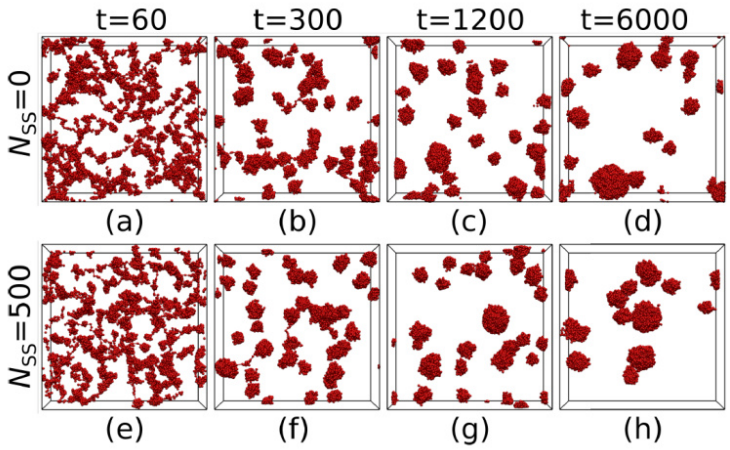
Hessisches Kompetenzzentrum
für Hochleistungsrechnen

Slip Spring DPD Simulations of Flash Nano-Precipitation from Polymer Solutions



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Project Term
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Clusters
Lichtenberg Cluster Darmstadt

Additional Software
Enhanced SlipLink Code v3

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Introduction

A recent and promising method to synthesize nanoparticles of defined size and structure is the so-called flash nanoprecipitation, where a polymer is dissolved in a solvent and precipitated by rapid mixing with a nonsolvent. A polymer chain undergoing this solvent-to-nonsolvent exchange will collapse into a globule. If multiple chains are present in the system, they will eventually form a nanoparticle. The aim of this project is to study the precipitation behavior of polymer solutions in dependence of e.g. the chain length. Additionally, the influence of entanglement effects on the stability of intermediate collapse states and thus on the precipitation dynamics is investigated. The use of long chains and an explicit solvent necessitates large systems of more than 1.1 million particles. Because only few chains are present in diluted solutions, results with sufficient statistics require multiple production runs. These prerequisites can only be met on a high performance computer such as Lichtenberg.

Methods

Simulations were performed using Dissipative Particle Dynamics, a mesoscale simulation technique incorporating correct hydrodynamic behavior. Because its soft-core interactions allow unphysical chain crossing, entanglement effects have to be restored using slip springs, i.e. artificial, mobile bonds. Slip-spring motion is governed by blocks of Metropolis Monte Carlo simulations. The combination of both methods is achieved in an in-house, MPI-parallelized Fortran code.

Results

An interesting, two-stage behavior is observed for the precipitation dynamics. Under initially good solvent conditions, chains are uniformly distributed through the simulation box. As they precipitate, polymer solutions form a high number of small blobs that are sometimes connected by bridging chains (see Figure 1). In this network-like state, these bridges are highly exposed to non-solvent and retract quickly, apparently under no influence of the number of slip-springs used. All globules eventually coagulate into a small number of nanoparticles. These observations, especially the short lifespan of the bridging chains, hold roughly independent of slip spring number or chain length (see monitoring of the chain dimensions in Figure 2). For more details, we refer to the respective article by Schneider et al. (see publications).

Discussion

Extensive simulations of precipitating polymer solutions were carried out to investigate the role of entanglement effects in flash nanoprecipitation. Our studies indicated an interesting collapse behavior of chains in dilute solutions, but did not expose any influence of entanglements. Early collapse stages showed dynamics independent of the chain length, which only became relevant on longer time scales. The process of single-chain collapse thus promises to be an interesting target for further studies.

Figures

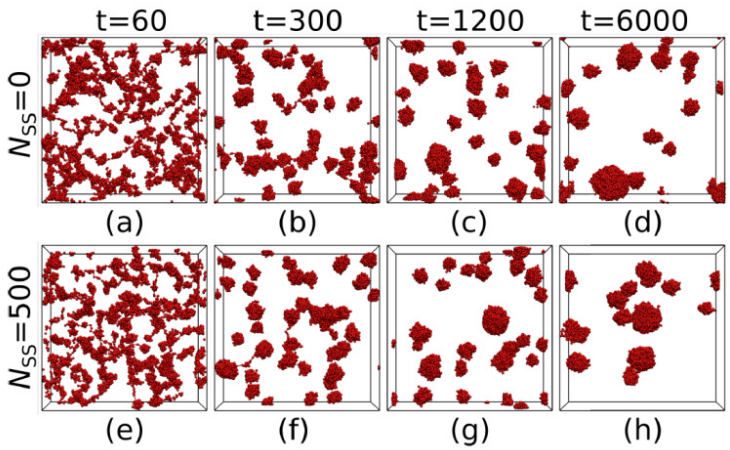

Figure 1: Snapshots of the precipitation of a solution of 56 chains (N = 200) with N_{SS} = 0 ((a)- (d)) and 500 ((e)-(h)). Solvent molecules are not shown. Snapshots are taken at 0, 300, 1200 and 6000 t_{DPD} after the solvent-to-antisolvent exchange using the VMD software.

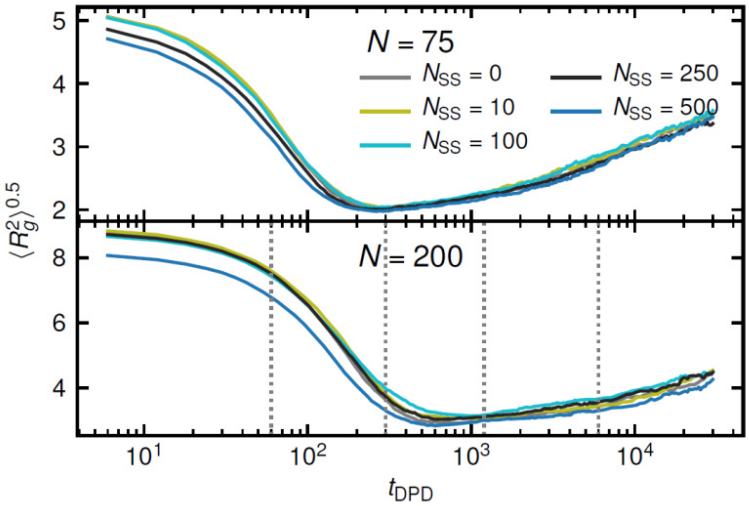

Figure 2: Root mean squared radius of gyration $[R_g^2]^{0.5}$ for chains of different lengths N with different slip spring numbers N_{SS}. At t = 0, 50 % of the solvent beads are exchanged for antisolvent. Dotted gray lines for N = 200 indicate the times when the snapshots displayed in Figure 1 are taken.

Publications

Schneider, J.; Süss, L. D.;Müller-Plathe, F.: The Influence of Entanglements on the Dynamics of Flash Nanoprecipitation: A Slip-Spring Dissipative-Particle-Dynamics Investigation. J. Chem. Eng., 2019 https://doi.org/10.1021/acs.jced.9b00679

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