

MD Simulation of Polymer Melts: Potential Model, Chain Architecture & DPD Thermostat

Yanwei Wang, Ole Hassager Flemming Y. Hansen, Guenther Peters
 Department of Chemical Engineering Department of Chemistry
 Technical University of Denmark, Lyngby, 2800, Denmark

Introduction

The aim of this study is to investigate the static and dynamic properties of polymer melts with different chain architectures using molecular dynamics simulations.

Flexible polymer chains are often modeled as united beads connected by FENE springs. In the literature, two types of beads are frequently used for the construction of a polymer chain, namely the hard beads and the soft beads.

One extensively studied hard-bead model is the so-called 'Kremer-Grest model', which combines the WCA potential and FENE spring potential [1]. A characteristic length scale σ , inherited from the Lennard-Jones potential, is used, although a clear physical origin of it is missing for a coarse-grained polymer model.

In DPD simulations, a commonly used polymer model is the soft-bead model with polymer beads interacting through a weak quadratic potential and spring potential [2,3]. The cutoff distance for the weak repulsion sets the length scale.

In this study, we sought to make a generalization between these two types of models. This is done by resetting a common length scale for both cases, and we chose to use the maximum extension of a spring. In coarse-grained simulations of flexible polymers, this quantity can be interpreted as the product of the Kuhn step length of the polymer chain and number of Kuhn steps within one spring. Besides, instead of using the purely repulsive WCA potential, we use the SHRAT potential, which has been used to approximate the LJ potential [4]. The SHRAT potential has an attractive tail that can be easily monitored and it vanishes naturally at the cutoff.

We studied polymer melts of different chain architectures (linear, ring, star) using the soft-bead model with DPD thermostat, and we also investigated the possible application of DPD as a thermostat in simulations of hard-bead model systems.

Potential Model

Kremer-Grest Model:
 bonded beads interact through WCA + FENE potential
 nonbonded beads interact through WCA potential

$$\phi^{WCA}(r) = \begin{cases} \frac{1}{2} \left[\left(\frac{r}{\sigma} \right)^{12} - \left(\frac{r}{\sigma} \right)^6 + \frac{1}{4} \right] & (r < 2^{1/6}\sigma) \\ 0 & (r \geq 2^{1/6}\sigma) \end{cases}$$

$$\phi^{FENE}(r) = -\frac{1}{2} H Q_0^2 \ln \left[1 - \left(\frac{r}{Q_0} \right)^2 \right]$$

$$Q_0 = 1.5\sigma$$

$$H = 30\epsilon/\sigma^2$$

$$\epsilon = k_B T$$

DPD Polymer Model:
 bonded beads interact through DPD + FENE potential
 nonbonded beads interact through DPD potential

$$\phi^{DPD}(r) = \begin{cases} \frac{9}{2} \left(1 - \frac{r}{r_c} \right)^2 & (r < r_c) \\ 0 & (r \geq r_c) \end{cases}$$

$$\phi^{FENE}(r) = -\frac{1}{2} H Q_0^2 \ln \left[1 - \left(\frac{r}{Q_0} \right)^2 \right]$$

$$\alpha = 18.75 k_B T$$

$$H = 6.0 k_B T / r_c^2$$

$$Q_0 = 3.0 r_c$$

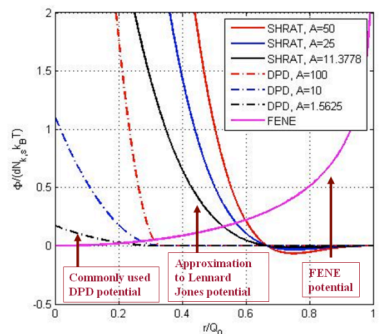
In the Kremer-Grest model, σ is used as a characteristic length scale
 In the DPD model, r_c is used as a characteristic length scale
 Instead, we use Q_0 as a common characteristic length scale and we also turn to use the SHRAT potential.

$$\frac{\phi^{FENE}(r)}{k_B T} = \frac{d}{2} N_{k,s} \ln \left[1 - \left(\frac{r}{Q_0} \right)^2 \right]$$

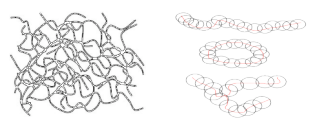
$$\frac{\phi^{SHRAT}(r)}{k_B T} = \begin{cases} A d N_{k,s} \left(\frac{1}{3} - \frac{r}{Q_0} \right) \left(1 - \frac{r}{Q_0} \right)^3 & (r < Q_0) \\ 0 & (r \geq Q_0) \end{cases}$$

$$\frac{\phi^{DPD}(r)}{k_B T} = \begin{cases} A d N_{k,s} \left(\frac{1}{3} - \frac{r}{Q_0} \right)^2 & (r < Q_0/3) \\ 0 & (r \geq Q_0/3) \end{cases}$$

Note that for gaussian chain $Q_0 = N_{k,s} l_k$
 where l_k is the Kuhn step length of a polymer
 $N_{k,s}$ is the number of Kuhn steps covered by one spring



Chain Architecture



Chain asphericity (A_3) is used to describe the equilibrium chain conformation. L_1, L_2 and L_3 are eigenvalues of the radius of gyration tensor Q

$$Q = \frac{1}{2N^2} \sum_{i=1}^N \sum_{j=1}^N (\mathbf{r}_i - \mathbf{r}_j)(\mathbf{r}_i - \mathbf{r}_j)$$

