The dynamics of polymers by novel mesoscopic methods
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Summary

The research presented in this thesis mainly considers the results of mesoscopic computer simulations on polymer solutions. This can be broken down into two parts, namely computer simulations and the behaviour of polymer chains in solution. Consequently, in the first two chapters we give an introduction to these topics. First, in chapter 1, we try to do this on a very basic level. We aim to make these concepts accessible to non-experts. Next, in chapter 2, we discuss the topics in more detail. In this chapter we describe for instance how and why we use a dissipative ideal gas coupled to a Lowe-Andersen thermostat as our simulation method. Furthermore, we introduce some of the important concepts in polymer physics, for instance the Gaussian chain and the excluded volume effect.

In chapter 3 we describe a novel method for implementing a solid boundary in mesoscopic simulations. We demonstrate this method on pressure-driven flow between two plates, in which case the flow profile must be the parabolic Poiseuille result. The solid boundary should result in a stick boundary condition at exactly the solid/fluid interface. Furthermore, the presence of the boundary should not influence the density and temperature distribution of the model solvent. The first requirement is easily fulfilled by imposing a simple bounce-back condition: the velocity of a particle impinging the surface of the boundary is reversed. The latter two requirements have proven to be more difficult, although from literature it is known that it is essential to have continuity of the stress over the interface. We propose a new method that, besides a bounce-back boundary, involves the introduction of a relatively small “dummy” layer, filled with particles identical to the other mesoscopic particles. Interactions between particles in the two areas proceed in the normal manner. The dummy region is closed by a slip boundary: particles impinging this surface bounce forward. This does not introduce additional momentum in the axial direction and the total force on the slip surface is zero. Consequently, the total force acting on the fluid is only the sum of the force exerted on the two sides of the “real” interface. By ensuring that the total force on the system is zero, we also ensure that the stress over the boundary is continuous. This is arranged by introducing an external force over the
dummy particles, opposite in direction to the force that is required to drive the flow in the real system, but with the same magnitude. We compare this method with two other alternative methods. First, a bounce-back boundary without dummy region at all and, second, a bounce-back boundary complemented by a dummy region filled with particles whose velocities are drawn randomly from the distribution of thermal velocities at zero flow velocity. All three methods correctly impose a no-slip boundary condition. However, only for the method we introduced the flow profile agrees exactly with theory. We also tested our method on flow through a tube with an elliptical cross-section and it works equally well.

In chapter 4 we use the boundary method discussed in chapter 3 to study the dynamics of ideal polymer chains in a solvent flowing through microfluidic capillaries. Using novel fabrication methods, it is now possible to construct microscopic flow devices. Therefore, it is of scientific interest to study the behaviour of polymer solutions on the micrometer scale. At low Reynolds numbers the flow profile of a pressure-driven flow in a tubular geometry is parabolic. Due to steric hindrance, the centre-of-mass of a big polymer chain spends less time close to the boundary than the centre-of-mass of a smaller polymer. Consequently, the bigger chains spend more time in the high velocity region than the smaller polymers, resulting in a higher average “accelerated” drift velocity. Based on this velocity difference, experimentalists can separate particles of different sizes. This technique is called hydrodynamic chromatography. We calculated the drift velocity as a function of the polymer radius of gyration, \( R_g \), relative to the size of the tube, \( R \). We find excellent agreement between our results and experiments for \( R_g/R < 0.25 \). We show that in this case one can neglect hydrodynamic interactions and is allowed to consider only the depletion effect arising from the steric hindrance with the boundary. That makes it surprising that theories including the hydrodynamic interactions correctly predict the drift velocity of polymer chains in this regime. Furthermore, we demonstrate that for higher confinement, \( R_g/R > 0.25 \), the hydrodynamics do play an important role. The polymer drift velocity is reduced, relative to the situation where hydrodynamic interactions are not included. We propose an empirical fit that correctly describes our results, up to \( R_g/R \sim 2 \). We conclude the chapter with a short discussion on the nature of ordering of polymer chains at higher flow velocities.

In the fifth chapter we consider pressure-driven non-dilute polymer solutions in microfluidic capillaries. The long relaxation time of the polymer chains strongly influences the properties of the surrounding solvent. As a consequence, the shape of the flow profile deviates from the normal Poiseuille profile. Many theories are available that predict the shape of the flow profile, but we demonstrate these cannot be correct. Because all our simulations
are at low flow velocities and the polymers are not evenly distributed across the channel, general theories for non-Newtonian fluids are not relevant in this case. Furthermore, we demonstrate that methods assuming a depletion layer with a width of roughly $R_g$ are also incorrect. The results of our simulations show that the polymer volume fraction determines the shape of the flow profile. We propose a new formula that successfully predicts the shape of the flow profile. This formula originates from the Brinkman theory for flow in inhomogeneous porous media. Once we assume that polymers in the solution behave like a porous medium with some “slight slip”, we find a dependence between the slip length and polymer volume fraction. Our new model does not only work for flow profiles generated with computer simulations. We show that the model can also qualitatively predict the shape of flow profiles obtained from experiments.

The thesis is concluded with chapter 6, in which we discuss a new model for mesoscopic simulations of excluded volume chains. In the previous chapters we only considered ideal chains, corresponding to “real” polymer chains at the so-called theta temperature. This new model allows us to also look at polymers away from the theta temperature. We construct an excluded volume polymer model that consists of “bloppy” monomers, each blob representing a long model polymer. In principle one can employ an arbitrary potential between the blobs because it has been shown that, when the model chains are long enough, they all behave identical. In this chapter we propose a potential that enables us to reach the point where all polymer chains behave identical using only a limited amount of monomers. We test this model on three different problems. First, the properties of our blob chains in the dilute limit, using the structure factor. Here we conclude that the behaviour is consistent with de Gennes’ model for the screening of excluded volume interactions above the so-called overlap concentration. Second, the osmotic pressure of a polymer solution as a function of concentration. We find that only a relatively small number of monomers is needed to recover the correct thermodynamic behaviour in the semi-dilute regime. Third, the pressure required to confine a polymer in a spherical cavity. The scaling of the pressure shows behaviour that is similar to the scaling of the osmotic pressure with concentration for semi-dilute polymer solutions. This finding agrees with recent theoretical predictions and with simulations. However, we also show that the analogy between the two is only approximate. Finally, almost all simulations in this chapter were performed using a modified version of the Lowe-Andersen thermostat, that proves to be significantly more efficient than simply thermostatting the complete system.