

Bridging Scales in Polymer Physics and Processing

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Abstract: Understanding both the flow behavior of polymers during processing and the end-use properties of finished plastic products from a molecular picture of the constituent polymers has been a long-standing dream in polymer engineering and science. It is the goal of our work in the Polymer Physics Group to reduce the considerable discrepancy between dream and reality. Close interaction between theory and experiment is of crucial importance for further progress towards achieving this goal. Furthermore, the bridging of the gaps between chemical polymer structure, viscoelastic flow behavior, and non-homogeneous anisotropic properties in the solid state requires massive use of computer simulations. The Polymer Physics Group thus comprises three strongly interwoven branches, *theory – experiment – simulation*, as shown in this article.

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1. Research Areas

Polymeric materials often behave fundamentally differently during processing than so-called low-molecular materials. For example, both flow-induced orientation and shear thinning under moderate deformation are due to the existence of long characteristic relaxation times in polymeric melts and solutions. Concerning polymer processing, the effect of flow-induced orientation is of major importance in injection-molding and fiber spinning in order to tailor the material properties of the final solidified material. The foundations of the rich microstructural behavior, the complex rheology, and generally the extremely wide range of relevant time-scales in polymeric systems are the main targets of the research conducted in our group.

The research interests of the Polymer Physics Group are summarized and correlated to each other in Fig. 1. In order to

understand the properties of polymers during processing, it is important to realize that there exists an extremely wide range of time-scales relevant to the dynamics of polymeric liquids. In any attempt to understand their flow behavior, one is therefore forced to pass from atomistic to coarse-grained models of polymer molecules in order to capture the interplay between rheology and microstructure. On one hand, it is evident that not all details of an atomistic model are relevant for studying and improving the processing of polymers. On the other hand, to describe the complex behavior of polymers using continuum mechanics on purely phenomenological grounds is certainly also not appropriate and it does not lead to deeper insight into the behavior of the material. It is therefore a key issue in the research projects in our group to link different levels of description in one way or the other in order to get a deeper understanding of the basic mechanisms in the material. In this sense, both the investigation of well-known coarse-grained kinetic theory models and the formulation of new ones constitute main points of emphasis in the work of the Polymer Physics Group. Moving from kinetic theory to traditional continuum mechanics is a further step of coarse graining, after which the effect of polymer dynamics on the balance equations for the conserved

hydrodynamic quantities (mass, momentum, energy) can be described only in a rather unspecific manner by phenomenological constitutive equations.

Finding the proper coarse-grained variables relevant to polymer processing, describing their dynamics, and going from one level of description to another are typical tasks of nonequilibrium thermodynamics and statistical mechanics. Hence, the foundations of the theory of nonequilibrium systems can be developed in connection with practical problems – an exciting field for polymer physicists. Based on our experience with complex fluids, a general equation for the nonequilibrium reversible-irreversible coupling (GENERIC) was developed [1]. The successful modeling of polymer melts strongly benefits from the guidance provided by the thermodynamic approach. Once a coarse-grained model has been formulated empirically or derived theoretically, its predictions need to be compared to experimental results on each level (basic material properties, flow behavior). For that purpose, unique experimental equipment is available in the rheology and fluid dynamics laboratory of the Polymer Physics Group. Rheology and fluid dynamics may even serve as tools for polymer characterization if the comparison between kinetic theory and experiment proves favorable.

