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Molecular dynamics studies of entangled polymer chains

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Chapter 1

Introduction

The more original a discovery, the more obvious it seems afterwards.

Arthur Koestler

This thesis presents three molecular dynamics studies of polymeric ensembles in which the chain entanglement plays the major role in the internal dynamics of the system. A coarse-grained model is used for representing the polymer chains as strings of beads connected by finite-extensible springs. In a dense ensemble of such chains, the strong bonds along the polymer backbone coupled with the repulsive Lennard-Jones interaction between unconnected beads prevent the chains from crossing each other. This results in an entangled system with motion restrictions for each chain imposed by the intertwining with the neighboring ones. Studying the chain dynamics inside entangled ensembles of identical chains is the main purpose of this thesis.

Due to the entanglement, the polymers are restricted to a reptation motion. The chain movement is influenced significantly by chain length (N), temperature (T) and chain stiffness. In order to analyze the effect of these parameters, three systems were investigated by computer simulation.

- **The polymer melt:** at relatively high temperatures, the ensemble of entangled polymers behaves like a highly viscous fluid. Above the entanglement length ($N > N_e$), in the reptation regime, the chain self-diffusion decreases with the square of the chain length (N^2). This is in contrast with a linear dependence on N predicted by Einstein's relations and applicable only to short chains in Rouse regime.
- **The polymer glass:** as the temperature is lowered below the glass transition temperature ($T < T_g$), the diffusion process ceases. The system enters the glassy state characterized by structural arrest in which the local random bead motion is ineffective in inducing large scale chain diffusion.

- **The adhesion between two polymer bulks via connector chains:** the adhesion strength is measured in debonding simulations. As the two polymer bulks are pulled apart the connector chains are forced to disentangle from the bulks following a reptation motion. Remarkably, the total work necessary to break the adhesion is again proportional to the square of the connector length (N^2). This confirms that the entanglement of the connectors inside the polymer bulks is the essential mechanism realizing the bondage.

The prominent contribution of this thesis is the systematic study of how these phenomena are influenced by the chain stiffness, modeled by a bending potential and a novel form of torsion potential acting on three, respectively four, successive beads along the polymer backbone. By incorporating chain stiffness, our study shows that the effects of chain entanglement become more evident: as chain stiffness is enhanced, the entanglement length (N_e) increases, the glass transition occurs at higher temperatures (T_g) and the adhesion via connector chains becomes stronger.

The results reported in this thesis are based on a massive computational effort amounting to about 10 CPU years.

1.1 Chain dynamics in entangled polymer ensembles

This thesis is concerned with the microscopic characterization of dense polymer chain ensembles by coarse-grained molecular dynamics simulations. Two main research goals are followed:

- the study of the conformation and motion of a polymer chain in entangled ensembles depending on chain length, chain stiffness and architecture, or temperature;
- the establishment of general relationships between the microscopic properties and the macroscopic behavior of the polymeric material such as the glass transition or the mechanical behavior.

It is important to mention that the results reported in this thesis are relevant in allowing a good understanding and prediction of the essential qualitative trends underlying the statistical behavior of polymeric systems. Obtaining exact quantitative predictions for a specific polymer with a given chemical structure remains a distant goal due to the enormous complexity of the physical interactions, largely exceeding the concrete computational power available. Nevertheless, the study performed in this thesis may be the first step in the selection, improvement and design of better polymer products in an industrial setting. This thesis will refer to one industrial application in particular: the adhesion between two glassy polymers reinforced with connector chains.

The beginning of the 20th century was marked by the invention of synthetic polymers. This fact has led in short time to a growing industry with large applications everywhere in our life. Today, plastics frequently replace most traditional materials such as wood, metal, glass, leather, paper and rubber because they can be more inexpensive, lighter, stronger, corrosion resistant or durable. In fact, since the seventies, polymeric materials used in the entire world quantitatively exceed any other material.

Polymeric materials are dense ensembles of large molecules formed by extremely many atoms linked together by covalent bonds. The motion of the chains inside such ensemble is ultimately revealed by the macroscopic properties of the material, which motivates the great interest in understanding chain dynamics.

It is obvious that this is a very complex multi-body problem that has to account for chain connectivity and for the interactions with the other chains that ultimately lead to chain entanglement. Two of the most widely used theories for polymer melt dynamics reduce the problem to a single chain moving in an effective medium: the *Rouse model* for the simple case of unentangled chains (Rouse 1953) and the *reptation model* for entangled chains (de Gennes 1979, Doi and Edwards 1989). In the Rouse model, a Gaussian chain of beads connected by springs interacts with a stochastic medium that mimics the presence of the other chains. As a consequence, the chain center of mass is subjected to particle-like diffusion. In the reptation model, on the other hand, the polymer chain is confined inside a “tube” formed by the constraints imposed by the entanglement with other chains. The chain length at which these models overtake dominance is known as the entanglement length N_e . This transition from the Rouse to the reptation regime has been proved already by molecular dynamics simulations of polymeric ensembles using coarse-grained models for polymer chains without chain stiffness enforcement (Kremer and Grest 1990).

