Downloaded from UvA-DARE, the institutional repository of the University of Amsterdam (UvA)
http://dare.uva.nl/document/110268

File ID 110268
Filename Chapter 1: Introduction

SOURCE (OR PART OF THE FOLLOWING SOURCE):
Type Dissertation
Title The dynamics of polymers by novel mesoscopic methods
Author A. Berkenbos
Faculty Faculty of Science
Year 2008
Pages vi, 130

FULL BIBLIOGRAPHIC DETAILS:
http://dare.uva.nl/record/278159

Copyright

It is not permitted to download or to forward/distribute the text or part of it without the consent of the author(s) and/or copyright holder(s), other than for strictly personal, individual use.

UvA-DARE is a service provided by the library of the University of Amsterdam (http://dare.uva.nl)

CHAPTER 1

Introduction

1.1 POLYMERS

Polymers form a very important class of materials in our modern world. Widely used polymeric substances are for instance plastics, Nylon, Teflon and Kevlar (see Fig. 1.1 C). The reason that polymers are so widely used, is that it is possible to change the properties of polymeric materials almost at will. Polymer chains are very large, built out of many repeating units called "monomers" (as depicted in Fig. 1.1 A). The monomers can be relatively simple, only consisting of a single carbon atom and two hydrogen atoms (see Fig. 1.1 B), or they can be much more complex, involving many (different) atoms. By changing the chemical composition of the monomers, the properties of the complete polymer can change dramatically. These properties are very diverse, for instance the electrical resistance, the mechanical strength, the solvent permeability and the resistance to heating. However, in this thesis the composition of the monomers and the properties listed in the previous sentence are not considered. I look at polymers on a more abstract level. Polymer chains are modelled as small spheres called "beads", connected by springs. Using such a simple model one cannot expect to incorporate all these diverse properties. However, what is incorporated are two very important concepts: the size of the polymer in a solvent and the rate at which the chain moves through this solvent.

The exotic behaviour of polymer solutions out of equilibrium is an interesting research area. Typical examples are shear thinning[1–3] and elastic turbulence at small flow velocities.[4,5] The viscosity of a polymer solution is higher than the viscosity of the solvent without the polymer chains. Shear thinning is the phenomenon that the viscosity of a polymer solution decreases if the solution is sheared. The shearing can for instance take place between two

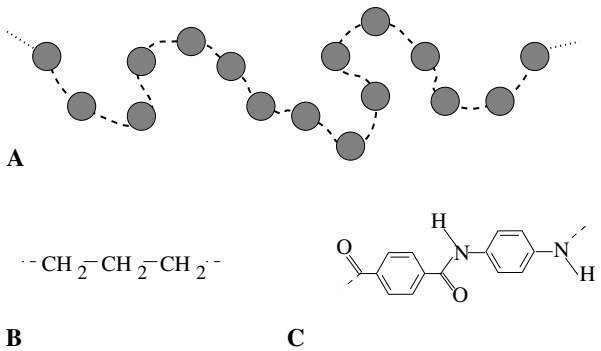

Figure 1.1: Schematic representation of a polymer chain (A). The chemical composition of monomers can be very different. Shown here are polyethylene (B) and Kevlar (C).

walls moving in opposite directions. Elastic turbulence at small flow velocities means that a polymer solution can behave like turbulent water flow at very low flow velocities. These phenomena are caused by the relative long relaxation time of the polymer chains. This influences the behaviour of the surrounding solvent particles. Despite a large volume of scientific publications, the mechanisms behind these phenomena are still not completely unravelled. A special class of polymers are the naturally occurring ones, such as DNA and proteins. With the development of novel fabrication techniques it is now possible to construct microscopic flow devices with dimensions of the order of one DNA chain. This enables researchers to manipulate single molecules and learn more about the behaviour of those. The fluid behaviour inside such devices ("microfluidics") differs dramatically from our day-to-day experience.

1.2 COMPUTER SIMULATIONS

Computer simulations can be an excellent tool to complement experiments in the microfluidic regime because they enable one to carefully examine single polymer chains in great detail. As such, I believe that computer simulations can lead to a more complete understanding of the complex behaviour of polymer solutions. Most computer programs that are used to perform dynamic simulations on molecules work in the same manner. Imagine balls on a pooltable. If they move in a straight line they keep on doing so until they bounce against a wall, or until they bounce against another ball. In that case the trajectory and speed of the balls change. In more physical terms:

the balls keep on moving with the same velocity and trajectory (this can also mean that they have a velocity that is exactly zero) until they interact with another ball or with the wall of the table. Dynamical computer simulations of particles proceed in a way similar to the balls on a pooltable. The particles continue following their trajectory until they interact with another particle or with for instance a boundary.

