

1.1 Complexity theory

Complexity theory as a science already exists for a few decades. My personal interest in complexity was raised in the summer of 1996 when I visited the Complex Systems Summer School of the Santa Fe Institute in New Mexico. After working on the modeling of microphase separation processes in polymer liquids for almost two years, I became interested in similarities between and underlying principles of different models that describe pattern formation in chemical, biological and physical systems, stimulated by an excellent paper in *Science*.¹ By that time I had already realized that working with people with very different backgrounds on a daily basis in a multi-disciplinary environment, stimulates creativity and enhances the exchange of principles from different sciences. It seemed a logical step to apply for the summer school and visit the Santa Fe Institute for a one-month stay. Many topics that I had encountered in my own research, such as nonlinearity, global order from local interactions, self-organization in complex systems and the importance of different scales in a system, were and are dealt with by the scholars of complexity. I enjoyed a month of stimulating lectures on 'complex' topics as diverse as brain imaging, the immune system, evolutionary modeling, neural networks, cellular automata, spin glasses, protein folding and energy landscapes, biological regulation and the measurement and definition of complexity. I discussed until late at night with scientists from a wide range of disciplines, got a taste for spicy food, visited Anasazi remains and Adobe-buildings (Fig. 1.1), hiked the astonishingly beautiful mountains around Santa Fe in the burning sun and filled my head with ideas. Back in Groningen, I thought and read more (popular books) about complexity²⁻⁶ and decided that the study of complex systems will probably not lead to a 'theory of everything'. Moreover, I do not believe in some basic complexity ideas such as that there are *always* simple rules that underlie complex patterns. Nor do I think that for similar properties in different systems to exist on macroscopic scales, the underlying theory must be irrelevant and replaceable. However, some of the principles in complexity theory are very appealing. Realizing that simple elements that interact via simple rules in a local manner, can give rise to global emergent properties due to nonlinearity and the presence of a hierarchical structure and disparate space and time scales, has definitely lead to more insight in a number of complex systems. Many complexity studies



Figure 1.1 Adobe-building in Santa Fe, New Mexico.

focus on the computer as a tool and use neural nets, genetic algorithms and evolutionary strategies to do statistical analysis of the huge amounts of possible outcomes that are generated by combination of simple rules. Although I make ample use of the computer in my own research, I believe that a good model should not only be based on statistics, but should also incorporate mechanisms. Complex structures should be studied as the result of *active* processes.

Complex polymer liquids, the topic of this thesis, form complex systems in which active processes (as in many pattern forming systems in chemistry and physics) play an important role. The polymer liquid is clearly complex in the sense of this introduction. The elements (polymers) are simple but put together (and quenched, mixed or sheared) they form a variety of emergent patterns due to phase separation and reaction processes. The phenomena of importance are active on different length and time scales and the system is self-organizing. Instead of

modeling a polymer liquid using a phenomenological approach incorporating a balance of competing interactions,¹ I have tried to go beyond phenomenology by including microscopic static and dynamic information in the system description. An approach in the spirit of complexity using as much microscopic information as possible and letting the simple basic elements (polymers) interact via more or less local rules (diffusion, reactions, convection), with additional attention to the active processes in the system, is in this thesis shown to lead to answers that are not accessible from a phenomenological point of view.

Pattern formation due to phase separation can be modeled on three different levels. On one end of the scale are the microscopic models, which are based on detailed molecular descriptions and which are integrated using e.g. Monte Carlo or molecular dynamics algorithms. On the other end of the scale are the macroscopic models which are often based on equations of state and fitted to macroscopic phase diagrams. This is the domain of the chemical engineer. In between in both length and time scales are the mesoscopic models, which may use local concentration variables as collective variables to describe self-organizing structures. Typical length scales are 10-1000 nm, typical time scales are up to milliseconds or even seconds. In the past years, both microscale and macroscale modeling has been very successful. However, physical, chemical and biological properties of materials are determined by mesoscale structures to a large extent. Models that are generally applicable to mesoscale materials are at present still missing.

1.2 Outline of this thesis

In this thesis I show how a mathematical model, that incorporates static microscopic information and dynamic phenomena, can be developed and used to predict structures in industrially processed complex liquids such as copolymer melts.

Mesoscale morphologies that develop as a result of molecular properties and processing conditions (mixing, quenching, extruding, shearing) determine industrially interesting material properties, such as tear strength, to a large extent. 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 nano- or microscale structure can be made in bulk quantities.

The basis of this work is the dynamic mean-field density functional theory as it is described in Ref. 7. The history of the dynamic mean-field density functional theory is rather short. From 1994 to 1997 the method was developed in an EC-funded pilot-project #8328 called CAESAR. Partners were the University of Groningen, IBM Heidelberg, MSI Cambridge and BASF Ludwigshafen. In a follow-up ESPRIT project #22685 called MesoDyn, the method is currently being further developed into a commercially available mesoscale chemical engineering software tool.