The reptation model was originally developed to describe the dynamics of a long chain inside highly dense polymer melts. Nevertheless it is generally accepted that this model might be applied, at least partially, also to the fracture behavior of amorphous polymers (Evans 1987). Two facts sustain this assumption: (1) the configurational statistics of amorphous polymers in the unstressed state, below their glass transition temperature, are equivalent to those in the polymer melts (Kirste and Kruse 1975); (2) the motion imposed to the polymer chains during the fracture process can be considered as an accelerated reptation. In order to break the interface, polymer chains have to be extracted (and maybe broken) from an entangled ensemble of other chains. Their natural diffusion process is accelerated in one direction, but the motion is restricted in the same way: the polymer chain is pulled-out in a worm-like manner along an imaginary tube, created by the neighboring chains (Prentice 1983, Prentice 1985).

Against this background, the present thesis is devoted to the study of the dynamics of dense polymer chains ensembles in the melt and glassy state, and during the fracture

of the interface between two polymer bulks reinforced with connector chains.

Following this challenging problem a number of fundamental research questions have been investigated:

- What is the influence of the chain stiffness on the entanglement length at which the motion of a polymer chain changes its style from Rouse to reptation behavior?
- Can the glass transition of a polymer ensemble be revealed by molecular dynamics simulations using coarse-grained models? How is the glass transition temperature affected by the stiffness of the polymeric chains?
- Is the motion of the polymer chain in melts similar with the motion of polymer connector during the fracture of the interface between two polymer bulks reinforced with connector chains? How can the adhesion strength be controlled by different connector architectures (chain length, chain stiffness, areal density of the connectors at the interface, number of effective stitches at the interface)? And what is the influence of the temperature or the separation rate in determining the adhesion strength?

1.2 Bridging the gap between polymer physics and continuum mechanics

Bonding together existing polymers is a technical solution for creating new materials with specific properties, at a relatively low cost. Unfortunately many useful polymers are immiscible, thus having a very weak interfacial interaction. One way to reinforce their junction is to add preformed copolymers at the interface as adhesion promoters (Creton et al. 2001). These act like connectors between the polymer bulks and can effectively "sew" the junction and strengthen the interface adhesion. The obtained adhesive bonding is required to resist a specific stress (a very high one in the construction or automotive industry or a relatively low one for the packaging industry) at different loading rates; to be adequate for different working environments and temperatures; and not the least, to be an integral part of the new material by not changing its properties.

There are many ways in which the reinforcement may be acquired depending on the areal density of the connector chains, their molecular weight and chain stiffness, the effective way in which they weave back and forth across the interface thus creating one or multiple stitches. In order to have a simple and inexpensive connector architecture to lead to a specific adhesion strength intended for particular applications, experimentalists usually employ a trial-and-error process that works reasonably well but is very expensive in cost and time. An attractive alternative for an effective selection is to use

computer programs to simulate such multiple possibilities and to give guidelines for synthesizing additives for specific effects wanted on the mechanical response and on the interface strength. However, such achievement is not straightforward due to the complexity of the adhesion process whose understanding involves multiple approaches coming from chemistry, interfacial physics, and mechanics.

The only available method for the quantitative evaluation of adhesion strength is the effective breakage of the interface. This justifies the traditional macroscopic approach of studying polymer adhesion using continuum fracture mechanics. But since this was developed especially for steel and other metals some modifications have to be considered to make it also applicable to polymeric materials (Williams 1984).

Fracture generally occurs because of the propagation of crack-like defects under the influence of the surrounding stress field. At room temperature this usually takes place in a rather brittle manner and, in a first approximation, the two bonded polymer bulks may be treated as linear elastic solids (Fig. 1.1a). A crack will grow between them if the energy-release rate reaches the value needed to create two dissimilar surfaces in the same way a cohesive fracture has to create two similar surfaces (Griffith 1920). This is indeed the case for brittle materials. However the polymeric materials are also well capable of large deformations to quite large strains. As a result, their fracture energy is many orders of magnitude greater than the surface energies. More than that the theoretical relation between fracture energy and surface energies is still unknown.

The generally accepted explanation for this difference is that the polymer–polymer fracture is not a reversible process, but rather comprises many irreversible dissipative processes, such as shear yielding and crazing. Furthermore, detailed investigation of the fracture surfaces, using ion beam and X-ray scattering techniques (Kramer 1991, Boucher et al. 1996), reveals that irregular material discontinuities appear at the crack tip, so that the true surface area becomes greater than the planar geometrical area assumed for the fracture initiation criterion.