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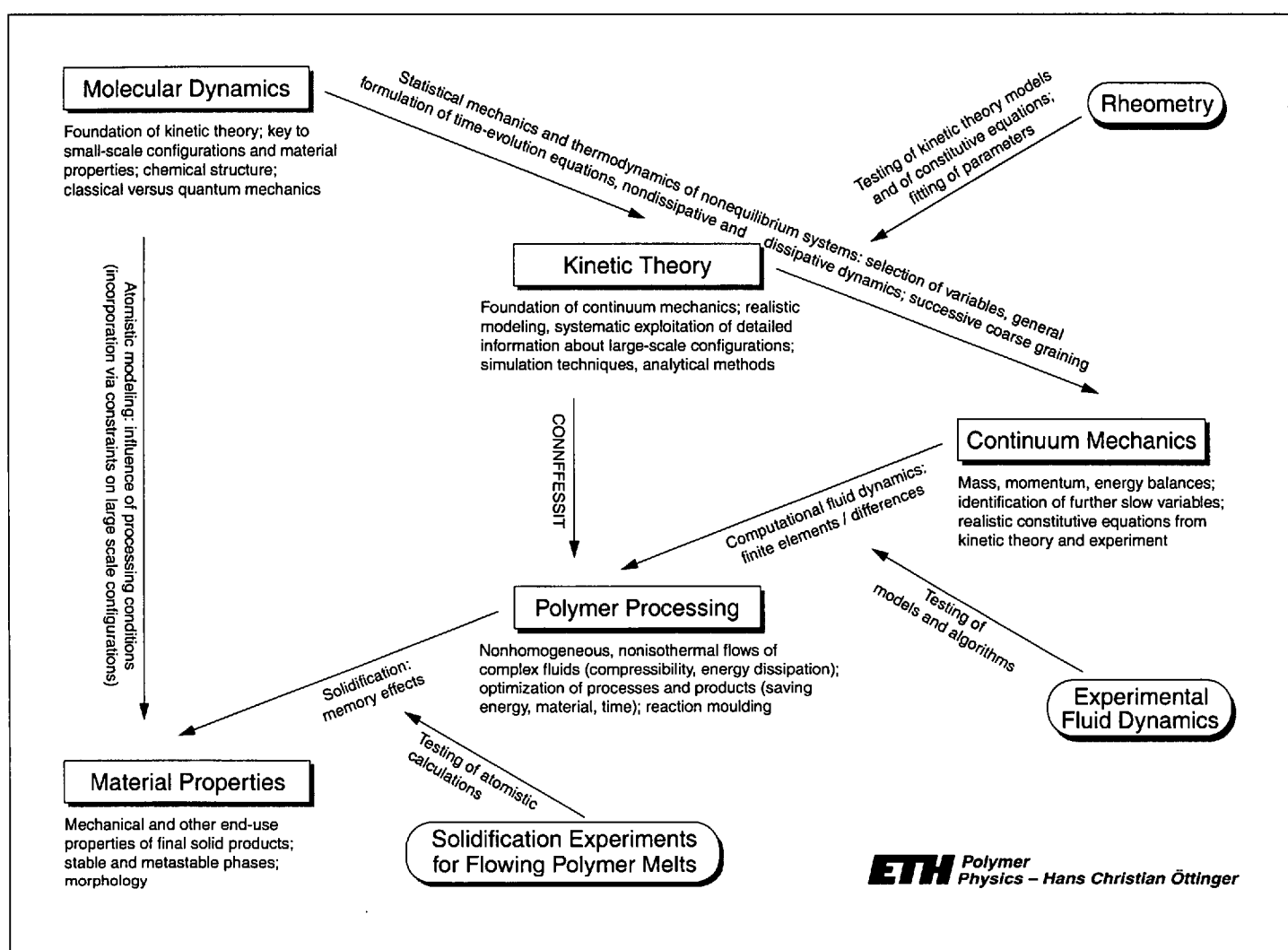


Fig. 1. Overview of the research interests of the Polymer Physics Group at ETH Zürich.

The flow calculation for kinetic theory models is now a standard tool in computational fluid dynamics initiated by the Polymer Physics Group. The basic idea is to use molecular models directly in flow calculations, that is, without going through continuum mechanics (CONNFESSIT) [2]. This approach builds a bridge for crossing easily and conveniently from molecular models to problems of practical importance. Great efforts are made to ensure that the most recent theoretical ideas can be exploited in industrial applications. Again, the success of numerical flow calculations needs to be checked against experimental data, that is, by experimental fluid dynamics. In the schematic diagram (Fig. 1), all experimental activities are indicated by round-shaped boxes.

