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## 10.1 Dreams and reality

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In this thesis, the current status of the dynamic mean-field density functional theory is described. This is by no means where it will end. On the contrary, the area of applications of this method seems to be growing ever faster.

The strength and versatility of the dynamic mean-field density functional method is mainly in its firm background of thermodynamics and statistical mechanics. The open formulation of the (Helmholtz) free energy and the flexible model for the dynamics allow for many different phenomena of interest in complex material formulation to be described. The goal of a mesoscale chemical engineer is to be able to design processing conditions in a rational way such that a particular mesoscale material can be produced in bulk quantities. Interesting mesoscale structures are the result of *active* processes. These structures are not only determined by e.g. a careful choice of the weight ratio of constituting materials but also by processing conditions. As this thesis illustrates, widening the area of applications for the dynamic mean-field density functional method can be achieved both by improving the description of the constituting materials (adding compressibility or viscoelasticity) *and* by extending the description of processing conditions (allowing for nonlocal kinetic coupling or including hydrodynamics).

Extensions, modifications and adaptations of the dynamic mean-field density functional method are called for by practical problems and applications. An important example in industry is emulsion (co)polymerization with applications in latexes and paints. In many cases (two-stage) (seeded) emulsion polymerization leads to core-shell morphologies, in which good properties of different materials are combined. In this case, a shell of one type of (co)polymer is grown around a core of another type. For instance in paint formulations the core is made of a glassy polymer to give gloss and mechanical stability. The shell is rubbery to enable the latex particles to form a uniform surface coating. A number of extensions must be made to the dynamic mean-field density functional method in order to describe emulsion polymerization processes. First of all, for a good description of the dynamics, reaction phenomena should be included on the level of the dynamics. This also implies that, second, polydispersity must be accounted for.

Another example from industry is thermoplastic polyurethane (TPU)

which offers a broad range of physical properties and characteristics (high tensile and tear strength, chemical and abrasion resistance and fabricability), making it a material which is produced in extremely large quantities. The TPU chemistry consists of a series of block copolymers with alternating hard and soft phases. The soft, flexible segments are scattered throughout the polymer chain. The ratio and molecular structure of these segments determines the specific characteristics of a TPU grade, which can range from a rigid material to a highly flexible TPU. Because of its different constituting segments, TPU combines the mechanical and physical properties of rubber with the advantages of thermoplasticity and processability. The original TPU reaction was conceived in 1937 by Otto Bayer. During its rather long existence, strong experimental knowledge has been built about TPU. During microphase separation under processing conditions, the hard segments tend to align and make hydrogen bonds with each other. Locally, the material hence becomes lamellar (crystalline), whereas the material remains amorphous in other domains. The hard/soft segment morphology is key to the TPU hardness or softness (durometer) and toughness. The dynamic mean-field density functional method in its current form can not describe semi-crystallinity and partial stiffness of polymers such as TPU in a straightforward way. The molecular description should be improved such that stiff and flexible parts within one molecule can be accounted for.

Other interesting phenomena and material properties that should be within range of the dynamic mean-field density functional description of complex materials are of viscoelastic nature, or involve an improved description of hydrodynamics. Recent work<sup>9</sup> in our group, which is not discussed in this thesis, entails the incorporation of confined geometries in the dynamic mean-field density functional method. It is known from applications in film casting,<sup>215</sup> that the local thickness of the film determines the observed morphology to a large extent. In SBS (styrene-butadiene-styrene) films, the equilibrium hexagonal morphology leads to an observed lamellar morphology in thick regions (where tubes orient parallel to interfaces) and an observed hexagonal morphology in thinner regions (where tubes orient perpendicular to interfaces) (Fig. 10.1). Confined geometries are not only interesting for applications in film casting, but more importantly, combined with the dynamic mean-field density functional method, it will ultimately describe filler particles (static or dynamic) in complex liquids and polymer liquids in porous environments. Within the MesoDyn ESPRIT project, the dynamic mean-field density functional method will also be extended to account for electrostatic effects using Donnan electrostatics,<sup>216</sup> which is based on the principle of electroneutrality.

In the next two sections I will explain to a limited extent some approaches that can be taken in order to describe reaction processes and semi-crystallinity within the dynamic mean-field density functional approach.

