Fast protocol for equilibration of entangled and branched polymer chains

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A B S T R A C T

Direct brute-force equilibration of well-entangled polymers is beyond the reach of the modern computational power because of slow reptation dynamics exhibited by high molecular weight chains. We have introduced a fast protocol to prepare well-equilibrated entangled polymer melts of various architectures. A soft, DPD-like potential is used to quickly equilibrate the melt at intermediate length-scale following with a replacement of the DPD potential with Lennard–Jones potential. The equilibrated structure is then subjected to a short MD simulation run that relaxes the melt configuration at the short length-scale. The topological characteristics of the final melt structure are excellent, and the method found to be computationally competitive to other state-of-the-art equilibration techniques.

1. Introduction

A major objective of computer simulations in the polymer science is to understand structure–property relationships for polymers with high molecular weight (MW). Some important industrial polymers, such as ultra high molecular weight polyethylene, have very long polymer chains with MW of 1000,000 or more. Mechanical properties of these polymers are dominated by topological constraints or entanglements. Direct atomistic modeling of dynamics of entangled polymers is still unattainable due to slow reptation dynamics exhibited by the high MW polymer chains of length N. The polymers diffusivity, D, decreases for longer chains according to the well-known relation $D \propto N^{-2.3}$ [1]. The calculation of polymer diffusion becomes feasible by using coarse-graining models that combine groups of atoms into a single particle or bead. This approach allows sampling longer time scales and larger system sizes, thus significantly reducing the computational time. Nevertheless, even for a case of coarse-grained chains, brute-force equilibration of well-entangled polymers can be prohibitively expensive.

Standard method (fast 'push-off') to equilibrate the polymer melt consists of fast introduction of the excluded volume into an ensemble of phantom chains with the correct end-to-end distance. This procedure yields chain deformation on the short to intermediate length scales [2]. Modern methods employ Monte Carlo-Molecular Dynamics (MC-MD) hybrid algorithms, which include the chain connectivity altering techniques ('double-bridging' algorithm), and those schemes are significantly faster than simple MD equilibration [2–4]. However, the bridging algorithms employ a set of complex moves with very low acceptance ratio. Recently, several

other algorithms were proposed to equilibrate well-entangled polymers, such as polymerization-like polymer growing techniques [5,6] and iterative method of affine scaling and equilibration [7,8]. Another attractive approach is slow 'push-off' method of phantom chains with correct end-to-end distance [2]. This method consists of MC moves that change position and orientation of phantom chains and subsequent MD simulation that removes spatial overlap by using modified Lennard–Jones potentials.

In this Letter, we introduce a fast protocol called 'DPD-push-off' to prepare well-equilibrated melts. This method is an extension of the slow 'push-off' method developed by Auhl et al. [2]. The main ideas of our approach are (1) to generate initial configurations that closely match equilibrium structures at large length scales so the MD simulation is only needed to relax the short to intermediate length scale configurations and (2) allow chains to pass through each other to speed up the polymer dynamics. Initially, we perform short simulation runs with soft repulsion potential used in Dissipative Particle Dynamics (DPD), U_{DPD} [9], on an ensemble of polymer chains with the correct end-to-end distance. After a gradual increase of the strength of the DPD potential, short simulation with target coarse-grained potential was performed. The idea of application of soft repulsive potentials for equilibration of polymer melts has been used earlier with parallel tempering MC technique, but this method has not been particular computationally efficient [10]. Here, we show that use of the soft potential is very effective if the potential is applied to the initial configurations that closely match equilibrium structures at large length scales.

The DPD-push-off algorithm does not contain MC moves, and it is fast and simple to implement with MD parallel simulators. Since our simulation approach preserves chain connectivity, it is not restricted to the linear polymers and therefore suitable for polymers of any complex architecture. We have demonstrated applicability of the method to equilibrate structure of a branched star polymer.

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2. Model and methods

Polymer chains are represented with the coarse-grained bead-spring model of Kremer–Grest (K–G) [11].