The MesoDyn project will run until 2000 and has as added end-user partners Shell Chemicals in Amsterdam and Norsk Hydro in Oslo.

In the dynamic mean-field density functional method, by using a free energy description for an *ensemble* of individual chains in a mean-field environment, the architecture of the copolymers, the connectivity of the monomers, the stretching of the copolymers and the cohesive and excluded volume interactions between the copolymers in the melt can be properly accounted for. The free energy is not truncated at a certain level as in many phenomenological models. Instead, the full path integral is retained using a numerical procedure.

A generalized convection-diffusion model accounts for the mobility of the copolymers, hydrodynamic effects and stresses on the system such that the static properties *and* dynamic processes are accurately represented. The model is very flexible and its parameterization is largely based on direct insertion of known values of (thermodynamic) polymer properties such as viscosity, compressibility, surface tension or vapor pressure. Since the method heavily depends on computer calculations, numerical aspects have also been studied. The outline of the remaining chapters of this thesis is as follows:

Chapter 2 - Dynamic mean-field density functional theory

In this chapter the dynamic mean-field density functional theory is explained in more detail. Since the other chapters are based on articles that were written as a result of my research, the contents of Chap. 2 will return a few times in condensed form. The interested reader can refer to this chapter for the details of the method that rely on statistical mechanics and thermodynamics. The basic underlying model for the dynamics is also discussed. Some aspects of the method, such as parameterization (which is discussed extensively in Ref. 8) and numerics that are not the topic of this thesis, but may be considered essential background information, are also treated.

Chapter 3 - Quadrature rules for a Gaussian chain polymer density functional in 3D

The cubic lattice model for the copolymer as it is originally used in the dynamic mean-field density functional theory is shown to lead to unphysical singularities in the inverse structure factor. In order to be able to do calculations in 3D, an essentially off-lattice algorithm should be used for calculating the (co)polymer density functional. New quadrature rules (stencil operators) are presented for the efficient integration of Gaussian chain polymer density functionals on a uniform 3D grid for different ratios of the Gaussian bond length parameter and the mesh width. The quadrature rules are such that the isotropy on the grid is maximal. The long length scaling of the numerical functionals is identical to analytical results and a good accuracy is achieved in the entire frequency domain. Comparison to other commonly used numerical integration techniques is

provided. The quadrature rules that are described in this chapter are currently being used for all dynamic mean-field density functional calculations of isotropic complex polymer liquids in which viscoelastic effects are of less importance.

Chapter 4 - Application of free energy expansions to mesoscopic dynamics of copolymer melts using a Gaussian chain molecular model

The dynamic mean-field density functional method is computationally quite intensive mainly because the dynamics is implicit in the densities. This chapter discusses the feasibility of an explicit expression for the dynamics, in which an analytical expression for the external potential as a function(al) of the densities would be required. An expansion of the external potential is introduced, similar to free energy expansions. This expansion is valid for both compressible and incompressible multicomponent copolymer melts using a Gaussian chain model. The expansion is similar to the well-known Random Phase Approximation (RPA) but differs in some important aspects. Also, the application of RPA-like free energy expansions to dynamics is new. The derivation in this chapter leads to simple expressions for the vertex coefficients, which makes numerical calculation of their full wave vector dependence possible, without assuming an ordered morphology as is common practice in most equilibrium studies of copolymer melts. The mathematically derived fourth order vertex is found to be negative for some wave vectors which has important consequences for especially the *simulation* of mesoscopic dynamics. Fitting the vertex coefficients by a special procedure to overcome the expensive calculation of the expansion is shown to also provide analytical parameters for a gradient free energy expansion. This allows for a whole new class of phase separation models to be defined. In principle the ideas in this chapter lead to new free energy models that may look phenomenological, but that have parameters which can be directly derived from molecular polymer properties. The free energy functional as it is used in the dynamic mean-field density functional method hence encompasses most phenomenological free energy models and is much richer in behaviour.

Chapter 5 -Mesoscopic phase separation dynamics of compressible copolymer melts

In this chapter the dynamic mean-field density functional method is extended to the mesoscopic dynamics of *compressible* polymer liquids. Although most polymer melts are only slightly compressible, some phenomena may be observed in experiments that are due to excluded volume effects. One example is the 'density dip' at domain interfaces. Different classes of compressibility models are discussed and compared: exactly incompressible, Helfand's harmonic penalty model and a cell model. Numerical results are discussed which show that the penalty model is a very

practical and easy-to-use solution, which correctly reproduces experimentally observable compressibility effects. In the current nVT -ensemble dynamics algorithms application of the cell model leads to a variation of the pressure and, depending on conditions, the system develops liquid-gas transitions. The morphology of a phase separated diblock copolymer melt around a gas bubble has intriguing structures, with lamellar phases oriented towards the gas-liquid interface. Similar morphologies can be observed in systems with solid particles, where lamellae are oriented perpendicular to the interfaces,⁹ depending on the size of the pores between particles.