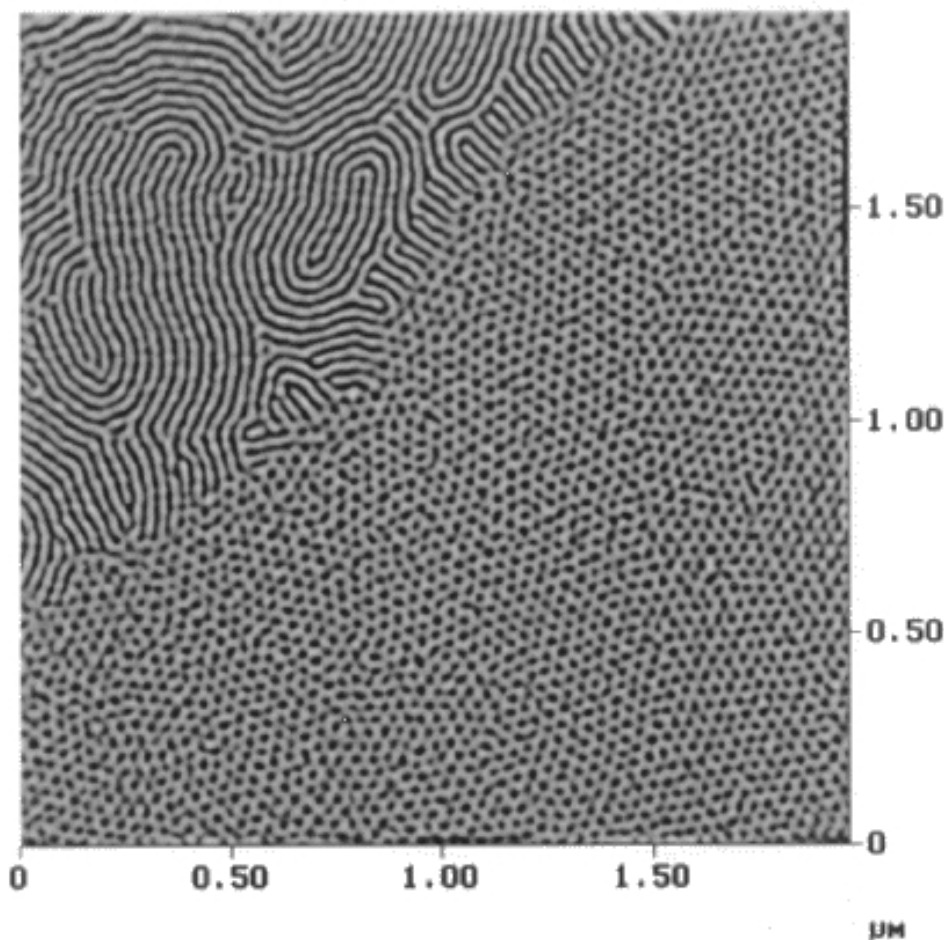


Figure 10.1 AFM-picture of an SBS-film where different morphology orientations can be observed in areas with different thicknesses. Courtesy of M. van Dijk, Shell Research and Technology Centre, Amsterdam.

## 10.2 Polymer reaction processes

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Emulsion polymerization methodology is not only commercially very important, it also provides a flexible basis for future extensions of the dynamic mean-field density functional method to other applications in reactive processing.

The simplest recipe for an emulsion polymerization consists of water, surfactant in a concentration above the CMC, water-insoluble monomer and water-soluble initiator. Usually, the system is first emulsified. This results in micelles swollen with monomer, surfactant stabilized monomer droplets and initiator in the aqueous phase. The system is then agitated e.g. by heating it. This leads to thermal decomposition of the initiator and free radical polymerization starts. A latex comprising polymer particles develops. The latex particles form a colloid, stabilized against coalescence by surfactant.<sup>217</sup>

Emulsion polymerization usually takes place in batch processes. The basic batch process consists of mixing all ingredients, stirring them and

discharging all contents after polymerization. In semi-batch processes (semi-continuous) a portion of the reactants is added at start-up and the reactor is charged with the remaining reactants in a controlled manner during the reaction cycle. The process which can best be simulated within the dynamic mean-field density functional approach is the simple batch process. An interesting idea is to incorporate morphological information that can be derived from a MesoDyn simulation on micrometer length scales into a macroscopic model for batch processing in a similar way as is done already for turbulent reactive flow processes.<sup>218</sup>

Until now, the most often used predictive models for polymer reaction engineering processes are based on kinetic models, which are treated extensively in the books of Odian<sup>219</sup> and Gilbert.<sup>217</sup> Most kinetic models divide the emulsion polymerization process into three distinguishable kinetic phases; a particle formation or nucleation interval and two particle growth intervals. The first particle growth interval is characterized by rapid diffusion compared to propagation and so-called zero-one kinetics.<sup>217</sup> The formed oligomers are very mobile. The second particle growth interval exhibits an increase in polymer weight fraction and viscosity and as more monomer is consumed, the system exhibits the gel effect. At very high conversions, the system becomes glassy. It is not so hard to incorporate the reactive processes during the second interval of zero-one kinetics into the dynamic mean-field density functional method. Since the chain propagates very fast in this interval due to the high monomer mobility, the stochastic reaction and microphase separation processes can be treated separately in the numerical algorithm. The other kinetic intervals are of less importance, since the specific morphology of the material is determined mainly in the first particle growth interval.

