

Part I

Illustrations & Applications

Simple Models for Polymeric and Anisotropic Liquids

We hope that the complexity of the world is neither in contrast with the simplicity of the basic laws of physics [1] nor with the simple physical models to be reviewed or proposed in the following. However, physical phenomena occurring in complex materials cannot be encapsulated within a single numerical paradigm. In fact, they should be described within hierarchical, multi-level numerical models in which each sub-model is responsible for different spatio-temporal behavior and passes out the averaged parameters to the model, which is next in the hierarchy (Fig. 1.1). Polymeric liquids far from equilibrium belong to the class of anisotropic liquids.¹ This monograph is devoted to the understanding of the anisotropic properties of polymeric and complex fluids such as viscoelastic and orientational behavior of polymeric liquids, the rheological properties of ferrofluids and liquid crystals subjected to external fields, based on the architecture of their molecular constituents. The topic is of considerable concern in basic research for which models should be as simple as possible, but not simpler. Certainly, it is also of technological relevance. Statistical physics and nonequilibrium thermodynamics are challenged by the desired structure-property relationships. Experiments such as static and dynamic light and neutron scattering, particle tracking, flow birefringence etc. together with rheological measurements have been essential to adjust or test basic theoretical concepts, such as a ‘linear stress-optic rule’ which connects orientation and stress, or the effect of molecular weight, solvent conditions, and external field parameters on shape, diffusion, degradation, and alignment of molecules.

During the last decade the analysis of simple physical particle models for complex fluids has developed from the molecular computation of basic systems (atoms, rigid molecules) to the simulation of macromolecular ‘complex’ system with a large number of internal degrees of freedom exposed to external forces. This monograph should be in certain aspects complementary to others. The foundations of molecular

¹ Greek: an (non) iso (equal) trop (to turn): Anisotropic materials exhibit properties with different values when measured in different directions. Material properties are rotation-invariant, usually either due to boundary conditions, anisotropic applied external fields, or the presence of nonspherical constituents.

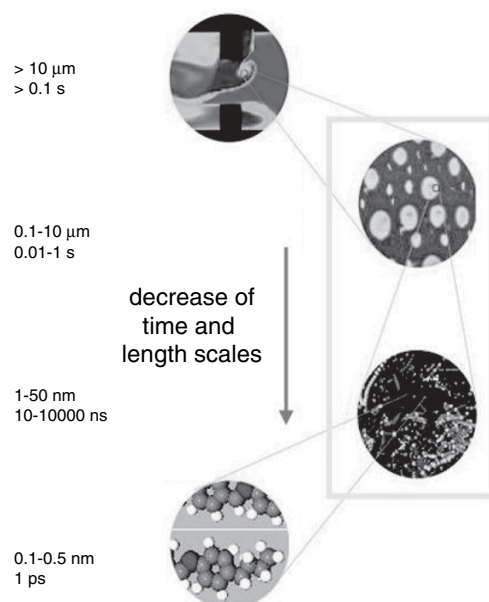


Fig. 1.1. Time and length scales of a typical polymer problem. In this review we are concerned with micro- and mesoscopic models (framed) which aim to describe physical behavior beyond equilibrium, beyond chemical details (*bottom*), and may be implemented into the macro-computation of complex flows (*top*)

and brownian dynamics methods for simple microscopic models for macromolecular systems have been extensively revisited [2]. Multiscale simulation in polymer science with special emphasis on coarse-grained models (incl. a soft-ellipsoid model) has been recently reviewed by Kremer and Muller-Plathe [3]. In the light of modern reviews on physical micro- and mesoscopic models to be mentioned below our focus is placed onto aspects which have been less extensively considered. Upon these are, in part 1 of this monograph, orientation and entanglement effects, the implications of stretchability, flexibility, order parameters, scission and recombination on material properties of anisotropic, dilute and concentrated polymeric bulk fluids in the presence of macroscopic flow and electromagnetic fields. Part II is an attempt to collect the minimum amount of information to implement and develop analytic theory and computational tools.