Once the behavior of polymers in processing situations is understood on a coarse-grained level, it is necessary to fall back on an atomistic description of the system in order to determine the end-

use properties of final products (*e.g.* anisotropic mechanical properties). In the atomistic modeling of the properties of solid plastic products, the large-scale molecular configurations determined by the processing conditions should be taken into account as constraints. This step of fine-graining, which leads back to the atomistic level after coarse-graining, breaks new ground in science and is of great practical importance. Herein lies the natural interface between polymer physics and theoretical polymer chemistry. Ideally, macromolecular structures, to be synthesized by chemists, can be designed to achieve certain desirable end-use properties. The experimental investigation of crystallization in elongational flows will eventually provide the challenge for the theoretical approach to fine-graining and solidification.

An important mission of the Polymer Physics Group is to provide a *broad scientific background for modern polymer technology*.

2. Illustrative Examples of Current Research Projects

In this section, an overview of current research projects is given. The section is organized as follows. The research areas described in the subsections 2.1.–2.3. are concerned with the fundamentals of nonequilibrium thermodynamics and with modeling specific nonequilibrium situations which appear in polymer processing. Some experimental activities are summarized in subsections 2.4.–2.5., concentrating on the rheology and microstructure of polymeric melts under shear and elongational deformation. Some projects which are concerned with developing appropriate simulation techniques and which study the manifold behavior of polymeric systems by means of computer simulation are discussed in subsections 2.6.–2.7.

2.1. Rheology and Thermodynamics (GENERIC)

The previously developed GENERIC framework [1] provides a powerful tool for treating nonequilibrium systems on a phenomenological level. Once the variables for describing a given system are chosen, mixed reversible and irreversible dynamics are expressed in terms of four building blocks: energy and entropy as generators, and the Poisson and friction matrices to multiply the gradients of the generators. With increasing complexity of the systems of interest, the phenomenological approach needs to be supplemented with statistical mechanics to calculate the GENERIC building blocks from atomistic principles. The foundations for doing this have been laid in [3][4].

Our current interest is focused on developing practical tools for calculating energy, entropy and the Poisson matrix by Monte-Carlo methods. This is done for melts of unentangled [5] and entangled [6] polymers. A most important feature is that the ensemble in a GENERIC Monte-Carlo simulation depends on the choice and atomistic definition of the coarse-grained variables for which the building blocks are sought; this situation is fundamentally different from simulations in which one tries to mimic directly an experimental situation. Powerful dynamic simulation techniques, such as molecular dynamics and Brownian dynamics, for evaluating friction matrices are under development.

2.2. New Models in Polymer Kinetic Theory

When the models of polymer kinetic theory are formulated in terms of stochastic differential equations one not only investigates established models, one can also develop new models [7]. Since, compared to the traditional approach, the borderline between 'simple' and 'difficult' is shifted, a multitude of new possibilities for the formulation of more realistic models becomes available, incorporating 'double reptation', 'convective constraint release', 'anisotropic tube cross sections', and 'chain stretching'. Recently, for example, a thermodynamically consistent reptation model to describe the shear and elongational rheology of linear entangled polymers was presented and tested numerically [8][9]. The model under consideration incorporates double reptation, convective constraint release and chain stretching, and it avoids the independent alignment approximation. The simulation results reveal that

the model at a highly simplified level with few structural variables is able to capture all features of the available experimental observations qualitatively and is hence a valuable model for describing the nonlinear rheological properties of linear entangled polymers.

2.3. Solidification of Polymer Melts

It is well known that material properties change drastically when going from (quasi-)equilibrium to highly nonequilibrium conditions. One of the most prominent examples in this respect is the liquid-solid (crystalline) transition. The fact that rapid cooling of the liquid state captures the system in a non-crystalline state below the crystallization temperature is attributed to the lack of rearrangement of the building blocks necessary to form the crystalline structure. In one part of this research project, the main goal consists of studying the liquid-glass transition upon rapid cooling in terms of thermodynamically consistent models.

However, rather than by rapid cooling, the system can also be drawn out of equilibrium by large deformations. It has been found, that large shear and elongation rates, respectively, enhance the rate of crystallization in polymer solutions and melts. In this case, the deformation is believed to promote the orientation of the polymer segments necessary for crystallization. Hence, the main goal of the second part of this project is to get an understanding of flow-induced/enhanced crystallization. In particular, we are interested in the formulation of a closed set of equations which enables the study of such transitions.

