukumar M, Edwards SF, Polymer, 23, 345 (1982).
22) Ewen B, Richter D, Adv Polym Sci, 134, 1, (1997).
23) Groot RD, Warren PB, *J Chem Phys*, **107**, 4423 (1997).
24) Harmandaris VA, Mavrantzas VG, Theodorou DN, Kröger M, Ramirez J, Öttinger HC, Vlassopoulos D, *Macromolecules*, **36**, 1376 (2003).
25) Takahashi KZ, Nishimura R, Yamato N, Yasuoka K, Masubuchi Y, *Sci Rep*, **7**, 12379 (2017).
26) Tzoumanekas C, Theodorou DN, *Macromolecules*, **39**, 4592 (2006).
27) Fotinopoulou K, Karayiannis N, Laso M, Kröger M, *J Phys Chem B*, **113**, 442 (2009).
28) Sukumaran SK, Grest GS, Kremer K, Everaers R, *J Polym Sci Part B Polym Phys*, **43**, 917 (2005).
29) Fetters LJ, Lohse DJ, Milner ST, Graessley WW, *Macromolecules*, **32**, 6847 (1999).
30) Pan G, Manke CW, *Int J Mod Phys B*, **17**, 231 (2003).
31) Auhl R, Everaers R, Grest GS, Kremer K, Plimpton SJ, *J Chem Phys*, **119**, 12718 (2003).
32) Langeloth M, Masubuchi Y, Böhm MC, Müller-plathe F, *J Chem Phys*, **138**, 104907 (2013).
33) JACI, “*Computer Simulation of Polymeric Materials*”, (2016), Springer Singapore, Singapore.
34) Kremer K, Grest GS, Carmesin I, *Phys Rev Lett*, **61**, 566 (1988).
35) Hirao H, Koseki S, Takano H, *J Phys Soc Japan*, **66**, 3399 (1997).
36) Takano H, Miyashita S, *J Phys Soc Japan*, **64**, 3688 (1995).
37) Hagita K, Takano H, *J Phys Soc Japan*, **71**, 673 (2002).
38) Kalathi JT, Kumar SK, Rubinstein M, Grest GS, *Macromolecules*, **47**, 6925 (2014).
39) Sukumaran SK, Likhtman AE, *Macromolecules*, **42**, 4300 (2009).
40) Nosé S, *J Chem Phys*, **81**, 511 (1984).
41) Andersen HC, *J Chem Phys*, **72**, 2384 (1980).
42) Ahlrichs R, Everaers R, Dünweg B, *Phys Rev E*, **64**, 40501 (2001).
43) Masubuchi Y, *Annu Rev Chem Biomol Eng.*, **5**, 11 (2014).