In part 1 this monograph is first of all concerned with the applicability and suitability of bead-spring multi chain models which incorporate finite extensibility of segments (so called FENE models, cf. Page 203), molecular architecture and flexibility, and capture topological interactions. Second, it aims to give an overview about the range of applications of simple mesoscopic theories, in particular primitive path models and elongated particle models, where topological aspects are either approximately treated or disregarded. In view of a rapidly growing amount of research and number of publications on these topics, we try to present a balanced selection of

simple, representative examples, connect them with related research, and thereby get in touch with a large – still not exhaustive – number of classical and modern approaches. In order to keep the monograph short, we do not summarize basic knowledge available from standard text books. We therefore do not provide an introduction to the theory of stochastic differential equations, the statistical physics of simple, molecular, and macromolecular liquids, linear response theory, rheology, or experimental methods. We are going to cite the relevant original literature where implementation details can be found. However, Part II of this monograph provides the reader with the basic ingredients needed to devise a simulation scheme and to derive equations of change for moments for a given model. In particular, it contains sample codes for various applications.

The existence of universality classes is significant for the theoretical description of polymeric complex fluids. Any attempt made at modeling polymer properties might expect that a proper description must incorporate the chemical structure of the polymer into the model, since this determines its microscopic behavior. Thus a detailed consideration of bonds, sidegroups, etc. may be envisaged. However, the universal behavior that is revealed by experiments suggests that macroscopic properties of the polymer are determined by a few large scale properties of the polymer molecule. Structural details may be ignored even for microscopic (beyond-atomistic) models since at length scales in the order of nanometers, different polymer molecules become equivalent to each other, and behave in the same manner. This universal behavior justifies the introduction of crude mechanical models, such as bead-spring chain models, to represent real polymer molecules (Fig. 1.2).

The FENE chain model and its variations can be considered as a maximum coarse-grained, still brute force simulation model to the physical properties of polymeric fluids. These models didn't fail to describe rheo-optical material properties quite satisfactory when solved without approximation, but are often numerically expensive while conceptually simple. FENE chains constitute the appropriate level of description in order to test polymer kinetic theory [4, 5], and assumptions made to simplify their analysis. This monograph discusses several realizations in detail, and hopes to stimulate for advanced treatments, therefore disregards many others (FENE chain models for star polymers, co-polymers, polymer blends, brushes, polyelectrolytes, in order to mention a few).

The dynamics of a single, fluorescing, DNA macromolecule held at one end by 'optical tweezers' and subjected to a uniform flow was successfully compared with simulations [6] of a FENE chain that accounted for the molecule's entropic elasticity, brownian motion, and hydrodynamic drag. Using self-diffusion data and analytical expressions to obtain this drag in the limits of the undeformed coil and of the fully stretched thread, these results once more confirmed the success of the FENE chain model in predicting the rheological properties of simple polymeric systems. Excellent agreement between the theoretical predictions based on the FENE models and data from experimentation indicated that the model also seemed able [7] to interpret the underlying physical mechanisms for the dynamics of polymer solutions [8–10], melts [11–13], copolymer melts [14, 15], brushes [16] not only in the quiescent state, but also subjected to flow fields [7, 8, 17–26]. During the last decade, the FENE chain

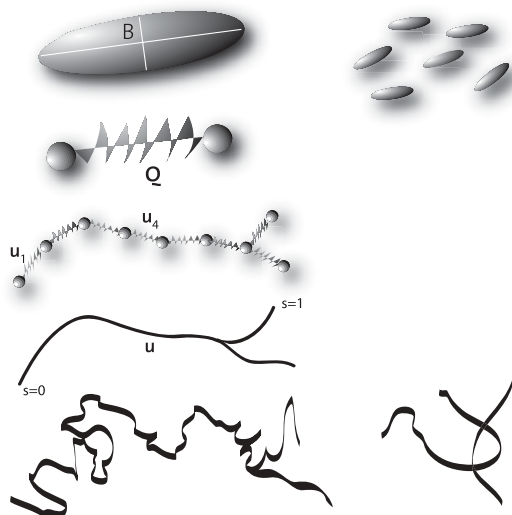


Fig. 1.2. Simple microscopic models for complex fluids with increasing level of abstraction and decreasing degrees of freedom (lhs, *bottom to top*), and their sketched range of application: (a) Atomistically detailed polymer which accounts for anisotropic intermolecular interactions incl. entanglements, (b) coarse grained model via a mapping (Sect. 8.10.1) to a ‘primitive path’, (c) further approximated by a multibead (nonlinear FENE) chain, (d) further coarse-grained to a (FENE) dumbbell which accounts for entropic elasticity and orientation but not for entanglement effects, and (e) ellipsoids of revolution – incl. rigid rods, dissipative particles, with spherical or mean-field interaction. Models must meet the requirement of being thermodynamically admissible