Since both solidification upon rapid cooling and flow-induced crystallization involve dynamics far from equilibrium, we seek to apply as guidelines recently developed general theories in nonequilibrium thermodynamics such as *e.g.* the GENERIC formalism.

2.4. Shear and Elongational Rheometry of Polymer Melts

Shear and elongational rheometry are important not only for material characterization but also for investigating the molecular structure of polymer melts. Improvements in the experimental techniques of polymer melt rheometry have enabled us to determine many rheological details with a small amount of sample material:

- to describe the linear viscoelastic behavior, we calculate the relaxation time spectrum from measurements of frequency-dependent viscoelastic material functions,
- for the nonlinear behavior, we measure the time- and strain rate-dependent shear stress as well as the two normal stress differences and the elastic recovery after steady shearing,
- in order to determine the elongational behavior, we have developed a new rheometer which only requires a small amount of sample material.

The Multiaxial Elongational Rheometer MAD (MultiAxiales Dehnrheometer; Fig. 2) was developed to determine elongational properties of polymer melts (LDPE, HDPE, PS, HIPS, ABS, PMMA) in the temperature range from 50 to 200 °C on disk-shaped samples of diameter 90 mm. The time dependent elongational

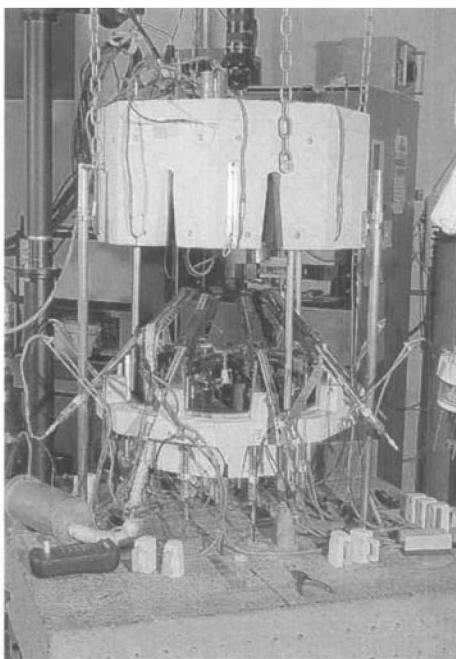


Fig. 2. Rheometer for equibiaxial elongation of polymer melts. The rheometer is opened for test preparation. Eight metal belt clamps radially stretch the disk-like sample (reference diameter 75 mm) that is floating on an inert gas cushion. The maximum temperature is 200 °C, the radial strain rates range from 0.003 to 0.1 s⁻¹.

viscosity is an important property of polymer melts during processing like blow molding (bottles), film blowing (plastic sheets), and deep drawing (packaging containers, housings, food containers, shields). The design of the instrument is based on approved components from the uniaxial elongational rheometer RME [10], such as nickel belts to grip and elongate the sample, frictionless sample support by a gas cushion, force measurement by leaf springs and inductive displacement transducers, and a video survey system to determine the true deformation behavior by means of a particle tracking system. The components of the rheometer allow the experiments to be performed in the equibiaxial and planar elongational mode. Such experiments yield valuable information for the establishment of constitutive equations.

2.5. Experimental Fluid Dynamics of Polymer Melts

Fluid dynamics of polymer melts connects the melt rheological behavior with polymer processing. Whereas in the literature there has been research in the theoretical field, we will focus on improving the experimental techniques. After the determination of the velocity field of a polyethylene melt in and in front of a die with the Laser-Doppler technique, we will now improve those measurements by tracing particles in the flowing polymer

melt by means of two video cameras [11]. Furthermore, the flow behavior at the die exit will be evaluated (problem of extrudate swell). In a new flow channel with cross-slot geometry, we produce two-dimensional flows of polymer melts by lubricating the front and back walls (Fig. 3). In addition to velocity measurements, this allows us the application of birefringence for full stress measurements (the stress-optical law is tested separately in elongational rheometers).