In the K–G model, the pair interaction between topologically nonconnected particles is described by the standard truncated Lennard–Jones pair potential:

$$U_{LJ}(r) = \begin{cases} 4\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^6 - \left(\frac{\sigma}{r_c}\right)^{12} + \left(\frac{\sigma}{r_c}\right)^6\right], & r \geqslant r_c \\ 0, & r \leqslant r_c \end{cases} \tag{1}$$

where ε is the depth of the potential well, σ is the distance where interparticle force is zero, and r_c represents the cutoff distance. Both the ε and σ are set to 1. The choice of $r_c = 2^{1/6}\sigma$ yields so-called Weeks–Chandler–Andersen excluded volume potential, U_{WCA}.

Topologically bound monomers interact according to the standard FENE/Lennard–Jones bonded potential, $U_{FENE/LJ}$. $U_{FENE/LJ}(r) = U_{FENE}(r) + U_{WCA}(r)$ and

$$U_{FENE}(r) = \begin{cases} -\frac{a}{2}R_0^2 \ln[1 - (\frac{r}{R_0})^2], & r \leqslant R_0 \\ \infty, & r > R_0, \end{cases} \tag{2}$$

where U_{FENE} is finite extensible nonlinear elastic potential. The standard parameter values for $R_0 = 1.5\sigma$ and $a = 30\varepsilon/\sigma^2$ were used. During all stages of our melt preparation, we have used molecular dynamics (MD) with DPD thermostat [12,13]. In a DPD simulation of polymers, particles interact with each other via a pairwise, two-body, short-ranged force, **F**, that is written as the sum of a conservative force, $\mathbf{F}^C$, dissipative force, $\mathbf{F}^D$, and random force, $\mathbf{F}^R$, as follows:

$$\mathbf{F}_i = \sum_{j \neq i} \mathbf{F}_{ij}^C + \sum_{j \neq i} \mathbf{F}_{ij}^D + \sum_{j \neq i} \mathbf{F}_{ij}^R. \tag{3}$$

The conservative force, $\mathbf{F}^C$, can be derived from excluded volume potential U_{WCA} or a soft repulsion potential U_{DPD}. $\mathbf{F}^C$ also includes a contribution from bonded particles ($\mathbf{F}^{FENE}$). The remaining two forces, $\mathbf{F}^D$ and $\mathbf{F}^R$ provide the thermostat in the DPD method. The dissipative force slows down the particles movement by decreasing their kinetic energy. This effect is balanced by the random force due to thermal fluctuations. $\mathbf{F}^D$ and $\mathbf{F}^R$ are given by:

$$\mathbf{F}_{ij}^D = -\gamma\omega^D(r_{ij})(\mathbf{e}_{ij}\mathbf{v}_{ij})\mathbf{e}_{ij}, \tag{4}$$

and

$$\mathbf{F}_{ij}^R = \sigma^R\omega^R(r_{ij})\xi_{ij}\mathbf{e}_{ij}, \tag{5}$$

where $\omega^D(r)$ and $\omega^R(r)$ are weight functions, γ is the friction coefficient, σ^R is the noise amplitude, and ξ_{ij} is the GAUSSIAN random number with zero mean and unit variance that is chosen independently for each pair of interacting particles. Here the vectors $v_{ij} = v_i - v_j$ are the velocity differences between particle i and j.

Español and Warren showed that the system samples the canonical ensemble and obeys the fluctuation–dissipation theorem if the following relations hold [14]:

$$\omega^D(r) = [\omega^R(r)]^2, \tag{6}$$

and

$$\sigma^2 = 2\gamma k_B T, \tag{7}$$

where T is the temperature and k_B is Boltzmann's constant. $\omega^R(r)$ is typically chosen as:

$$\omega^R(r) = \begin{cases} 1 - \frac{r}{r_c} & \text{for } r < r_c \\ 0 & \text{for } r \geqslant r_c \end{cases}. \tag{8}$$

All the equilibration stages were done with $T = 1\sigma/k_B$ and $\gamma = 4.5$. Time steps were $\Delta t_{DPD} = 0.01\tau_{DPD}$ and $\Delta t_{LJ} = 0.01\tau_{LJ}$. We measured time in terms of characteristic $\tau_{LJ} = \sqrt{m\sigma^2/\varepsilon}$ and $\tau_{DPD} = \sqrt{mr_c^2/k_B T}$.