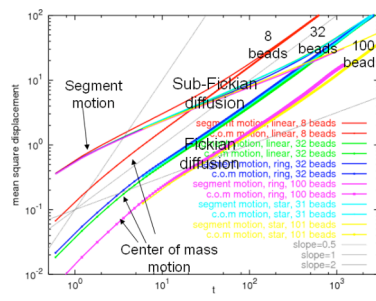
$$A_3 = \frac{L_1^2 + L_2^2 + L_3^2 - L_1^2 L_2^2 - L_2^2 L_3^2 - L_1^2 L_3^2}{L_1^2 + L_2^2 + L_3^2}$$

chain type	Asphericity (A_3)
sphere	0
star 4 x 25 + 1	0.2179
ring 32	0.2184
ring 100	0.2352
star 3 x 10 + 1	0.2740
star 3 x 33 + 1	0.2849
linear 8	0.3524
linear 32	0.3965
3D random walk (analytical)	0.3943
rod, cigar shape	1

Table 1: chain asphericity, calculated for system of soft beads
 Equilibrium DPD simulations, soft-bead model, the same parameters as [3] are used, linear polymers show gauss chain behavior, star and ring polymers investigated show tendency to be more close to sphere than linear polymers.

Dynamics: MSD

For the soft-bead model, the predicted diffusion behavior depends more on the number of beads along than chain than the chain architecture, in agreement with the Rouse model. A comparison with the hard-bead model is in proceeding.



Equilibrium DPD simulations, soft-bead model, the same parameters as [3] are used.

DPD Thermostat

Hamilton's equation of motion:

$$\frac{d\mathbf{r}_i}{dt} = \frac{\mathbf{p}_i}{m_i}$$

$$\frac{d\mathbf{p}_i}{dt} = \mathbf{F}_i^c = -\frac{\partial\Phi}{\partial\mathbf{r}_i}$$

Nosé-Hoover thermostat:

$$\frac{d\mathbf{r}_i}{dt} = \frac{\mathbf{p}_i}{m_i}$$

$$\frac{d\mathbf{p}_i}{dt} = \mathbf{F}_i^c - \zeta \mathbf{p}_i$$

$$\frac{d\zeta}{dt} = \frac{1}{\tau_T} \frac{T - T_0}{T_0}$$

Dissipative Particle Dynamics:

$$\frac{d\mathbf{r}_i}{dt} = \frac{\mathbf{p}_i}{m_i}$$

$$\frac{d\mathbf{p}_i}{dt} = \mathbf{F}_i^c + \mathbf{F}_i^D + \mathbf{F}_i^R$$

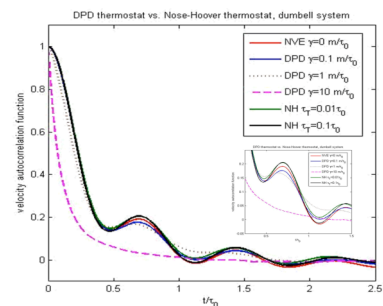
$$\mathbf{F}_i^D = \sum_{j \neq i} \mathbf{F}_{ij}^D = \sum_{j \neq i} [-\gamma \omega^D(r_{ij}) (\hat{\mathbf{r}}_{ij} \cdot \mathbf{v}_{ij}) \hat{\mathbf{r}}_{ij}]$$

$$\mathbf{F}_i^R = \sum_{j \neq i} \mathbf{F}_{ij}^R = \sum_{j \neq i} [\sigma \omega^R(r_{ij}) \xi_{ij} \hat{\mathbf{r}}_{ij}]$$

$$\sigma \omega^R(r) = \sqrt{2k_B T \gamma \omega^D(r)}$$

Velocity Autocorrelation

DPD, as a thermostat, controls the temperature through a combination of dissipative and random forces, and besides that, it also has an impact on the dynamics. Care should be taken when using DPD thermostat in MD simulations.



Equilibrium MD simulation. Hard-bead model (A=50), system of dumbbell molecules.

Conclusion

- The connection between MD and DPD simulations of polymer melts may now be better understood in terms of soft-bead model and hard-bead model.
- For polymer melts with different chain architectures, the soft-bead model gives rather reasonable predictions on static properties, while for dynamic properties, it produces results similar to the Rouse prediction.
- DPD, as a local thermostat, not only controls the temperature of the system, but it also contributes to the dynamic properties of the system.
- To understand the effect of chain crossing on polymer dynamics, a direct comparison of the hard-bead model and soft-bead model may be helpful (in proceeding).

References

- K. Kremer, G. S. Grest, J. Chem. Phys. 92 (8), 1990.
- R. D. Groot, P. B. Warren, J. Chem. Phys. 107 (11), 1997.
- S. Chen, N. Phan-Thien, X. J. Fan, B. C. Khoo, J. Non-Newtonian Fluid Mech. 118, 2004.
- S. Hess, M. Kröger, Physical Review E, 64, 011201, 2001.
- J. Rudnick, G. Gaspari, J. Phys. A: Math. Gen. 19, 1986.
- H. W. Diehl, E. Eisenriegler, J. Phys. A: Math. Gen. 22, 1989.
- M. Doi, S. F. Edwards, the theory of polymer dynamics, Oxford University Press, 1986.
- C. P. Lowe, Europhys. Lett., 47 (2), 1999.

Yanwei Wang, Ph.D student
 Danish Polymer Center
 DTU, Building 423, nr 112,
 Lyngby 2800, Denmark
 Email: www@kt.dtu.dk