2.6. Simulation Techniques

In the equations of motion for the coarse-grained models investigated in the kinetic theory of polymeric liquids there occur Brownian forces which lead to stochastic differential equations. In traditional kinetic theory, the direct treatment of the stochastic equations of motion is rather unusual even though it has important advantages. For example, the numerical integration of stochastic differential equations immediately leads to simulation algorithms. Simulations constitute an extremely powerful and versatile tool for investigating models for which the usual determination of probability densities in configuration space is very tedious or, more often, hopeless. In a simulation, all relevant properties (such as diffusion coefficients or rheological material functions) can be obtained as averages over a large ensemble of stochastic trajectories.

The multitude of possibilities for benefiting from the comprehensive mathematical theory of stochastic differential equations when developing simulation algorithms for kinetic theory models are illustrated in [7]. Among the rather elementary ideas for designing improved algorithms is the formulation of higher-order integration schemes. In a recent approach [12] approximate solutions for a given model are exploited in order to transform the equations of motion in such a way that the statistical error bars in a simulation become smaller (variance reduction), after having resolved some mathematical difficulties in formulating simulation algorithms for models with internal constraints (such as fixed bond angles or bond lengths [13]). Detailed simulations of models using variance reduction are now in progress (*e.g.* [14]). For simulating complex fluids, the construction of improved numerical methods may also be achieved by implementing the GENERIC structure in discretized schemes such as smoothed particle hydrodynamics or dissipative particle dynamics [15].

2.7. Nonequilibrium Dynamics Computer Simulation of Polymer Fluids

The methods of nonequilibrium molecular dynamics (NEMD) and Brownian dynamics (NEBD) computer simulation are applied to solve the equations of motion for diluted or concentrated polymeric systems modeled by an ensemble of multibead chains (*e.g.* [16–18]). Since our group is interested in the (macroscopic) flow and bulk properties of polymers and in order to keep the simulations feasible (on super computers), a coarse-grained description is desired. Actually, dense linear polymer systems, branched polymeric systems, polymer networks, equilibrium polymers, polymer brushes, actin filaments and micellar systems are under study, subjected to shear and elongational flows. From the knowledge (by means of computation of microscopic trajectories) about the full microscopic dynamics of the system one obtains the time resolved macroscopic quantities such as the

- optical behavior – flow induced alignment, scattering intensities
- rheological behavior – shear thinning/thickening, non-Newtonian viscosities
- dynamic behavior – diffusion coefficients, dynamics of entanglements.

Since most of these quantities are well defined within the framework of statisti-

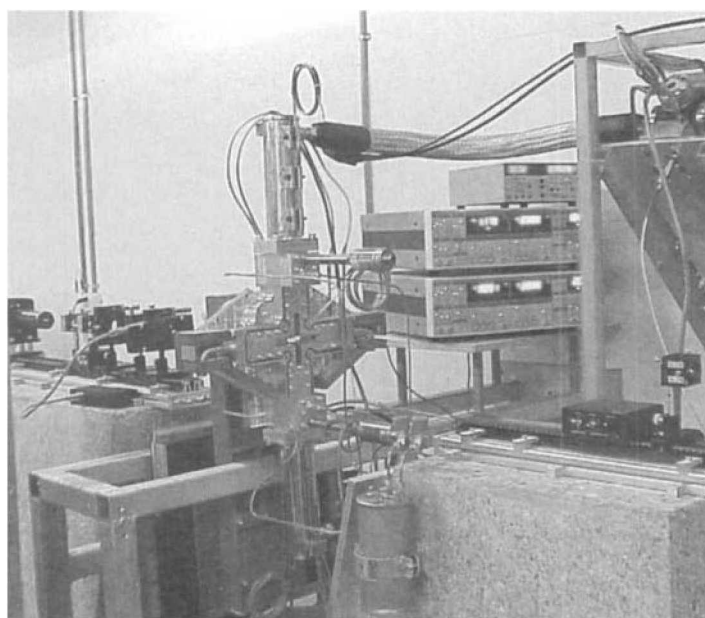


Fig. 3. Flow channel in cross-slot geometry for polymer melts. The melt is subjected to a planar elongational flow in the symmetry plane and to a mixed shear and elongational flow elsewhere. Stresses are determined from high-resolution point-by-point flow birefringence measurements. Gear pumps (right) provide a constant volume flow.