All simulations were executed using LAMMPS, a molecular dynamics program from Sandia National Laboratories [15].

2.1. Algorithm for preparation of equilibrated polymer melts

The DPD-push-off algorithm includes polymer building and equilibration techniques, and it consists of the following four stages:

(1) Polymer chains are generated inside a periodic cubic box with the correct end-to-end distance $R^2(n)$ on large length scales,

$$R^2(n) = l^2 C_\infty n, \tag{9}$$

where n is a number of bonds, l is a bond distance, and C_n is the Flory characteristic ratio and $C_n = C_\infty$ at $n \to \infty$. For freely rotating chain model (FRC), C_∞ is calculated from the relation $C_\infty = \frac{1 + \langle\cos\theta\rangle}{1 - \langle\cos\theta\rangle}$, where θ is a bond angle [1]. The fully flexible Lennard–Jones chains used in this work are characterized with $r_c = 2^{1/6}\sigma$ and $C_\infty = 1.88$.

Chains are built via non-reversal-random-walks [2] in 3D space with a random angle $\alpha = \pi - \theta$ that is sampled around $\langle\cos\alpha\rangle$. The standard number density for coarse-grained polymer melts [11], $\rho = 0.85\sigma^{-3}$ was selected.

(2) Short simulations of the melts prepared at stage 1 are carried out by substituting U_{WCA} for nonbonded particles with a soft repulsion potential in a form that is commonly used in DPD, U_{DPD}:

$$U_{DPD}(r) = \begin{cases} \frac{a_{DPD}}{2} r_c(1 - \frac{r}{r_c}), & r \leqslant r_c \\ 0, & r \geqslant r_c, \end{cases} \tag{10}$$

(3) where maximum repulsion parameter a_{DPD} is set to 25 $k_B T$ and cutoff radius r_c is equal to 1 in the length units [9]. At this stage, the simulation time was $t_2^{sim} = 500\tau_{DPD}$. Next stage is a fast 'push-off' to the full Lennard–Jones potentials by gradual increase of the strength of DPD potential from $a_{DPD} = 25$ $k_B T$ to $a_{DPD} = 1000$ $k_B T$. The fast 'push-off' time was $t_3^{sim} = 5.5\tau_{DPD}$, the shortest time interval to switch to full Lennard–Jones without generating numerical instabilities.

(4) In the final stage, the MD simulation with the U_{WCA} potential was performed for time equal to $t_4^{sim} = 10^4\tau_{LJ}$. This procedure improved structure on the short length scale caused by usage of the U_{DPD} potential.

In Section 3, we have justified our choice of t_2^{sim} and t_4^{sim}.

2.2. Model development

We compared a topology of the melts obtained by two different methods: (1) DPD-push-off method and (2) brute-force equilibration. Validation of the DPD-push-off algorithm was conducted for a melt with $M = 500$ chains of $N = 500$ beads. Simulation box was chosen as $66.5 \times 66.5 \times 66.5$ σ^3. The calculated topological characteristics were averaged from the six different initial configurations.

3. Results and discussion

The structure of melt obtained with the brute-force method is considered to be a reference structure for topological analyses, as
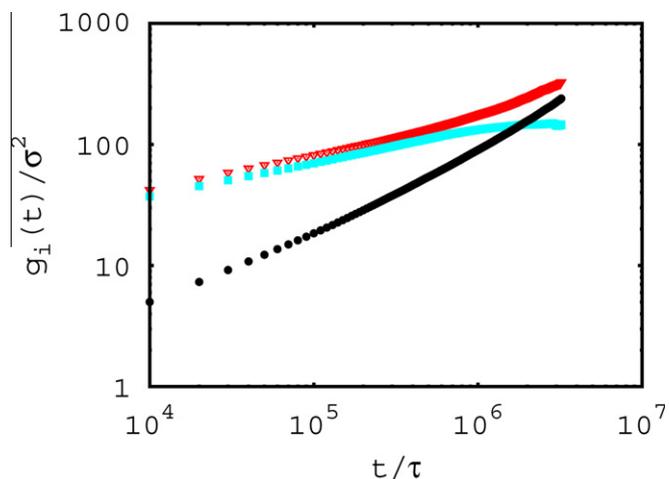
Figure 1. Mean-square displacements (MSD) for a melt $M = 500$ chains of length $N = 500$. Triangles, squares and circles represent MSD of the inner monomer, $g_1(t)$, the inner monomer with respect to center of mass, $g_2(t,)$ and center of mass, $g_3(t)$, respectively.

