Coarse Grained Model of Entangled Polymer Melts

By

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ABSTRACT

A coarse graining procedure aimed at reproducing both the chain structure and dynamics in entangled polymeric melts is presented. The reference, fine scale system is a bead-spring-type representation of the melt. This model is used to calibrate the coarse model for a specific monodisperse melt of linear chains. The coarse model is then used to represent the structure and dynamics of various other systems in thermodynamic equilibrium and non-equilibrium. Extensive comparison with equivalent fine scale models is performed to verify the coarse model.

The level of coarse graining is selected equal to the number of beads in the entanglement segment, N_e. The coarse model is discrete and contains blobs each representing N_e consecutive beads in the fine scale model. The mapping is defined by the following conditions: the probability of given state of the coarse system is equal to that of all fine system states compatible with the respective coarse state, the dissipation per coarse grained object is similar in the two systems, constraints to the motion of a representative chain exist in the fine phase space and the coarse phase space is adjusted such to capture them. Specifically, the chain inner blobs are constrained to move along the backbone of the coarse grained chain, while the end blobs move in the 3D embedding space. The end blobs continuously re-define the diffusion path for the inner blobs. The input parameters governing the dynamics of the coarse grained system are calibrated based on the fine scale model behavior. These are the characteristic length scale, N_e, and the effective friction coefficient per coarse grained object. Although the coarse model cannot reproduce the whole thermodynamics of the fine system, it ensures that the pair and end-to-end distribution functions, the rate of relaxation of segmental and end-to-end vectors, the Rouse modes and the diffusion dynamics are properly represented.

The model intrinsically captures contour length fluctuations and reptation behavior. Constraint release is additionally implemented by tracing the position of the ends of all chains in the system and performing a local relaxation of the chain backbones once end

retraction is detected. This algorithm takes advantage of the multibody nature of the model and requires no heuristic input parameters that would control, for example, the frequency and the magnitude of these fluctuations. The model is used, without additional calibration, to study start-up and step strain shear flows and reproduces features observed experimentally such as the overshoot during start-up shear flow, the Lodge-Meissner law, the monotonicity of the steady state shear stress with the strain rate, and shear thinning at large $\dot{\gamma}$. Most of the simulations reported are performed in conditions in which using a fully refined model of the same system would have been extremely computationally demanding or simply impossible with the current methods.

Chain diffusion is studied in mixtures of bi-disperse linear polymers of same chemical identity by means of the coarse grained model with no additional calibration. The two sub-populations are moderately to highly entangled, with the shorter chain length N_S fulfilling $N_S / N_e \geq 5$. Its performance in reproducing chain dynamics in a polydisperse melt is tested by extensively comparing the results with those obtained from an equivalent fine scale representation of the same system. The coarse grained model is used further to investigate for the first time by means of simulations the scaling of the diffusion coefficient with the length of the two types of chains and its dependence on the respective fractions. The model reproduces many features observed experimentally. For example, the diffusion coefficient of one of the chain types decreases with increasing the length of the other type chains. It is shown that, in this model, this effect is not linked to constraint release. When the matrix chains become sufficiently long, their length does not influence the diffusion coefficient of the short chains anymore. The diffusion coefficient of the short chains scales with their weight fraction in a manner consistent with experimental observations. In mixtures, the dynamics of the short chains is slower and that of the long chains is marginally faster than in their respective monodisperse melts. This type of simulations are not feasible at present using classical methods, due to the large system size required and the long relaxation times observed in such entangled melts.