LECTURE NOTES IN PHYSICS

M. Kröger

Models for Polymeric and Anisotropic Liquids

Springer

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Simplicity is the ultimate sophistication
Leonardo da Vinci (1452–1519)

Preface

Part I of this monograph is concerned with the theoretical, analytical as well as numerical prediction of field-induced dynamics and structure for simple models describing soft matter. It presents selected results and demonstrates ranges of applications for the methods described in Part II. Special emphasis is placed on the finitely extendable nonlinear elastic (FENE) chain models for polymeric liquids, their dynamical and rheological behavior and the description of their inherently anisotropic material properties by means of deterministic and stochastic approaches. A number of representative examples are given on how simple (but high-dimensional) models can be implemented in order to enable the analysis of the microscopic origins of the dynamical behavior of polymeric materials. These examples are shown to provide us with a number of routes for developing and establishing low-dimensional models devoted to the prediction of a reduced number of significant material properties. Concerning the types of complex fluids, we cover the range from flexible polymers in melts and solutions, wormlike micelles, actin filaments, rigid and semiflexible molecules in flow-induced anisotropic, and also liquid crystalline phases. Fokker–Planck equations and molecular and brownian dynamics computer simulation methods are involved to formulate and analyze the model fluids.

Part II allows the reader to redo simulations and motivates for further investigation of polymeric and anisotropic fluids. It contains computational recipes for devising simulation methods and codes, including Monte Carlo, molecular and brownian dynamics (written in Mathwork's Matlab, thus allowing for simple visualization and animation). A special chapter on isotropic and irreducible tensors allows for comfortable conversion between stochastic differential equations, tensorial balances, and equations for coefficients, including the testing of closure approximations. We explicitly derive coupled equations for alignment tensors for arbitrary tensor fields suitable for nth order approximations strictly valid close to equilibrium, and also highly anisotropic states.

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Part I

Illustrations & Applications

1

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 anlaysis 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.

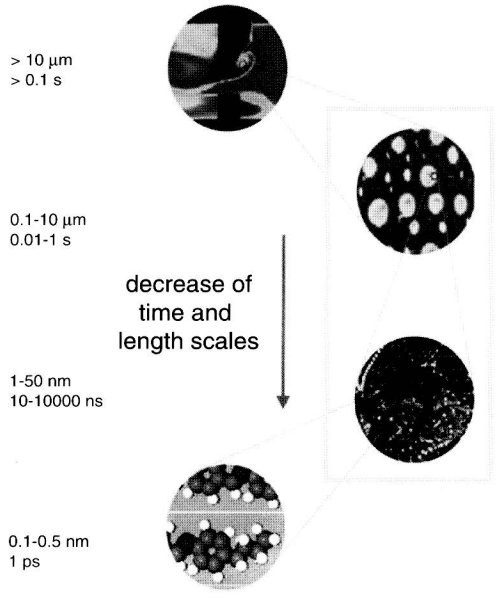

Fig. 1.1. Time and length scales of a typical polymer problem. In this review we are concerned with micro- and mesoscopic models (framed) which aim to describe physical behavior beyond equilibrium, beyond chemical details (*bottom*), and may be implemented into the macro-computation of complex flows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