described below. For the brute-force equilibration, the long MD simulations were performed, and motion of the chains were

evaluated by computing mean-square displacements (MSD), $g_i(t)$. Displacements of the polymer were calculated from:

$$g_1(t) = \langle [\mathbf{r}_i(t_0 + t) - \mathbf{r}_i(t_0)]^2 \rangle$$
$$g_2(t) = \langle [(\mathbf{r}_i(t_0 + t) - \mathbf{r}_c(t_0 + t)) - (\mathbf{r}_i(t_0) - \mathbf{r}_c(t_0))]^2 \rangle \qquad (11)$$
$$g_3(t) = \langle [\mathbf{r}_c(t_0 + t) - \mathbf{r}_c(t_0)]^2 \rangle,$$

where $g_1(t)$, $g_2(t)$, $g_3(t)$ are MSD of inner monomer, inner monomer with respect to center of mass, and the chains' center of mass, respectively. Since an entangled chain relaxes at the relaxation time, t_d if $g_1(t) \propto t^1$ [1], the simulation was carried out for time long enough that $g_1(t) \propto t^{0.93}$ (the run time was $t = 6.5 \times 10^6 \tau_{LJ}$). Figure 1 shows that simulation was carried out for time long enough that the chains moved three times their own size. The brute-force generated structures were averaged from six conformations of long equilibrated melt taking coordinates at simulation times equal to $t = 4 \times 10^6$, 4.5×10^6, 5×10^6, 5.5×10^6, 6×10^6, 6.5×10^6 τ_{LJ}. The mean square internal distances of chains $\langle R^2(n) \rangle/n$ were computed to characterize the chain conformations. $\langle R^2(n) \rangle/n$ was averaged over all possible combinations of segments of size $n = |i - j|$ along the chains, where $i < j \in [1, N]$ are monomer indices [2]. Since $\langle R^2(n) \rangle/n$ it is nearly independent of chain length, N for a given chemical distance $n = |i - j|$, this metric is an excellent indicator of chain configuration at all length scales [2]. $\langle R^2(n) \rangle/n$ has been
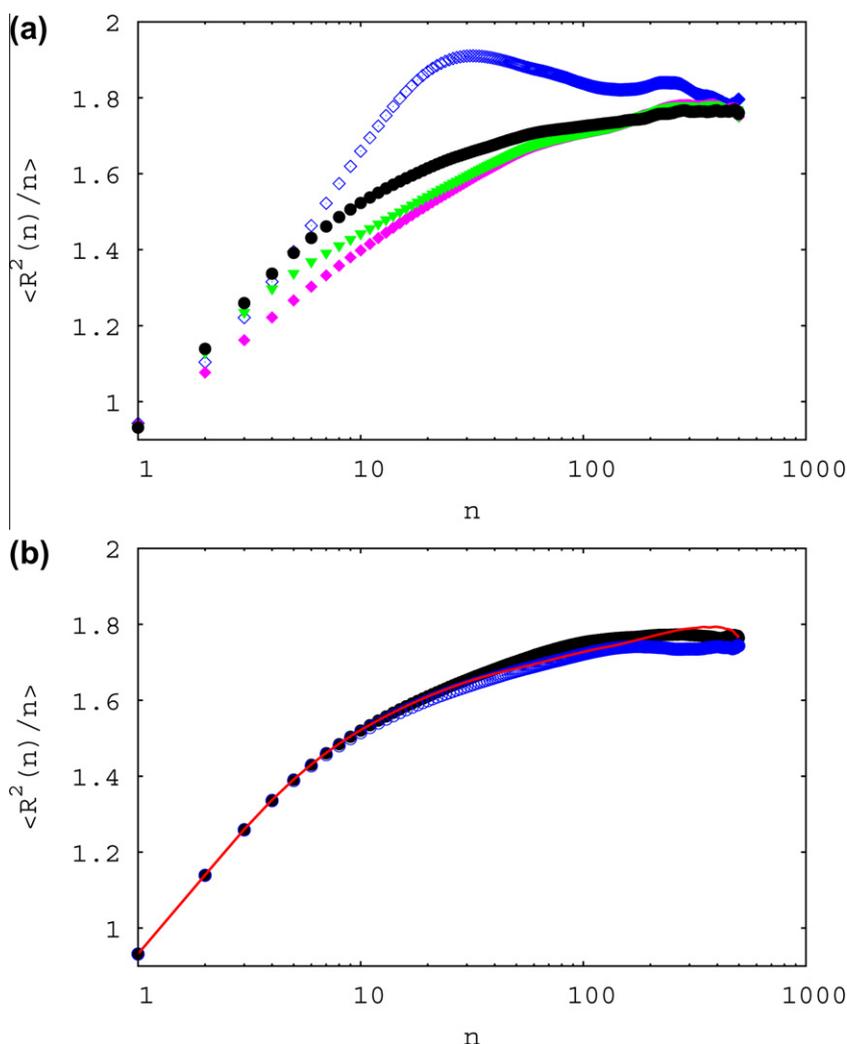