The dissipative processes are intimately connected to the nature of the polymer materials that are formed by long and entangled chains. In order to fracture such materials, polymer chains have to disentangle from the bulk region around the crack tip, individually or in fibrils of many chains that continue to deform plastically until complete fracture.

During fracture it might happen that the size of the plastic deformation spans an extended zone around the crack tip, comparable with the size of the sample (Fig. 1.1b). One may describe this plastic deformation by means of a macroscopic continuum model. An isotropic, strain-hardening model developed originally for metals, gives rise to singular stress–strain fields referred to as HRR fields (Rice and Rosengren 1968, Hutchinson 1984). To be more specific to the polymeric behavior a generalization of the HRR model for non-linear viscoelastic materials can be used (Schapery 1984) or, instead, a phe-

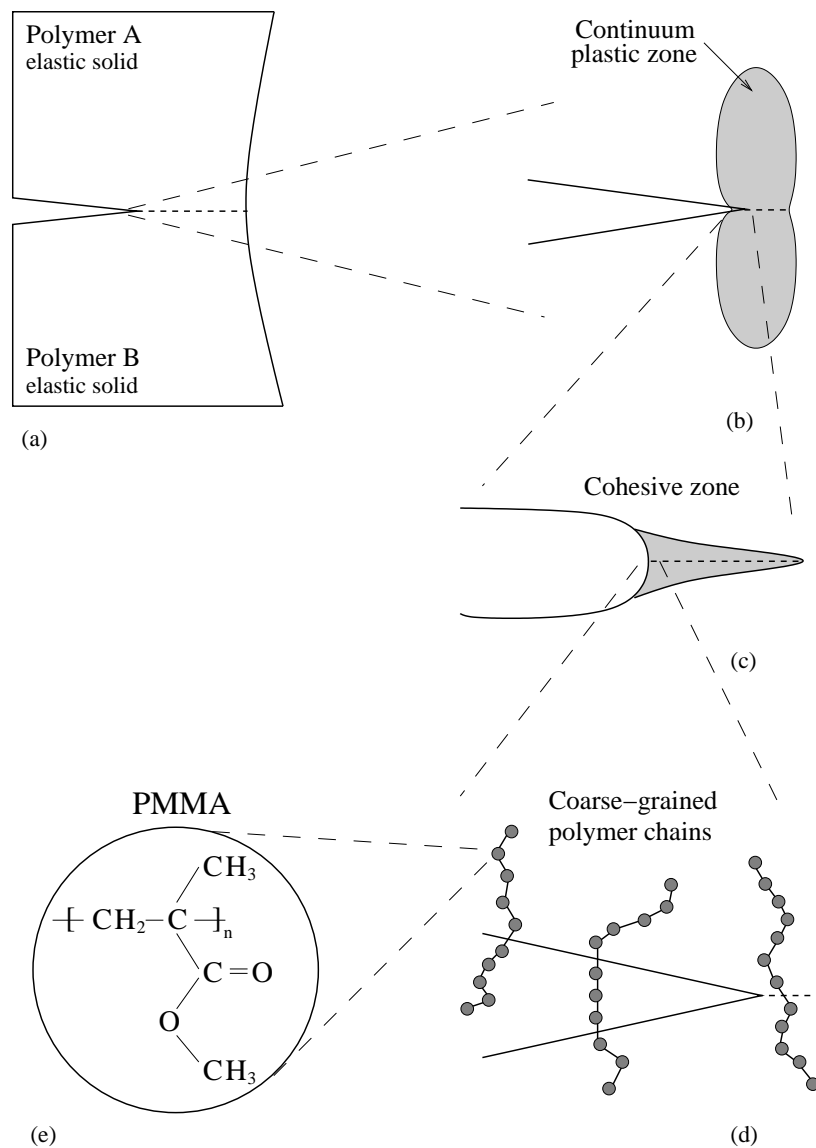


Figure 1.1: A multi-scale model for polymer fracture: (a) the macroscopic scale at which the two polymer bulks may be considered elastic solids, (b) the local plastic zone near the crack tip due to shear yielding, (c) the small cohesive zone in which the molecular fracture mechanisms occur (e.g. pullout of the connector chains) (d) the mesoscopic molecular scale in which the polymer chains are treated as strings of beads connected by springs, (e) the atomistic scale that considers the chemical detail of the polymer chain.

nomenclological model based on micromechanical considerations of the strain softening and re-hardening characteristics of glassy polymers (Wu and Van der Giessen 1995, Wu and Van der Giessen 1996, Lai and Van der Giessen 1997).

