Supplemental Material for: Atomistic Hybrid Particle-Field Molecular Dynamics Combined with Slip-Springs: Restoring Entangled Dynamics to Simulations of Polymer Melts

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Determining the Number of Slip-Springs from MD Simulations

This section provides more details about the determination of the number of slip-springs in our model. The number of slip-springs N_{ssp} per chain is expected to depend linearly on the chain length. In practice, we conduct slip-spring hPF-MD simulations with different concentrations of slip-springs $\rho_{ssp} = N_{ssp}^{\text{total}}/N^{\text{total}}$, where N_{ssp}^{total} is the total number of slip-springs and N^{total} is the number of atoms in the system. Then we compute the mean square displacements of the chain centers and extract the values of g_1^{mid} at $t = \tau_R$. After that, comparing $g_1^{\text{mid}}(\tau_R)$ of different ρ_{ssp} with the reference MD values, the optimum total number of slip-springs N_{ssp}^{total} for each chain length is identified. In this work, chain length $N = C_{150}$, C_{200}, C_{250}, C_{300} and C_{350} and values of ρ_{ssp} from 0.03 to 0.08 are chosen for determining the number of slip-springs. An example is shown in Figure S1 for the mean square displacements of chain centers of PE (C_{350}) with various ρ_{ssp} and the reference MD result. It is worth noting that the MD simulation shows the same qualitative behavior as the slip-spring hPF-MD simulations with different ρ_{ssp}. As seen in Figure S4, the number of slip-springs per chain N_{ssp} is found to follow the linear relation with the chain length quite well. The linear relation is shown below:

$$N_{ssp} = k\,N + b \tag{1}$$

where $k = 0.037$ and $b = 4.12$ are the fitting parameters. This linearity between the number of slip-springs per chain and the chain length is also found in other slip-spring models [1,2]. With this relation, the number of slip-springs can be extrapolated for long polymers.

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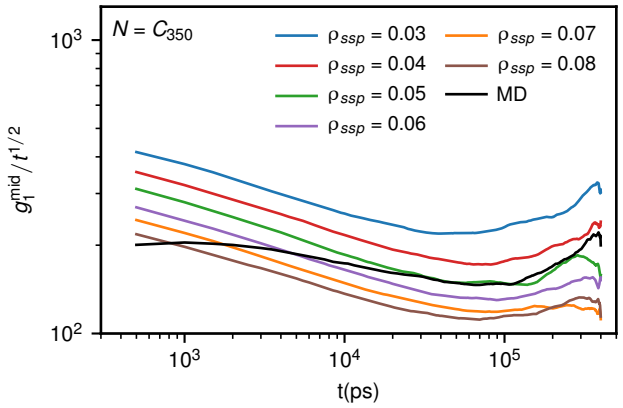


Figure S1: Mean square displacements of chain centers of PE (C_{350}) normalized by $t^{1/2}$ for slip-spring hPF-MD with various concentrations of slip-springs and the corresponding MD simulation.

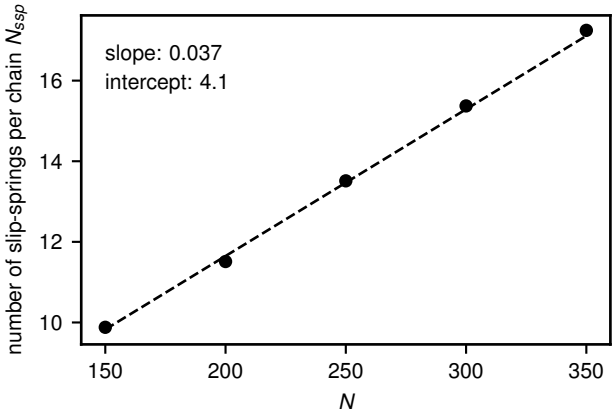
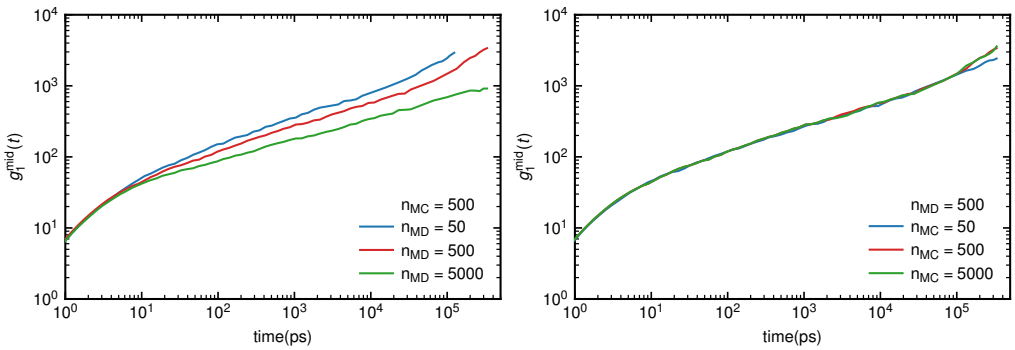


Figure S2: Dependence of the number of slip-springs per chain N_{ssp} on the polymer chain length N. The dashed line is a linear fit.