Figure 2. Mean square internal distances $\langle R^2(n) \rangle/n$ for a melt with $M = 500$ chains of length $N = 500$. (a) Evolution of $\langle R^2(n) \rangle/n$ throughout the preparation procedure. Open and solid diamonds represent a chain in the beginning ($t = 10\tau_{DPD}$) and at the end of stage 2 ($t = 500\tau_{DPD}$) – simulation with soft potential, respectively. Triangles correspond to the chain after 'push-off' (stage 3). Circles correspond to the final structure after stage 4 ($t = 10^4\tau_{LJ}$). The results are shown for one initial conformation. (b) $\langle R^2(n) \rangle/n$ for the melt prepared by our method using U_{DPD} (solid circles) and U_{cos} (open circles). The reference melt is shown with solid line. Results are averaged over six conformations.

Table 1
Evolution of chain topology throughout the preparation procedure: primitive path dimensions $\langle L_{PP} \rangle$, entanglement length N_e, and number of kinks $\langle Z \rangle$ for Z1 for a melt $M = 500$ chains of length $N = 500$. Deformed conformation was obtained in the beginning of stage 2 ($t = 10\tau_{DPD}$). The results are shown for one initial conformation.

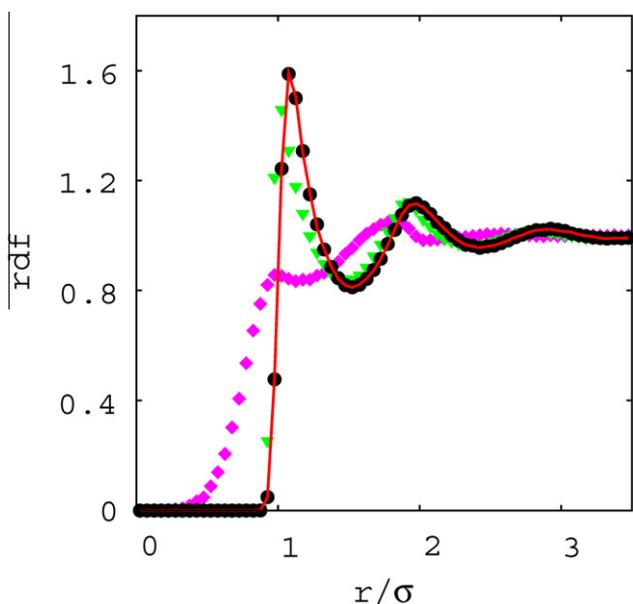| Conformation	$\langle L_{PP} \rangle$	$\langle L_{PP}^2 \rangle^{1/2}$	N_e	$\langle Z \rangle$
Deformed	91.16	93.13	53.82	13.99
After stage 2	70.44	71.93	87.86	9.37
After stage 3	70.34	71.81	88.16	9.33
Final	72.43	74.02	83.56	9.82

