

Chapter 1

Introduction

Polymers are of considerable interest both in industry [Ber91] and in biology [Hua05]. In the context of industry it is important to understand the properties of polymers while they are liquid and undergo flow because at some point during the production of most polymeric products the material is liquid. The utility of polymeric liquids has meant that they have been analysed in significant detail. The resulting models for the flow of polymeric liquids require constitutive equations or models which can largely be divided into two groups: firstly microscopic models based explicitly on some level of molecular detail and secondly models which are based on principles of continuum mechanics. Microscopic models include the influential model of Doi and Edwards [DE78a, DE78b, DE78c, DE78d, DE86] and a model of Curtiss and Bird [CB81b, CB81a, BSC82a, BSC82b, SBC82, BCAH87]. As we will discuss further in Chapter 2 models like these two have seen many variations over the last thirty years, incorporating additional detail required for the accurate prediction of the behaviour of polymeric liquids under flow.

Increasingly computer simulations have been used to calculate thermodynamic properties of polymeric liquids from a molecular basis [KG90]. In these simulations a suitable choice of molecular potential needs to be made and some compromise must be made between atomic detail and computa-

tional efficiency. Two molecular models which have been used, one of which is the model considered by Kröger *et al.* [KLH93] which uses the so called *finitely extensible nonlinear elastic* potential (FENE) as the bonding potential between beads of the model polymer; in this thesis we use the name FENE molecule for this example. A second molecular model which has had considerable use, particularly in the nonequilibrium literature, constrains the length of bonds between beads in the chain. We use the name *freely jointed chain* molecule or FJC molecule for this model. In addition to these last two examples there are also a considerable number of models which seek to incorporate specific chemical detail of molecules. One of the main aims of this thesis is to compare results from the simulation of the FENE and FJC molecules.

A key property of the microscopic models mentioned above is the assumed behaviour of diffusion in the polymer melt. In particular both the Doi-Edwards model and the Curtiss-Bird model use the *reptation* assumption, that polymer molecules in the melt are forced to diffuse in the direction of the contour of a polymer and are constrained to some extent from diffusing in the transverse direction. In the case of nonequilibrium molecular dynamics simulations the anisotropic nature of the diffusion becomes apparent when liquids are far from equilibrium. This behaviour has had some analysis under planar Couette flow using algorithms developed for NEMD. However, this property has not been previously investigated for molecular systems under planar extensional flow (PEF) and in addition previous simulations which have been performed under planar Couette flow (PCF) have only measured these properties for a limited range of molecular weights. Considerable attention is paid to these properties in this thesis and furthermore, correlation functions are used to analyse the dynamics of molecules under extensional and shear flows.

Our simulations of PEF rely on the Kraynik-Reinelt periodic boundary

conditions (pbcs) [KR92, TD98, BC99, TD99]. These pbcs allow simulations of PEF of indefinite duration. In Chapter 3 we show that these pbcs are related to the Arnold cat map which is an example of a simple chaotic map. More particularly, the usual Arnold cat map corresponds to one lattice from the family of lattices found by Kraynik and Reinelt [KR92] which are mapped back onto themselves under PEF. The cat map provides an illustration of the Kraynik-Reinelt pbcs which is in many respects more tangible than previous descriptions. Our observations have led to a better understanding of the chaotic properties of NEMD simulations of extensional flows [Tod05] and have informed subsequent studies by Frascoli, Todd and Searles [FTS07, FST06, FT07].

We now give a chapter by chapter outline of this thesis: Chapter 2 introduces the theory of polymeric liquids and flow. We also introduce the idea of constitutive equations and then introduce the Doi-Edwards model and some theory of polymers. We also outline the calculations required to compare the Doi-Edwards model with results from simulation. Chapter 3 presents the NEMD algorithms we have used and, as mentioned above, the second half of the chapter describes the connection between the pbcs used for PEF and the Arnold cat map. Following these detailed descriptions of the algorithms used, Chapter 4 presents results for the comparison between the FENE and FJC molecules. Properties presented in this chapter include macroscopic viscometric functions and some structural and dynamical properties such as molecular spin angular velocity and molecular alignment. Chapter 5 is devoted to the diffusive properties of the systems studied. In this chapter methods and results from the calculation of the diffusion in these systems out of equilibrium are presented. Alongside these results are presented the velocity autocorrelation functions which are analysed in conjunction with the results from Chapter 4. A summary of conclusions of the thesis is presented in Chapter 6 together with several recommendations for further work.