

Complex polymer liquids form a system in which active processes play an important role. The constituting elements (polymers) are in principle very simple, but put together and quenched, mixed or sheared, they form a variety of emergent patterns due to phase separation and reaction processes. In principle, phase separation processes can be described and modeled on different levels, varying in scale from microscopic to macroscopic. The scale of interest in this thesis is mesoscopic. Many industrially interesting polymer material properties are determined by mesoscale morphologies. The model that is developed in this thesis should eventually lead to a tool that allows a chemical engineer to design processing conditions such that a particular mesoscale structure can be made in bulk quantities. To achieve this goal it is essential to incorporate both microscopic properties of the polymers in the liquid or melt *and* the processing conditions into the model. Models that are generally applicable to mesoscale materials are at present still absent. In this thesis it is shown how a mathematical model can be developed that incorporates static microscopic information and dynamic phenomena and that predicts structures in industrially processed complex polymer liquids.

The basis of the mathematical model is the dynamic mean-field density functional method which is derived from principles based on thermodynamics and statistical mechanics. A free energy description for an ensemble of individual chains in a mean-field environment is used, in which the architecture of the polymers, the connectivity of the monomers and the cohesive interactions between chains are properly accounted for. The free energy is not truncated at a certain level as in many phenomenological models, but instead the full polymer path integral is retained using a numerical procedure. The open formulation of the free energy and the flexible model for the dynamics allow for many different phenomena of interest to be described. The extensions and adaptations of the method as described in this thesis are called for by practical problems and applications.

Some of the extensions are of numerical mathematical nature. Since the method is computationally very intensive it is very important to optimize the numerical algorithms. Therefore new quadrature rules are presented for the efficient integration of Gaussian chain polymer density functionals on a uniform 3D grid. Another considerable improvement in the numerical efficiency of the method would be furnished by an explicit expression for the dynamics in terms of the densities. The current implicit formulation implies that the whole algorithm is iterative and

hence time consuming. An expansion of the external potential is studied, similar to well-known expansions of the free energy. Although this expansion does not directly lead to an explicit dynamics model, it provides analytical parameters for a gradient free energy expansion, giving rise to a whole new class of phase separation models. It is also shown that the free energy description in the dynamic mean-field density functional method encompasses most phenomenological free energy models, being much richer in behaviour.

The other extensions of the dynamic mean-field density functional method that are described in this thesis aim at widening its application area. Although most polymer melts are only slightly compressible, some phenomena can be observed in experiments that are due to excluded volume effects. In order to represent these phenomena properly, different compressibility models are discussed and compared both analytically and numerically. Currently, a penalty model is used which correctly reproduces experimental observations. The kinetic model of the method has also been improved. Experimental results show that the Onsager coefficient is nonlocal. Instead of using a simple local coupling approximation, a model has been developed that includes the essential physical features of nonlocal coupling in the Rouse model. Surprisingly, this model also leads to different (external potential) dynamics. As there is a lot of rheological interest in polymer liquids, an expression for the stress tensor was derived analytically using a virtual work principle. This method automatically provides an equation of state, which can in principle be used to perform constant pressure simulations. An important step towards incorporating processing conditions in the dynamic mean-field density functional method is the inclusion of hydrodynamic effects. It is shown that it is justified to use a simple approximation for the velocity field, which incorporates an effective local friction force. This simple model reproduces experimentally observable hydrodynamic effects. In order to represent strange effects such as shear-thinning in rheological flow experiments, the effect of simple steady shear on polymer orientation and elongation is explicitly taken into account by adapting the polymer configuration distribution function. A simplified model is used in which the connected beads in a polymer chain react to the flow as independent dumbbells. This model correctly reproduces conformational changes.

Finally, a few application areas of the dynamic mean-field density functional method are discussed which may be expected in the near future.