

Chapter 6

Conclusion

We have presented results of nonequilibrium molecular dynamics simulations (NEMD) of concentrated systems of two types of linear chain molecule: the FENE molecule and FJC molecule. The first of these uses the flexible FENE potential and the second uses a constraint force algorithm to fix the separation between bonded atoms. These simulations have been performed under planar Couette flow (PCF) and planar extensional flow (PEF) using the molecular SLLOD algorithm. We have compared the behaviour of these molecules, calculating a range of viscometric, structural and dynamical properties. Having established the similarity of the properties of these two molecules we have focused on the calculation and analysis of the self-diffusion tensor and velocity autocorrelation functions under PCF and PEF. The PEF simulations represent the first NEMD calculation of the diffusion tensor in a concentrated system under an extensional flow. Our ability to perform these simulations under PEF have been brought about by the recent development of the Kraynik-Reinelt periodic boundary conditions (pbcs). We have shown in this thesis that these pbcs are closely related to the Arnold cat map, a simple dynamical map, which is commonly used as an example of a chaotic system. In addition we have calculated the predictions of the Curtiss-Bird model for PEF and briefly compared these with results from the NEMD

simulations.

Model liquids of both FENE and FJC molecules have been used by previous authors in a wide range of NEMD investigations. This has motivated us to present the results in this thesis of a direct comparison of these two models. To clarify the comparison we chose to simulate FJC molecules with the fixed bond length $b = 0.97$ which corresponds to the average bond length of the FENE molecule which we have observed over a wide range of strain rates under both PCF and PEF. The comparisons between the molecules have been made for systems of 2,4,10,20 and 50-site molecules. Data for 100-site systems have been presented for FENE molecules only. The properties on which we have based our comparison include: the shear viscosity, the two extensional viscosities, the first and second normal stresses, the mean squared end to end length of molecules, the radius of gyration and the order parameter. Specifically under PCF we have also calculated the spin angular velocity of molecules ω_z and the alignment angle. In all cases we have found that there is very little difference between the FENE and FJC molecules. The similarity of the rheological properties of these two molecules arises because, despite using different algorithms, the molecular structure varies only slightly and because the pressure tensor calculation involves just intermolecular forces and kinetic contributions. We have briefly tested the computational efficiency of the FENE and FJC force calculations finding that FENE calculations were more efficient than FJC calculations, particularly for longer molecules. However, comparisons of efficiency should be performed with recent improvements to the FJC constraint algorithms made by Daivis.

Our data for the order parameter under both flows, as well as our data for the spin angular velocity ω_z under PCF, represent the most extensive data for these properties in the literature. From the order parameter results we have noted that alignment is significantly enhanced under PEF, going

through a fairly abrupt transition with strain rate when compared with the alignment under PCF. This difference between the flows is due to the rotation of molecules under PCF which leads to some suppression of the alignment of molecules, while for PEF, having no spin angular velocity, molecules are able to align with the stream lines of the flow. Our results for spin angular velocity ω_z of molecules under PCF show trends which have not been seen in previous data. At low strain rates data follow or approach the relation $\omega_z = -\dot{\gamma}/2$ which is predicted by irreversible thermodynamics. However, in general, for higher strain rates, we have observed that the data follow a power law behaviour $\omega_z = -\alpha\dot{\gamma}^\beta$ with coefficients α and β dependent on the molecular weight. The exponent β was found to decrease with the molecular weight, which is clearly explained by the increased obstruction of motion for larger molecular weights. As yet we do not know the reason for the wide applicability of the power law relation. Further investigations might compare this behaviour with structural properties of the liquid. Clarification of the dynamics would also come from comparisons of the spin angular velocity of individual molecules with their individual alignment angle, as has been performed in previous studies of shorter molecules by Edberg *et al.* [EEM87, EME87]. Trends in the other properties we have used to compare FENE and FJC molecules have been reported by previous authors.

There is a very significant body of literature which presents microscopic models of polymeric liquids based on assumptions about the dynamics at the molecular level. In Chapter 2 we summarised several of these models including the Doi-Edwards model and the Curtiss-Bird model (CB-model). Our calculation of the predictions of the CB-model under steady state PEF is to the best of our knowledge the first presentation of this result in the literature. Having the Curtiss-Bird prediction of the extensional viscosity for different values of the link tension coefficient ϵ we have been able to compare NEMD results with the results of the model. Both NEMD results

at constant volume and results of the CB-model show an increase in the extensional viscosity with strain rate and a plateau viscosity at high strain rates. However, we have found that the ratio between the zero strain rate viscosity and the plateau viscosity falls outside the range allowed by the CB-model. In particular the NEMD results do not correspond at all with the prediction of the Doi-Edwards model which is equivalent to the CB-model with $\epsilon = 0$. In future work it would be interesting to compare our NEMD results with predictions of more recent models which incorporate more features of polymer dynamics.