Chapter 6 - External potential dynamics: nonlocal kinetic coupling in mesoscopic dynamics of copolymer melts

Nonlocal kinetic coupling is applied to the dynamic mean-field density functional method, which in its first version only incorporated a local coupling approximation. Experimental results show that the Onsager coefficient is dependent on spatial frequencies. The general theory of time evolution of density variables with general kinetic coefficients that was developed by Kawasaki and Sekimoto is discussed in this chapter. The limits of the theory that yield the local coupling approximation, the collective Rouse dynamics model and the reptation dynamics model are treated. A simple approximation to the Rouse dynamics model is shown to lead to a feasible numerical model that includes the essential physical features of nonlocal kinetic coupling. This results in a dynamic equation for the external potential instead of the density which allows for calculations of microphase separation in copolymer melts with increased relevance to experimental results. As might be expected from a numerical model that includes nonlocal kinetic coupling, the numerical results show less defects in the final morphology and a faster increase of the order parameter compared to local kinetic coupling.

Chapter 7 - Equation of state and stress tensor in inhomogeneous compressible copolymer melts

In order to study rheological properties of copolymer melts and npT -ensemble simulations, the pressure and stress components have to be calculated. In this rather theoretically oriented chapter, an expression for the global stress in *inhomogeneous* complex copolymer liquids is derived by applying the principle of virtual work to the free energy as defined in the dynamic mean-field density functional method. This method automatically provides the full stress tensor (deviatoric and isotropic parts) and hence an equation of state for inhomogeneous compressible copolymer melts. The excluded volume interactions and cohesive interactions between chains have been explicitly taken into account. Therefore the expressions for the stress and thermodynamic pressure have a wide range of validity. The connectivity of the chains is automatically accounted for and the free energy adapts very well to changes in the molecular proper-

ties. In the limiting case of homogeneous systems it simplifies to known results. In this chapter it is also shown how the pressure and stress can be numerically evaluated during simulations using a Green propagator algorithm, instead of having to calculate the time dependent configuration distribution function explicitly from a Smoluchowski equation. A numerical simulation illustrates how the pressure changes during microphase separation. In principle the results from this chapter can be used in a pressure coupling method to perform npT -ensemble simulations of microphase separation, which are more realistic. Moreover, the expression for the stress tensor enables the study of the stress-strain relationship in a phase separating copolymer melt under shear.

Chapter 8 - Hydrodynamic effects in 3D microphase separation of block copolymers

An important step towards incorporating processing conditions in the numerical simulations of industrial complex liquids is the inclusion of hydrodynamic effects. The effect of shear alone was already demonstrated in Ref. 10. In this chapter it is shown that it is justified to use Darcy's approximation for the velocity field. This simple model accounts for a velocity field that is proportional to an effective local friction force and reproduces both the increased domain growth and the faster removal of defects that are a result of hydrodynamics. A simulation of a diblock copolymer melt is performed to study the viscous effects in 3D. The free energy is shown to decrease twice as fast as in a simulation which only includes diffusion. The hydrodynamics are shown to be of second order nature and to become important only in the later stages of phase separation as is also predicted from theoretical analysis. The separation process proceeds faster because the growth of bulk domains is accelerated compared to the purely diffusive case.

Chapter 9 - Viscoelastic effects in 3D microphase separation of block copolymers

In this chapter, the dynamic mean-field density functional method is extended to account for viscoelastic effects in polymer liquids under shear. In rheological flow experiments of polymer liquids a number of unusual effects such as shear-thinning and normal stress effects can be observed. Rheologists aim at understanding these phenomena from a microscopic point of view. In this chapter, the effect of simple steady shear on polymer orientation and elongation is taken into account by adapting the polymer configuration distribution function. We propose a simplified model for Gaussian chains in a simple steady shear flow in which the connected beads in the chain respond to the flow as independent dumbbells. It is shown numerically that this model correctly reproduces expected conformational changes. The conformational effect is demonstrated to be of importance only for high viscosity liquids and/or high shear rates.

Chapter 10 - Outlook to the future

In this thesis, the current status of the dynamic mean-field density functional method is described. The area of applications of the method seems to be growing ever faster due to its firm basis in thermodynamics and statistical mechanics and its versatility. In this concluding chapter, I indicate what application areas may be expected in the near future and, in more detail, in what ways the method has to be extended and adapted to account for polymerization processes and semi-crystalline materials which are of great industrial interest.