However, even though these are explicitly non-linear treatments, they do not take into account the energy losses inside the confined zone in the proximity of the crack tip as the crack propagates (Fig. 1.1c). This is a crucial zone since here the main fracture mechanisms occur and compete with each other to give the final properties.

In the absence of knowledge of what really happens at this scale, the response of this region is traditionally synthesized in a "cohesive zone", following the approaches suggested by Dugdale (1960) and Barenblatt (1962). This zone could represent purely brittle behavior in case of cleavage-like crack propagation or the behavior of a craze formed by polymer fibrils being pulled-out from the bulk. Whatever the mechanism, the properties of such a zone are collapsed into a cohesive law connecting traction on the interface to the separation of the materials on either side.

Despite the importance of the molecular processes in adhesion strength, until the present, the analysis of polymer fracture has mostly concentrated on macroscopic phenomena. Nevertheless, some attempts have been made to incorporate the molecular fracture mechanisms into continuum models by using phenomenological cohesive laws. But, due to the lack of development of such laws for polymeric materials, these constitutive relations were just borrowed from those developed for metals, in spite of the clear distinction between the phenomenology of plastic deformation in amorphous polymers compared to metals. For example, Rahul-Kumar et al. (1999, 2000), modeling fracture during the peel test of viscoelastic polymers, has demonstrated the failure of metallic cohesive law in describing polymer fracture. The major insufficiency of the cohesive law used was its insensitivity to rate dependence specific for polymeric materials.

A long-term goal of the present work is to contribute to the development of reliable constitutive relations specific for the debonding of a polymer-polymer interface reinforced with connector chains by performing molecular-dynamics simulations for the polymeric material localized in front of the crack tip, see Fig. 1.1d. These novel constitutive relations can be used as cohesive laws at the continuum level in a multi-scale simulation. Such an implementation has been already done for simulating crack growth in homopolymers: using a micromechanical model, a cohesive law for crazing was derived and subsequently introduced in continuum fracture simulations (Tijssens et al. 2000, Tijssens and Van der Giessen 2000).

The major contribution of the molecular dynamics outcome is that it naturally contains the rate-dependent behavior of the system.

The model used at the molecular level, in our molecular dynamics simulation of polymer-polymer adhesion, is a coarse-grained representation of polymer chain as connected beads that replace one or more monomer units, see Fig. 1.1e. Such a simple treatment was preferred for this study since it captures the nature of the polymer chain ensembles (Kremer and Grest 1990) while allowing the simulation of sufficiently big systems for relatively long time.

1.3 Overview of the thesis

This thesis is structured in three main parts:

1. Basic concepts
2. Characterization of a dense ensemble of entangled polymer chains
3. Polymer-polymer adhesion reinforced with connector chains

The first part is written as a rather brief presentation of the theoretical concepts and computer simulation technique further referred in the thesis.

First of all, in Chapter 2 a short introduction into polymer physics is given. It recapitulates different polymer chain models and fundamental theories describing the polymer chain motion in dense chain ensembles. Next, the macroscopic behavior is discussed as it appears in more general applications: the glass transition, and the polymer adhesion.

The molecular dynamics technique used to simulate the polymeric materials is described in Chapter 3. Without going in great detail, this chapter presents the backbone of the molecular dynamics code developed during this PhD study. The emphasis is on the description of the polymer chain stiffness as included in the coarse-grained model used for polymer chain representation throughout this thesis.

Second part concerns the problem of how the chain stiffness and molecular weight influence the chain motion in polymer chain ensembles at a specific temperature (Chapter 4) and in a large temperature interval (Chapter 5).

The main objective of Chapter 4 is to see how the chain motion compares to the classical theories (Rouse and reptation models) when the chain stiffness is enhanced. Special importance is given to the chain stiffness influence on the entanglement length N_e . This aim is acquired by diffusion coefficient calculations, Rouse mode analysis and chain visualization.

Many polymer applications are found at temperatures below the glass transition temperature, where the polymeric materials have special macroscopic properties induced by, a still poorly understood behavior at the molecular scale. This motivated the work from Chapter 5 to investigate the possibility of the model used here to capture the glass transition in the simulated systems. Diffusion coefficient results combined with the analysis of the autocorrelation functions for the torsion angle and for the end-to-end distance are employed for the evaluation of the glass transition temperature in systems with different chain stiffness.

Chapter 6 presents a detailed investigation of polymer-polymer adhesion reinforced with connector chains. This chapter builds on the knowledge gained in previous chapters in order to understand the motion of the polymer chains induced by the fracture of the interface. The ambition here is to provide valuable recipes of how to reinforce the adhesion (areal density of the connectors, chain length and stiffness, number of stitches at the interface) in order to obtain specific adhesion strength for different technical applications.

Finally, the conclusions and some further research directions envisaged for the future are gathered in Chapter 7.