In modeling a simultaneous reaction/phase separation process, the different time scales in the system and especially their relative sizes, are of major importance. If diffusion is slow, as in a system with a very high fraction of polymer, the overall rate coefficient is given by that for diffusion. If the chemical reaction is much slower than diffusion, the overall rate coefficient is determined by the chemical step. The dynamic equations of the dynamic mean-field density functional method can straightforwardly be extended with reaction terms by applying a terminal model (first order Markov process<sup>219</sup>) in which the reaction probabilities are time-independent. In this case, it may be necessary to explicitly distinguish chain end beads. Using the terminal model it is also possible to keep track of the chain distribution, without having to perform complex statistical analysis.

As can be concluded from the previous paragraphs, a number of extensions must be made to the dynamic mean-field density functional method in order to account for emulsion polymerization and generalized reactive processes. Various types of molecules develop during the emulsion polymerization. This effectively influences the polydispersity in the system. The different types of polymers can be accounted for by introduction of multiple polymer density functionals. In this case, separate density fields

for the radically active chain ends may also be necessary. This approach to polydispersity implies a huge increase of memory requirements, but ensures the one-to-one relationship between all densities and external potentials. Other approaches such as modeling the dynamics of a given distribution of polymer chain architectures are in principle feasible, but too complex in practice.

If only a few of the intermediate products in an emulsion polymerization are represented in a model, it is harder to reproduce experimental results. It has to be very carefully considered which part of the kinetics can be left out without losing the important aspects of the phenomenology.

### 10.3 Semi-crystalline polymer materials

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Another possible future application of the dynamic mean-field density functional method is to predict the phase diagram of (semi-)crystalline materials. The object is to foresee material properties such as abrasion resistance and tensile/tear strength, based on the molecular parameters and process conditions. As an example, it is generally believed that the hard segment length, volume fraction in the polymer and 'solubility' with the soft segment of TPU are primarily responsible for the stress/strain strength. The varying crystallinity in the material dictates its behaviour. With the currently used Gaussian chain model in the dynamic mean-field density functional method, partly stiff or crystalline polymers can not be represented satisfactorily. However, by making use of the fact that  $\chi$  interaction parameters consist of an enthalpic and an entropic part, it may be possible to qualitatively describe crystallization behaviour by detailed modeling of the temperature/density dependence of  $\chi$ .

In general, there are many models described in literature that deviate from the Gaussian chain molecular model.<sup>37,73,220</sup> In semi-flexible chains, the chain is modeled by the local coordinate and a local orientational parameter, which provides a measure for the local bend.<sup>73</sup> The disadvantage of this approach is that it involves a six-dimensional order parameter. In nematic liquid crystals, any good order parameter should take into account that the local orientation has equal probability of pointing parallel or anti-parallel to a given direction. Since this property can not be properly represented by vector order parameters, a tensor orientational order parameter is used. Some phenomenological equations for the dynamics of the order parameter tensor were proposed by de Gennes.<sup>73</sup> In principle, the full Smoluchowski equation for the dynamics is known, but it is extremely hard to work with.

## Polymers with stiff and flexible parts

The stiff parts of a semi-crystalline polymer will behave as (nematic) liquid crystals. In microphase separation, they will orient parallel with respect to each other. The flexible parts of the polymer will behave as 'normal' Gaussian chains. A model for e.g. a TPU, to be included in the dynamic mean-field density functional approach, should incorporate both types of behaviour.

In the next paragraphs I propose an extension to the dynamic mean-field density functional method that will make application of the method to semi-crystalline polymer materials feasible. In order to describe a polymer that combines the two types of behaviour, the persistence length of the flexible chain must first be made position dependent (this is where the main intrinsic molecular information will be incorporated into the model). The intrinsic Hamiltonian of the system becomes:

$$\beta H^{\text{intrinsic}} = \frac{1}{2} \int_0^N K_s \left| \frac{\partial \mathbf{u}(\mathbf{R}(s))}{\partial s} \right|^2 ds, \quad (10.1)$$

instead of the usual (discrete) Gaussian chain Hamiltonian

$$\beta H^{GC} = \frac{3}{2a^2} \sum_{s=2}^N (\mathbf{R}_s - \mathbf{R}_{s-1})^2. \quad (10.2)$$