model has been extended to incorporate the effect of scission, recombination (FENE-C) and branching of chains in order to investigate the formation and development of complex micellar systems and networks [14, 27–30], cf. Fig. 1.3. The model has been further extended (FENE-B) to incorporate semiflexibility of chains [31–34], and studied in confined geometries. To give an overview about the range of applicability of the sufficiently detailed and simple microscopic models, we restrict ourselves to the formulation and analysis of models for particulate fluids and validate them against experimental data.

The nomenclature given at Page 203 is recommended in order to make the search for results obtained for extensions of the original FENE dumbbell more comfortable. Actually, the most complete summary of the various ‘analytic’ FENE models may be found in [35]. Configuration tensor models such as the FENE-P and more general quasi-linear models (Johnson-Segalman, Gordon-Schowalter, Phan-Thien/Tanner etc.) have been also developed in a fully nonisothermal setting [36–38]. NEMD together with a dissipative particle dynamics (DPD) thermostat had been successfully applied to study the shear-induced alignment transition of diblock copolymer melts, surfactants and liquid crystals in a large-scale system [14], based on an effective simplified continuum model for FENE dumbbells [39] biased towards phase separation. Simplified versions of FENE chain models neglect flexibility or finite

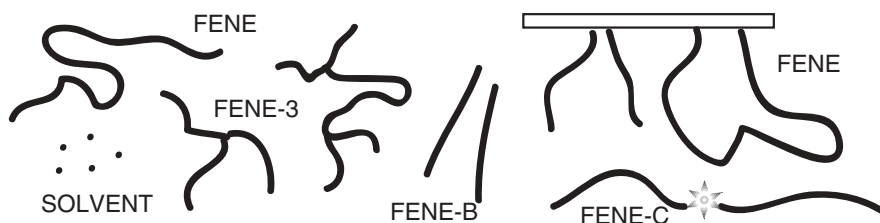
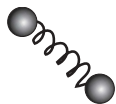


Fig. 1.3. Simple FENE models for a range of macromolecular fluids to be treated in a unified fashion: with/without solvent (simple fluid) for linear/star/branched, flexible/semiflexible, bulk/confined/tethered, non-/breakable macromolecules, cf. Table 14.1. Charged, tethered polymers have been excluded from the review since an excellent review is available in this series [40]

extensibility and have been widely used. Rigid elongated particles further neglect stretchability. Models dealing with these objects will be reviewed in certain detail as long as the simplified description turns out to be appropriate (unentangled: dilute polymers, rigid molecules: liquid crystals). Some space will be reserved for the discussion on the connection between the different levels of description, projection operators, coarse-graining procedures, and the theory of nonequilibrium thermodynamics which sets a framework for simple physical models.

1.1 Section-by-Section Summary

Part I

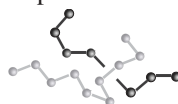


Chapter 2: In the quiescent state, polymers in dilute solution should have negligible interactions with each other on purely geometrical grounds, in contrast to semi-dilute or concentrated solutions and melts. The flow behavior of polymer solutions is, however, more complex than that of the familiar Newtonian fluids. Within these solutions shear thinning and the Weissenberg effect [4] are typical phenomena of technological importance. These effects are found to be strongly correlated with flow-induced conformational changes of the dissolved polymer chains and they can be dramatic in dilute solutions. Orientation and deformation of chain molecules can, and has been measured in flow birefringence light scattering and neutron scattering experiments (for methods and references see [41]), and via computer simulation [42–45]. For a review on molecular orientation effects in viscoelasticity we refer to [46]. For this introductory section we will be concerned with approximate solutions for FENE dumbbells (with $N = 2$ beads) in the infinitely dilute and semi-dilute regimes.