It is only possible to perform simulations if the exact position and velocity (and the direction of the velocity) of all particles in the system is known. With this knowledge the position of all particles a moment later can be computed. Next, all interactions between all particles are evaluated and the new velocities are determined. A moment later all positions are calculated again, and the new velocities of all particles are determined, and so on, and so on. The time it takes to be "a moment later" is called a time step. The time steps cannot be too big because then one might miss collisions between particles. However, if the time step is set too small it will take very long before the simulation is finished. The trick is to choose the time step such that it is as big as possible, without missing interactions between particles.

In nature, all processes have their own characteristic length and time scale. On the smallest scale there is for example the motion of electrons, on the largest scale there is the motion of planets and galaxies. Electrons can move to another atom in less than a femtosecond,[6] whereas astronomers use light years to describe the distance between galaxies. In between these two extremes are polymer molecules, diffusing their own distance in seconds, or, if they are very large, hours or even days. Each process, with its own relevant time scale, requires a different simulation technique. As an example imagine using a computational method where the movement of electrons is taken into account. By definition the time step of this method must be smaller than the typical relevant time. Using this method to calculate a diffusing polymer chains will take at least more than 10^{15} time steps, a number far too high for any supercomputer.

The time and length scales on which polymer molecules show interesting behaviour is called the mesoscopic regime. As a mesoscopic model solvent a dissipative ideal gas is used, coupled to a Lowe-Andersen thermostat.[7] One of the big advantages of this simulation technique is that the particles move in continuous space, whereas with other methods their movements are sometimes restricted to a grid. This is an important feature of this simulation method, considering the complex morphology of polymer chains. Other advantages of this method over other mesoscopic simulation methods are that it is computationally efficient in the microfluidic regime we are interested in,[8] it is simple to implement and, finally, it is a particle model with correct

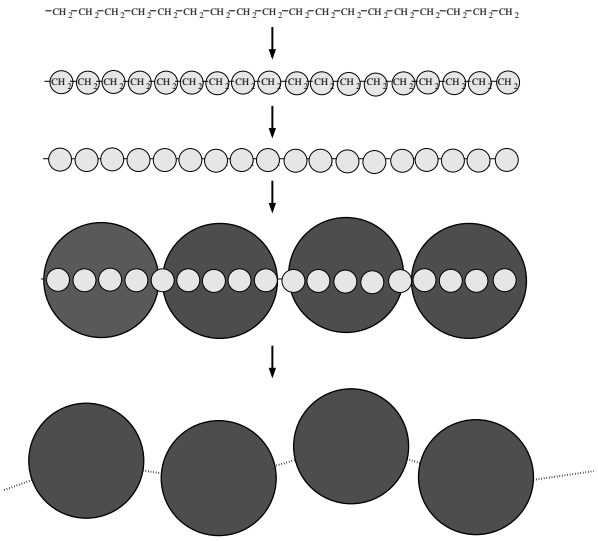

Figure 1.2: From a "real" polymer chain to a simplified model polymer.

hydrodynamic interactions included by construction.

Turning to the polymer chains, despite the fact that all atomic details are ignored, they still need to be drastically simplified (such that the polymer model will not be longer than a hundred particles). In Fig. 1.2, I demonstrate how a "real" polymer is simplified to a very short model polymer. However, it only makes sense to renormalize the original polymers to a much shorter model chain if the dynamics of the real polymer can also be captured by the model chain. Lowe *et al.* have developed a method that enables one to reproduce the hydrodynamic properties of real polymer chains using a very short polymer model.[9]

1.3 OUTLINE OF THIS THESIS

The techniques described in this chapter are more thoroughly explained in chapter 2. First an introduction to polymer physics is presented. In the second part of chapter 2 the most important concepts of mesoscopic simulations are discussed, followed by a section with a description of how long polymer scaling can be retrieved using short model chains. In the following chapters research results are presented. In chapter 3, I introduce a novel method for the inclusion of solid boundaries in mesoscopic particle meth-

ods. Many practical problems involve the flow of confined fluids, polymer solutions in porous media for example. On a mesoscopic scale the boundary should not introduce artificial density fluctuations and, on average, the fluid velocity at the interface should be zero. The new method meets these requirements and is based on simple physical arguments. This method is employed in chapter 4, where the drift velocity of single polymer chains flowing in a pressure-driven flow in a microfluidic capillary is investigated. The influence of the polymer size relative to the tube width on the results is compared with experimental data. In chapter 5 the same system as in chapter 4 is considered, but this time with polymer solutions at much higher volume fractions. In this case the polymer chains alter the shape of the fluid flow profile. A new model is proposed that correctly describes the different shape of the profile. Finally, in chapter 6 a novel method for modelling excluded volume polymer chains is presented. This method treats the beads as blobs, which each in itself represent big pieces of polymer. The model is applied to investigate some interesting research questions, among which is the behaviour of excluded volume chains in spherical confinement.