

Review

Quantitative study of equilibrium and non-equilibrium polymer dynamics through systematic hierarchical coarse-graining simulations

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Study of complex macromolecular systems through molecular simulations is a very intense research area. Here we present an overview concerning the development and application of hierarchical particle coarse-graining molecular dynamics simulations on the quantitative prediction of the dynamics and the rheology of polymers. Through a systematic time mapping approach that involves data from detailed atomistic dynamic simulations the coarse-grained polymer model can be used to quantitatively predict the dynamics and the rheology of the polymeric chains in a very broad range of characteristic length and time scales. Data from the application of these approaches on the dynamics of polystyrene melts under equilibrium and under shear flow conditions are presented.

Keywords: molecular dynamics simulations, shear flow, coarse-grained models, segmental relaxation, terminal dynamics

1. Introduction

Accurate knowledge of the dynamical and rheological behavior of complex macromolecular fluids is very important both for scientific questions and technological applications of macromolecular materials. From the technological point of view data about the dynamics and the rheology of complex systems are extremely useful for their processability, as well as for the prediction of their final rheological, mechanical and electrical properties (Larson, 1999). This knowledge is also important from the scientific point of view and, for example, it could be used to check the predictions of theoretical models, such as the Rouse model and the reptation theory (Doi and Edwards, 1986). Therefore, efforts to obtain and ultimately predict these properties, either through experimental methods or theoretical and simulation approaches have been reported in the literature (see for example Larson, 1999; Binder, 1995 and references within).

Main goal in this field is the study of the dynamics and the rheology of complex macromolecular systems at the molecular level. This is a very challenging issue for both experiments and simulation approaches due to the enormous range of length and time scales involved. The latter is a general characteristic of all macromolecular systems, due to the different characteristic time scales associated with the motion of various parts-segments (length scales) of the polymer chain (Doi and Edwards, 1986; Evans and Morriss, 2008). For example, concerning the length scales,

the dynamical behavior in the monomer level is determined by the actual structure and friction in the monomeric level (typical lengths of a few (1–5) Å), whereas the critical length for the chain conformations is the Kuhn segment (length scale of a few (1–2) nm), and the macroscopic rheological properties of the entire system are characterized by the radius of gyration or the conformation tensor of the macromolecular chains. Concerning the relevant time scales, things are even more complicated. Chemical bond vibrations within a polymer chain are typically characterized by times of a few fs (10^{-15} s), whereas conformational changes associated with dihedral transitions take place in times of the order of a few ps (10^{-12} s), for temperatures well above the glass transition, T_g , and much longer times (~1 s) for temperatures close to T_g . Even more, relaxation of the entire chain can be of the order of seconds even for temperatures far from T_g , whereas the dynamics of various segments along the chain is characterized by all intermediate time scales. In addition the relevant length and time scales of systems under non-equilibrium conditions can be even broader.

Because of all the above several simulation and experimental studies of the dynamics and rheology of macromolecular soft matter appeared in the literature. In this aspect molecular simulations can be of particular importance because of their direct connection to the microscopic (atomistic) structure of the molecular system. Therefore, such simulation methodologies are nowadays a valuable tool for studying dynamics and rheology of complex fluids and in particular of macromolecular (polymeric) materials. Among these, molecular dynamics (MD) and non-

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