Chapter 3 is next on the hierarchy and treats multibead chains ($N > 2$ beads) in dilute solutions. We start from a stochastic approach to polymer kinetic

theory. The model takes into account configuration-dependent hydrodynamic interaction (HI) and simplifies to the Zimm bead-spring chain model in the case of preaveraged HI, for which parameter-free ‘universal ratios’ such as the ratio between radius of gyration and hydrodynamic radius are known. The Chebyshev polynomial method and a variance reduction simulation technique [47] are revisited to implement an efficient NEBD simulation. The full dependence of several characteristic ratios vs. both chain length and hydrodynamic interaction parameter is resolved, and compared with analytical and experimental results. Polymer solutions under good solvent conditions have been also studied extensively via NEMD by taking into account explicit solvent particles, e.g., in [42–45, 48]. In that case, hydrodynamic interactions and excluded volume are incorporated through momentum transfer and a WCA potential between beads, respectively.



Chapter 4 demonstrates insights obtained by NEMD into the microscopic origin of the nonlinear viscoelastic properties of (dense) polymer melts by using a FENE chain model. Stress-strain relationships for polymer melts are the main requirement for the conventional flow simulation of polymer processing, useful in modelling industrial applications including injection moulding, film blowing, and extrusion. The reliability and accuracy of such simulations depends crucially on the constitutive equations. Although closed-form phenomenological models have been widely used in research and commercial codes, their degree of success is limited because of a lack of physical ingredient on the molecular level. For the purpose of realistic modelling, and further development of semiempirical constitutive equations, full FENE chain models are shown to be uniquely suited.



Chapter 5 extends the FENE chain system in several directions. We offer explicit examples of recently established models: wormlike micellar systems modelled by a FENE-C potential, model liquid crystals composed of semiflexible FENE chains, as well as a model for semiflexible (FENE-B, actin) filaments and networks. Results for the models are obtained by NEMD or NEBD, though we will also discuss analytic descriptions that are able to guide the interpretation of important aspects of the results.

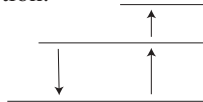


Chapter 6 offers illustrative examples on how to formulate and handle kinetic model equations for primitive paths (coarse-grained atomistic chains) by approximate analytical or ‘exact’ numerical treatments. The role of topological interactions is particularly important, and has given rise to a successful theoretical framework: the ‘tube model’. Progress over the last 30 years had been reviewed in the light of specially-synthesized model materials, an increasing palette of experimental techniques, simulation and both linear and nonlinear rheological response in [5]. Here we review a selected number of improved versions of primitive

path models which allow to discuss the effect of approximations on the linear and nonlinear rheological behavior of polymer melts. Brute force FENE chain simulation results summarized in the preceding chapters are used to test the assumptions made in the formulation of these kinetic models.



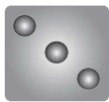
Chapter 7 deals with elongated particle models. There are many early approaches in the literature to the modelling of fluids with simple microstructure. For example, equations for suspensions of rigid particles have been calculated by averaging the detailed motion of the individual particles in a Newtonian fluid. In particular, the solution for the motion of a single ellipsoid of revolution in a steady shear [49] in terms of a Fokker–Planck equation has been used to determine the governing equations for the slow flow of a dilute suspension of non-interacting particles. In more concentrated systems, various approximations to the particle motions have been used. Hinch and Leal [50] have named this approach, based upon a detailed analysis of the microstructure, ‘structural’. Alternatively, ‘phenomenological’ continuum theories for anisotropic fluids have been postulated. These theories tend to be quite general, being based upon a small number of assumptions about invariance. Perhaps the most successful and well-known example is the Ericksen–Leslie (EL) director theory for uniaxial nematic liquid crystals. Additionally, numerous models have been developed and discussed in terms of symmetric second and higher order tensorial measures of the alignment. Given these diverse methods of derivation and apparently diverse domains of application, one may ask if, and how, such diverse approaches may be interrelated. The answer and several examples (incl. concentrated suspensions of rod-like polymers, liquid crystals, ferrofluids) are given in this section.