(a) (b)

Figure S3: Influence of sequence length of the molecular dynamics and Monte-Carlo blocks on the diffusive dynamics of polyethylene melts composed of 350 carbons.

Influence of Sequence Length of Molecular Dynamics and Monte-Carlo Blocks

The influence of the sequence length of Molecular Dynamics (n_{MD}) and Monte-Carlo (n_{MC}) blocks on polymer dynamics in the combination of slip-springs and the hybrid particle-field simulation is similar to the initial work of Langeloth et al., which introduces the slip-springs into the dissipative particle dynamics simulation. Basically, the number of MD steps between two MC blocks determines the duration time of the topological constraints (entanglement) imposed by the slip-springs on the polymer chains. Meanwhile, the number of MC steps between two MD blocks dictates the mobility of the slip-springs. In detail, we measure the mean square displacements of the chain center in polyethylene melts of chain length N=C_{350} to show the impact of different pairs of MD/MC sequence lengths. As seen in Figure 3(a), with the same MC block length $n_{\mathrm{MC}} = 500$, the mobility of the polymer melts is profoundly decreasing with increasing MD block length from $n_{\mathrm{MD}} = 50$ to $n_{\mathrm{MD}} = 5000$. On the other hand, the dynamics of polymer melts is expected not to be altered significantly by varying MC block length once it is larger than a critical value at which the slip-springs are mobile enough. Figure 3(b) shows the diffusive dynamics varying as the MC block length from $n_{\mathrm{MC}} = 50$ to $n_{\mathrm{MC}} = 5000$. when $n_{\mathrm{MC}} = 50$, the diffusive dynamics is unchanged in the short time regime, while slightly slower than that of both $n_{\mathrm{MC}} = 500$ and $n_{\mathrm{MC}} = 5000$ in the long time regime. The overlap of the mean square displacements of $n_{\mathrm{MC}} = 500$ and $n_{\mathrm{MC}} = 5000$ indicates that $n_{\mathrm{MC}} = 500$ sufficiently ensures that the slip-springs are mobile enough in our current systems. To achieve better computational efficiency, we employ $n_{\mathrm{MC}} = 500$ for all slip-spring hPF-MD simulations.

Parameters in Slip-Spring Hybrid Particle-Field Simulation

Table 1: Parameters in slip-spring hybrid particle-field simulation

parameters	explanation	units
T	temperature of the system	K
$\chi_{i,j}$	density-field interaction parameter between particles of type i and j	kJ/mol
κ	compressibility factor	1/(kJ/mol)
N	number of carbons of the polymer chain	-
M	number of polymer chains in the system	-
ρ	density of the system	kg/m^3
K_{ssp}	slip-spring bond force constant	kJ/mol
$r_{0,ssp}$	equilibrium distance of the slip-spring bond	nm
N_{ssp}	number of slip-springs in the system	-
n_{MD}	time steps for one molecular dynamics block between Monte-Carlo blocks	-
n_{MC}	time steps for one Monte-Carlo block between molecular dynamics blocks	-

Relationship between the Entanglement Length and Number of Slip-Springs per Chain

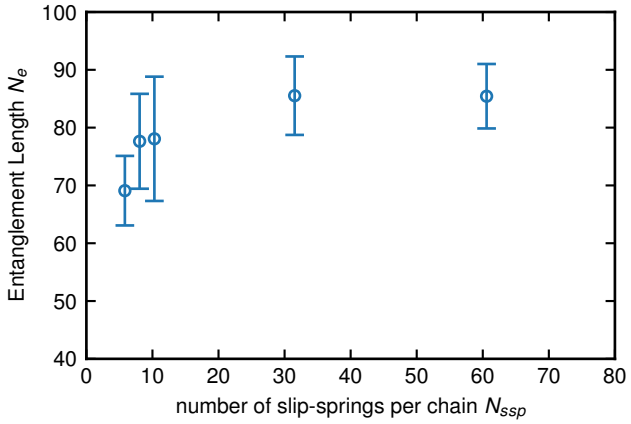


Figure S4: Dependence of the entanglement length N_e on the number of slip-springs per chain N_{ssp}.

References

1. Langeloth, M.; Masubuchi, Y.; Böhm, M. C. and Müller-Plathe, F., *The Journal of Chemical Physics*, 2014, **141**(19), 194904.

2. Sgouros, A. P.; Megariotis, G. and Theodorou, D. N., *Macromolecules*, 2017, **50**(11), 4524–4541.