Figure 3. Radial distribution function of nonbonded monomers for a melt with $M = 500$ chains of length $N = 500$. Diamonds represent the melt after stage 2. Triangles and circles correspond to the melt after fast 'push-off' (stage 3) and final structure, respectively. The reference melt is shown with solid line.

subsequently used as a target function in the other studies on equilibration of polymer melts [6–8].

Additionally, the topology of the melt was characterized by computing the average contour length, L_{pp}, the entanglement length, N_e, and the number of 'interior' kinks, Z. For this analysis, Z1 code was utilized [16]. This program performs geometrical analysis of the melt by calculating the number of interior 'kinks' Z [16]. The averaged value of Z, $\langle Z \rangle$, is proportional to the number of entanglements [16–18], n_e. The N_e value was estimated by using a 'classical' S-coil formula, $N_e = (N-1) \frac{\langle R^2(N) \rangle}{\langle L_{pp} \rangle^2}$ [19]. The topological parameters $\langle R^2(n) \rangle / n$, L_{pp}, N_e, Z, were measured at all stages of the DPD-push-off procedure and are reported in Figure 2 a and Table 1.

Analysis of results indicates that the introduction of U_{DPD} at stage 2 of the equilibration protocol leads to immediate deformations of polymer chains on the intermediate length scale, producing a 'characteristic bump' in $\langle R^2(n) \rangle / n$ plot (Figure 2a). Figure 3 demonstrates that this deformation of polymer chains is due to some degree of excluded volume brought into the simulation system by the repulsive U_{DPD} potential. The local chain stretching decreases the entanglement length, N_e (Table 1). This significant deformation of the polymer chains is similar to distortion of the chain after application of fast 'push-off' [2]. However, simulation time of $t_2^{sim} = 500\tau_{DPD}$ is sufficient to remove this 'bump' since U_{DPD} allows chains to pass through each other. This procedure causes also a modest compression of the chains on the short length scale (Figure 2a) and reduction of the entanglement density (Table 1). This compression is due to a soft nature of U_{DPD} that allows beads

to overlap to some extent. Subsequent fast 'push-off' (stage 3) increases separations between monomers, which become large enough allowing for replacing the U_{DPD} potential with the full Lennard–Jones potential (see Figure 3). Interestingly, the fast 'push-off' does not significantly modify the structural properties of the melt. Remarkably, deformation of the chains occurs only at the initial stage (beginning of stage 1) of simulation as can be seen in Figure 2a and Table 1. Finally, at stage 4, we observe that the MD simulation with the U_{WCA} potential for $t_4^{sim} = 10^4\tau_{LJ}$ removes the distortions of structures on the short length scale caused by use of the U_{DPD} potential at earlier stages of the procedure (Figure 2a and Table 1).

The structural properties of the melt obtained with the DPD-push-off method are virtually indistinguishable from the reference melt calculations (see Figure 2b). The mean square bondlength, $\langle l^2 \rangle$, remains constant during the entire equilibration procedure. The radial distribution function of the equilibrated and reference melts are practically identical (Figure 3). Table 2 shows the results of topological analysis obtained from the Z1 code. The standard deviations of N_e and $\langle Z \rangle$ for the reference melt were ±2.39 and ±0.13, respectively, and are comparable to values obtained with the DPD-push-off method of ±2.08 and ±0.13 for N_e and $\langle Z \rangle$, respectively. The discrepancy between results of our method and reference, brute-force simulations are within ∼3% for all topological parameters, as evident from Table 2. Similar error was found with respect to the results obtained by double-bridging hybrid (DBH) algorithm for the same melt [18]. However, the DPD-push-off method is more efficient and shortens computational time by an order of magnitude as compared to the DBH simulations.