Chapter 8 is an attempt to review several strategies and open questions concerning the thermodynamically admissible description of complex non-equilibrium fluids on different levels (conc. length and time scales or structural details) of description. We will touch the theory of projection operators which act on the space coordinates of atoms such that the resulting quantities serve as slow variables needed to proceed with a separation of time scales in the corresponding Langevin equations. Attempts being made to characterize the system with (a few) structural quantities, known to be within reach of analytical theoretical descriptions and/or accessible through experimentation will be reviewed. A similar formal structure, namely a symplectic structure, for thermodynamics and classical mechanics was noted early by Peterson [51] in his work about the analogy between thermodynamics and mechanics. He notes that the equations of state, by which he means identical relations among the thermodynamic variables characterizing a system, are actually first-order partial differential equations for a function that defines the thermodynamics of the system. Like the Hamilton–Jacobi equation, such equations can be solved along trajectories given by Hamilton’s equations, the trajectories being quasi-static

processes, obeying the given equation of state. This gave rise to the notion of thermodynamic functions as infinitesimal generators of quasi-static processes, with a natural Poisson bracket formulation. In this case the formulation of thermodynamic transformations is invariant under canonical coordinate transformations, just as with classical mechanics. These illuminating ideas have been further developed [52, 53] and generalized Poisson structures are now recognized in many branches of physics (and mathematics). We are therefore also concerned with the formulation of so called ‘thermodynamically admissible’ simple models for complex fluids, where admissibility is assumed whenever the complete set of state variables characterizing the systems possess the ‘General Equation for the Non-Equilibrium Reversible-Irreversible Coupling’ (GENERIC) structure [38, 54]. This structure (a special representation of a less predictive ‘Dirac’ structure which also contains the Matrix model by Jongschaap [55] as a special case, connections between thermodynamic formalism are revisited in [56]) requires a Poisson bracket for the reversible part of the dynamics. Specifically, the time-structure invariance of the Poisson bracket as manifested through the Jacobi identity has been used to derive constraint relationships on closure approximations [57]. Explicit coarsening procedures from connected or disconnected atomistic chains (or FENE chains, Chap. 4) to primitive paths (Chap. 6, Fig. 1.2) are given in Sects. 8.10.1–8.10.2.

Part II



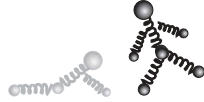
Chapter 9. Monte Carlo methods use random numbers, or ‘random’ sequences, to sample from a known shape of a distribution, or to extract distributions by other means. and, in the context of this monograph, to i) generate representative equilibrated samples prior being subjected to external fields, or ii) evaluate high-dimensional integrals. Recipes for both topics, and some more general methods, are summarized in this chapter. Advanced Monte Carlo ‘moves’ for polymers, required to optimize the speed of algorithms for a particular problem at hand, are outside the scope of this brief introduction.

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Chapter 10 summarizes definitions and properties of cartesian, anisotropic, irreducible and isotropic tensors and related tensor operators. Tensors rather than scalars allow to describe the anisotropic behavior of structural fluids subjected to external fields. The formulas presented in this chapter help to evaluate tensor operators (differentiation, integration) without performing a differentiation or an integral, to rewrite arbitrary tensors of arbitrary rank made of unit vectors in terms of the corresponding dyadics, and vice versa. This sets us in position to write down (coupled) moment equations starting from a given differential equation for (orientational) distribution functions, to derive approximate sets of coupled equations for moments of the distribution functions.



Chapter 11 introduces Fokker–Planck, Smoluchowski, and stochastic differential equations, their interrelation and methods to solve them numerically. We focus on the dynamics, in particular, the orientational dynamics of structured fluids subjected to orienting fields. The dynamics and anisotropy is properly modeled by using orientational distribution functions, their equation of change, and the corresponding balance equations for moments (here, alignment tensors) of the distribution function. We restrict ourselves to discuss the case of one-particle (single-link) orientational distribution functions and explicitly derive coupled set of moment equations which cover all cases discussed in Part I.



Chapter 12 offers basic recipes and sample applications which allow the reader to immediately start his/her own simulation project on topics we dealt with in the foregoing chapters. The chapter provides simulation codes and underlying equations. We concentrate on the necessary, and skip anything more sophisticated. Codes have been used in classrooms, they are obviously open for modifications and extensions. Codes are short, run without changes, demonstrate the main principle in a modular fashion, and are thus in particular open regarding efficiency issues and extensions. Algorithms are presented in the MatlabTM language, which is mostly directly portable to programming languages like fortran, c, or MathematicaTM.