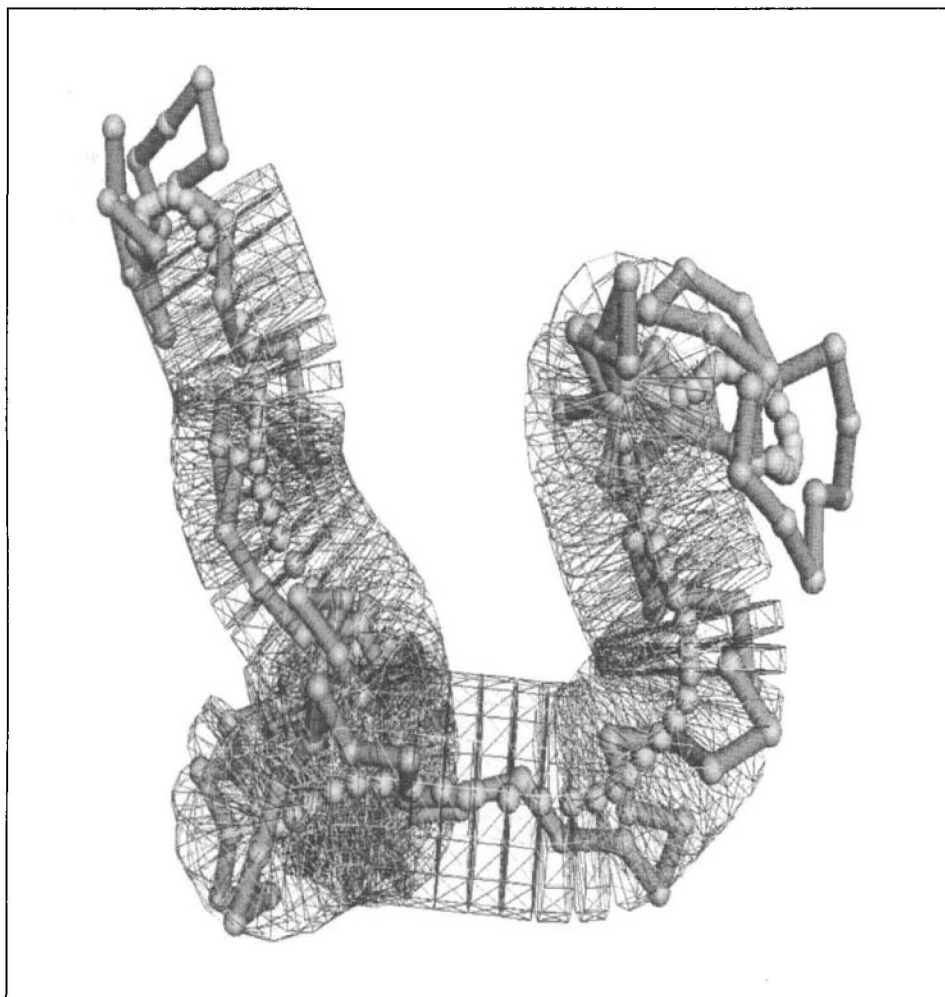


Fig. 4. Multibead-chain configuration (chain of rods and spheres) surrounded by a 'tube' (mesh) along its coarse-grained path (chain of spheres). This 'primitive' path, and the orientation of the tube is constructed from the multibead-chain configuration; the local radius of the tube contains information about local intermolecular spacings.

cal mechanics and all accessible at the same time by means of computer simulation, the method allows the validity of empirical and theory-based relationships between stress and deformation history (constitutive equations) to be checked. In collaboration with the Institute of Theoretical Computer Science, ETH Zentrum, we develop algorithms for the efficient generation of equilibrated polymers with prescribed local and global characteristics (Fig. 4).

3. Conclusion

The selected research topics illustrate the possibilities of obtaining new insights in polymer physics and new routes in processing when

- theory, experiment and simulation are done in close interaction, and
- scales are bridged, with the guidance of nonequilibrium thermodynamics.

These ingredients are indispensable for further progress in understanding polymer dynamics and processing.

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