The mean-square radius of gyration of the melt obtained with the DPD-push-off method is about one-sixth of its mean-square end-to-end distance according to the Gaussian expectation [1]: $\frac{\langle R^2 \rangle}{\langle R_g^2 \rangle} = 5.95$. The reference melt has $\frac{\langle R^2 \rangle}{\langle R_g^2 \rangle} = 5.96$.

It is important to mention that instead of the U_{DPD} potential, other forms of the soft repulsion potentials could be employed in our method, although that may decrease the computational efficiency. For example, we have found that a cosine soft potential, U_{cos} [2], requires longer simulation time to remove the initial deformation. The simulation time using U_{DPD} and U_{cos} were $t_2^{sim} = 500\tau_{DPD}$ and $t_2^{sim} = 5000\tau_{cos}$, respectively. U_{cos} is given by [2]

$$U_{cos}(r) = \begin{cases} A_c(1 + \cos(\pi \frac{r}{r_c})), & r \leqslant r_c \\ 0, & r \geqslant r_c, \end{cases} \qquad (12)$$

where the amplitude $A_c = 4\varepsilon$. Surprisingly, the subsequent fast 'push-off' (stage 3) from $A_c = 4\varepsilon$ to 200ε for $t_3^{sim} = 10\tau_{cos}$ [2] does not deform the chains. Figure 2 b shows that the equilibration with U_{cos}, as well as the equilibration with U_{DPD}, produces final chain configurations that match the reference configurations.

The DPD-push-off method is applicable for polymer chains of various lengths and architectures. Since internal distances on long scales ($n > 100$) are changed only slightly, our approach is valid for chain of any length. We have built and equilibrated the linear polymers of different chain length with $N = 250$, 875, 1000, and results

Table 2
Chain topology: primitive path dimensions $\langle L_{PP} \rangle$, entanglement length N_e, and number of kinks $\langle Z \rangle$ for a melt $M = 500$ chains of length $N = 500$. The equilibrated reference melt was simulated via MD for $t = 6 \times 10^6\tau_{LJ}$.

Method	$\langle L_{PP} \rangle$	$\langle L_{PP}^2 \rangle^{1/2}$	N_e	$\langle Z \rangle$
Reference	72.81	74.21	83.14	9.85
DPD-push-off	72.08	73.55	84.56	9.64
DBH[*]	74.34	75.75	86.10	10.26

[*] Values for DBH are taken from [18], where Ne was averaged for several chain lengths.
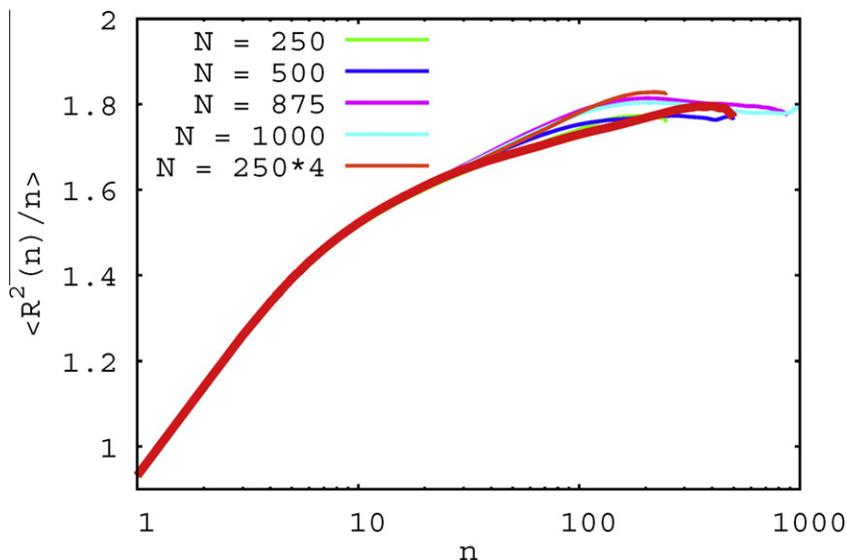
Figure 4. Mean square internal distances $\langle R^2(n)\rangle/n$ for chains of varying length N calculated with the DPD-push-off method. $\langle R^2(n)\rangle/n$ for the reference melt of $N = 500$ equilibrated for $t = 6 \times 10^6 \tau_{LJ}$ shown as a thick solid line for comparison.