An important consideration of many of the microscopic models of polymer rheology is the self-diffusion of individual molecules in the tangle of surrounding molecules. Thus, along with the collection of properties we have calculated in comparing the FENE and FJC molecules, we have also calculated the elements of the self-diffusion tensor and velocity autocorrelation functions for systems under both PEF and PCF. Previous works by other authors have investigated these properties for concentrated systems of molecules under PCF and have shown that at moderate strain rates Curie's principle, which predicts that diffusion and the velocity gradient do not couple, breaks down and the diffusion tensor becomes anisotropic. The simulations presented here under PEF represent the first calculation of the diffusion tensor of concentrated molecular systems under an extensional flow and the range of molecular weights we have investigated for both shear and extensional flows represents the greatest range of systems for which the anisotropic diffusion has been studied using NEMD techniques. We have found that the alignment of the molecules is a key property which affects the diffusive behaviour. Our derivation of the Green-Kubo type expression for the diffusion tensor, is to the best of our knowledge the first explicit presentation of this derivation in the literature.

Under both PEF and PCF we have observed that there is a significant

enhancement of the diffusion in the $\hat{\mathbf{n}}_x$ direction (with diffusion coefficient D_{xx}), which in the case of the extensional flow corresponds to the direction of extension. In contrast for both flows at low strain rates the diffusion in the $\hat{\mathbf{n}}_y$ and $\hat{\mathbf{n}}_z$ directions (D_{yy} and D_{zz} respectively), in general, increases only slightly with strain rate and in some cases decreases. At higher strain rates under PEF we have noted that the diffusion coefficients D_{yy} and D_{zz} follow a power law relation. Comparing these diffusion data with order parameter data it is clear that the power-law region corresponds to regions of high alignment. This also explains why the same coefficients under PCF do not show a power law behaviour, since these systems are not as strongly aligned as the systems under extensional flow.

We have also calculated and analysed the centre of mass velocity autocorrelation functions for these systems. These correlation functions have provided information about the dynamics of systems, intermediate between the full details of trajectories and the diffusion tensor data. The correlation functions indicate that in aligned systems there is less obstruction in the direction of alignment, corresponding to an increased diffusion coefficient in that direction. Correlation functions in the directions transverse to the alignment indicate that there are sharper collisions between molecules in this direction which lead to observed weaker diffusion. Components of the kinetic temperature can also be obtained from the correlation functions and it has been found that these are unequal, particularly for short molecules under PEF. The lower kinetic temperature T_x at high strain rates under PEF gives rise to the weaker diffusion D_{xx} for longer molecules. Further investigation of this anisotropic temperature would be interesting because these quantities are essentially second moments of the nonequilibrium distribution in momentum space. More generally the diffusive properties that we have presented here have to our knowledge not been incorporated into Doi-Edwards type models of polymer dynamics, and we note that one direction

for further investigation would be to first check that these properties persist in the entangled regime *i.e.* with $N_s > 100$ [KH00] and then to consider models which effectively accounted for this behaviour. The diffusive properties found here should also be investigated experimentally as they provide significant information about the nonequilibrium state of these systems under flow.

We have also presented our observation that the Kraynik-Reinelt pbc's used for the NEMD simulation of PEF are closely related to the Arnold cat map, a simple dynamical map with the properties of a chaotic system. In addition we have also clarified the relationship between similar dynamic maps and the pbc's for PCF and equilibrium simulations. These observations have significantly enhanced our intuition for these simulation techniques and the chaotic properties of extensional flows. In particular, Todd [Tod05] related the Hencky strain of the Kraynik-Reinelt map to the Lyapunov exponent of the map. The relationship between the pbc's and the cat map also clarifies the source of the instability in the technique previously observed and rectified by Todd and Daivis [TD00]. Encouraged by our better understanding of the Kraynik-Reinelt pbc's we have described in the appendix how they might be extended to the simulation of planar mixed flows with superposed shear and extensional components. We have also noted that Adler and Brenner [AB85] give suitable lattices for elliptical flows. This leads to the possibility of simulating all types of planar homogeneous flows using NEMD algorithms. As yet we have not implemented these schemes and any exploration of this range of flows would probably need an application for which the fidelity of NEMD using the SLLOD algorithm was required, or perhaps a theoretical question which would profit from simulations with the additional range of flow fields.