To describe the semi-crystalline polymer chains within the dynamic mean-field density functional method, two order parameters are now required:

$$\rho_s(\mathbf{r}) = n \langle \delta(\mathbf{r} - \mathbf{r}(s)) \rangle, \quad (10.3)$$

$$S_{sij}(\mathbf{r}) = n \langle \mathbf{u}_{si} \mathbf{u}_{sj} \delta(\mathbf{r} - \mathbf{r}(s)) \rangle, \quad (10.4)$$

where the average is taken with respect to the equilibrium Boltzmann distribution, corresponding to the partition function. In this case  $s$  is a continuous variable along the chain and  $S$  is newly introduced as a second order tensor. In going from a discrete description of the chain to a continuous description, the notation that is used in the previous chapters of this thesis has to be adapted. The functional integration

$$\int \delta \mathbf{R}_s = \int d\mathbf{R} \int_{\mathbf{R}_0=\mathbf{R}'}^{d\mathbf{R}'} \int_{\mathbf{R}_N=\mathbf{R}} \delta \mathbf{R}_s, \quad (10.5)$$

now replaces  $\int d\mathbf{R} = \int d\mathbf{R}_1 \cdots d\mathbf{R}_N$ . In order to determine the distribution function  $\Psi$  the free energy  $F$  must be optimized for all  $\Psi$  under a constraint (cf. Chap. 2 for a single density species):

$$\begin{aligned} F'[\Psi] &= \int \delta \mathbf{R}_s \Psi \frac{1}{2} \int_0^N K_s \left| \frac{\partial \mathbf{u}_s}{\partial s} \right|^2 ds + k_B T \int \delta \mathbf{R}_s \Psi \ln \Psi + F^{\text{nid}}[\rho^0] \\ &+ \int U(\mathbf{r}[\rho[\Psi](\mathbf{r}) - \rho^0(\mathbf{r})]) d\mathbf{r} + \int T(\mathbf{r}) : [S[\Psi](\mathbf{r}) - S^0(\mathbf{r})] d\mathbf{r} \\ &+ \lambda \left[ \int \delta \mathbf{R}_s \Psi - 1 \right]. \end{aligned} \quad (10.6)$$

Here an additional Lagrange multiplier tensor field  $T$  has been introduced. The additional term to  $\delta F'/\delta\Psi$  resulting from the orientational order parameter is now given by:

$$\int_0^N T(\mathbf{R}(s)) : \mathbf{u} \mathbf{u} ds. \quad (10.7)$$

Hence the optimal distribution function  $\Psi$  for a single density species is given by:

$$\Psi \propto \exp \left\{ -\beta \left[ \frac{1}{2} \int_0^N K_s \left| \frac{\partial \mathbf{u}(\mathbf{R}(s))}{\partial s} \right|^2 ds + \int_0^N U(\mathbf{R}(s)) ds + \int_0^N T(\mathbf{R}(s)) : \mathbf{u} \mathbf{u} ds \right] \right\}. \quad (10.8)$$

For more than one species in the system the optimal distribution function becomes:

$$\Psi \propto \exp \left\{ -\beta \left[ \frac{1}{2} \int_0^N K_s \left| \frac{\partial \mathbf{u}(\mathbf{R}(s))}{\partial s} \right|^2 ds + \int_0^N U_s(\mathbf{R}(s)) ds + \int_0^N T_s(\mathbf{R}(s)) : \mathbf{u} \mathbf{u} ds \right] \right\}. \quad (10.9)$$

The density can again be calculated according to a Green propagator algorithm.<sup>37</sup> We now have the following expressions for the conjugate external fields  $U$  and  $T_{sij}$ :

$$\rho_s(\mathbf{r}) = -\frac{1}{\beta} \frac{\delta \ln Q}{\delta U_s(\mathbf{r})}, \quad (10.10)$$

$$S_{sij}(\mathbf{r}) = -\frac{1}{\beta} \frac{\delta \ln Q}{\delta T_{sij}(\mathbf{r})}, \quad (10.11)$$

where  $Q$  is the partition function of the ideal chain. The expression for the free energy can be found by inserting a normalization of Eq. (10.9) into Eq. (10.6) (without the constraining terms). The modeling of the new kinetic models for the dynamics of both order parameters remains to be done. From symmetry considerations, the general form however will be given by:

$$\frac{\partial \rho(\mathbf{r}, t)}{\partial t} = \Gamma_{\rho\rho} \frac{\delta F}{\delta \rho(\mathbf{r}, t)} + \Gamma_{\rho S} : \frac{\delta F}{\delta S(\mathbf{r}, t)}, \quad (10.12)$$

$$\frac{\partial S(\mathbf{r}, t)}{\partial t} = \Gamma_{S\rho} \frac{\delta F}{\delta \rho(\mathbf{r}, t)} + \Gamma_{SS} \frac{\delta F}{\delta S(\mathbf{r}, t)}, \quad (10.13)$$

where the  $\Gamma_{ij}$  are appropriately chosen dynamic scalar/tensor operators.