are presented in Figure 4. We expect the method will be particularly useful in simulations of branched polymers. This was demonstrated by equilibrating a polymer with four-arm star of arm length of $N_{arm} = 250$. This system, indicated as $(250 * 4)$ in Figure 4, shows $\langle R^2(n)\rangle/n$ curve similar to other polymers of that size. This is because the core region of the stars is negligibly small due to the small number of arms [20], and therefore the arms display structural characteristics of linear polymers.

We have found that DPD-push-off method is 10^3 faster than brute-force equilibration for $N = 500$. Since the relaxation time of the entangled melt increases with N as $t_d \propto N^{-3.4}$ [1] and our equilibration time is independent of N, we expect that our method greatly surpasses the brute-equilibration method for long chains.

4. Conclusions

We have developed a computationally very efficient algorithm capable of equilibrating long entangled polymer chains of any architecture. The DPD-push-off algorithm includes polymer building and equilibration techniques that utilize soft DPD-like potential, allowing chains to pass through each other. In the final stages of the algorithm, the soft potential is replaced by the full Lennard–Jones potential. This procedure yields the melt structure with topological characteristics very close to those calculated from reference, brute-force calculations based on the long MD simulations. This approach significantly accelerates the polymer dynamics and makes the method orders of magnitude faster than the brute-force equilibration technique and faster than the current state-of-the-art, MC 'double bridging' technique. This approach is easily applicable to any polymer architecture, in particular to highly branched polymers. In this work, the DPD-push-off method was applied to generic, bead-spring 'Kremer–Grest' chains. However, the described protocol is general and applicable for any coarse-grained model.

References

[1] M. Rubinstein, R.H. Colby, Polymer Physics, Oxford, 2003.
[2] R. Auhl, R. Everaers, G.S. Grest, K. Kremer, S.J. Plimpton, J. Chem. Phys. 119 (2003) 12718.
[3] N.C. Karayiannis, V.G. Mavrantzas, D.N. Theodorou, Phys. Rev. Lett. 88 (2002) 105503.
[4] B.J. Banaszak, J.J. De Pablo, J. Chem. Phys. 119 (2003) 2456.
[5] J. Gao, J. Chem. Phys. 102 (1995) 1074.
[6] M. Perez, O. Lame, F. Leonforte, J.-L. Barrat, J. Chem. Phys. 128 (2008) 234904.
[7] G. Subramanian, J. Chem. Phys. 133 (2010) 164902.
[8] G. Subramanian, Macromol. Theory Simul. 20 (2011) 46.
[9] R.D. Groot, P.B. Warren, J. Chem. Phys. 107 (1997) 4423.
[10] A. Bunker, B. Dünweg, Phys. Rev. E 63 (2001) 16701.
[11] K. Kremer, G.S. Grest, J. Phys.: Condens. Matter 2 (1990) SA295.
[12] P.J. Hoogerbrugge, J.M.V.A. Koelman, Europhys. Lett. 19 (1992) 19155.
[13] J.M.V.A. Koelman, P.J. Hoogerbrugge, Europhys. Lett. 21 (1993) 363.
[14] P. Español, P.B. Warren, Europhys. Lett. 30 (1995) 191.
[15] S. Plimpton, J. Comp. Phys. 117 (1995) 1.
[16] M. Kröger, Comput. Phys. Commun. 168 (2005) 209.
[17] R.S. Hoy, M.O. Robbins, Phys. Rev. E 72 (2005) 061802.
[18] R.S. Hoy, K. Foteinopoulou, M. Kröger, Phys. Rev. E 80 (2009) 031803.
[19] S.F. Edwards, Br. Polym. J. 9 (1977) 140.
[20] M. Daoud, J.P. Cotton, J. Phys., France 43 (1982) 531.