Entangled polymer systems

Kurt Kremer a,∗, Sathish K. Sukumaran a, Ralf Everaers b, Gary S. Grest c

a Max-Planck-Institut für Polymerforschung, Postfach 3148, D-55021 Mainz, Germany
b Max-Planck-Institut für Physik komplexer Systeme, Nöthnitzer Str. 38, Dresden, Germany
c Sandia National Laboratories, Albuquerque, NM 87185, USA

Available online 7 April 2005

Abstract

Topological constraints, referred to as entanglements in the literature, dominate the viscoelastic behavior of high molecular weight polymeric liquids. To give a microscopic foundation of the phenomenological tube models which successfully describe this behavior, we have recently introduced a method for identifying the so-called primitive path mesh that characterizes the microscopic topological state of (computer generated) conformations of long-chain polymer networks, melts and solutions. Here we give a short account of this approach and discuss some applications.

Keywords: Molecular dynamics; Polymers; Reptation; Tube model; Primitive path analysis; Elastic modulus; Structure property relations

1. Introduction

The relation between the complex viscoelastic properties of polymer liquids and their microscopic structure and dynamics is a key issue in modern polymer science and biophysics [1–6]. A prototypical system is a melt or semi-dilute solution of long (flexible) chain molecules. On a microscopic scale, their Brownian motion is dominated by the restriction that the chains may slide past but not through each other. Consequently the motion of each polymer chain is confined to a tube-like region around a so-called primitive path along the coarse grained chain contour [7,8]. Recent, more refined analytical [3,9] and numerical models [10–14] concentrate on the dynamics of these primitive paths. These models are able to quantitatively describe most rheological and single chain dynamics data with a small set of material-specific parameters such as the tube diameter, \( d_T \).

2. Experiments/simulations

The key quantity of the theory, the mesh of primitive paths or equivalently the tubes with diameter \( d_T^2 \sim N_e \), the entanglement molecular weight, is not experimentally a directly accessible observable. A variety of experiments have been performed leading to...
different estimates of $d_T$ (or equivalently, $N_e$). Here we mention just three of the different approaches.

The motion of the chain beads can be monitored and the diffusion of individual beads or the whole chain can be studied, both by a variety of experiments as well as computer simulations. Taking the diffusion constant of the whole chain in a melt or semi-dilute solutions of identical other chains one expects ($N$ being the chain length):

$$D(N) \sim \begin{cases} N^{-1}, & N \leq N_e, \\ N^{-2}, & N \gg N_e. \end{cases}$$

(1)

Recent experiments even suggest a somewhat stronger decay for longer chains. When plotting the ratio of $D(N)$ over the hypothetical short chain diffusion constant of the same chain length vs. $N/N_e$ one would expect a universal curve, if the “correct value” of $N_e$ is used in the fit. This “correct” value then is based on a master plot, in the present case originating from experimental data on polyethylene [15]. This allows, similar to an analysis of the motion of simple computer polymers, all scattering lengths can be taken equal and $S(k, t)$ reads

$$S(k, t) = \frac{1}{N} \sum_{i,j} \exp[i k \cdot (\mathbf{r}_i(t) - \mathbf{r}_j(0))].$$

(2)

where $\mathbf{r}_i(t)$ is the position of bead $i$ at time $t$. For intermediate times the scatterer observes a smeared out bead density in the tube, akin to the effect described by the Debye–Waller factor in solid state physics. This leads to a plateau in the decay of $S(k, t)$, which then is related to $d_T$ in the following way [16–18]

$$\frac{S(k, t)}{S(k, 0)} = \left[1 - \exp\left[-(kd_T/6)^2\right]\right] f(k^2b^2\sqrt{12Wt/\pi})$$

$$+ \exp\left[-(kd_T/6)^2\right] \times \frac{8}{\pi^2} \sum_{p=1, \text{odd}}^{\infty} \frac{\exp[-tp^2/\tau_d]}{p^2},$$

(3)

where $f(u) = \exp[u^2/36]erfc(u/6)$, $b$ is the bond length and $W$ is the bead friction. From this expression, the corresponding tube diameter $d_T$ can be estimated. Again, $d_T$ is the parameter, which is used to fit the data to the above equation. If we assume that $d_T^2 = R^2(N_e) = N_e c_{\infty} b^2$, $R^2(N_e)$ being the mean square end-to-end distance of a chain of $N_e$ beads and $c_{\infty}$ the Flory characteristic ratio [19], it is then possible to calculate the entanglement length $N_e$. A third approach, which goes back to the origin of the tube models, employs the analogy between long chain polymer melts and long chain polymer networks. Under elongational or shear strain the initial stress relaxes rapidly towards the so-called plateau value $G_0^p$. In a network it remains there essentially forever, while in a melts the stress decays after the disentanglement time, $\tau_d \sim N_e^{1/4}$. In reality the behavior of course it more complex, however the plateau regime can be clearly identified in experiments. In a simulation, the normal stress $\sigma_n$ can be determined by the microscopic virial tensor and the plateau values were fitted to the stress strain formulas for classical rubber elasticity (CRE) (e.g., elongational strain in the limit of small deformation $\lambda$) [20,21]

$$\sigma_n = G \left(\lambda^2 - \frac{1}{\lambda} \right),$$

(4)

to determine $G_0^p$, which in turn is related to $N_e$ [1,3] by the expression

$$G_0^p = \frac{4 \rho k_B T}{5 N_e},$$

(5)

where $\rho$ is the bead density. This is the most direct experimental way to determine $d_T$ and $N_e$, respectively, as no fitting is required and only the underlying (approximate) theory is applied. However, this is not a direct measurement of $N_e$. Therefore, there certainly is a need to develop an approach, by which we can obtain the material specific quantity $N_e$, directly from the polymer conformations by taking into account its dependence on the melt topology. Such an approach would be particularly valuable, as the different experimental ways to determine $N_e$ lead to rather conflicting results (see Table 1 in which results from two different simulation studies are listed).

The data for polycarbonate (BPA-PC) at $T = 570$ K were obtained from a simulation of the coarse grained PC model [15,22], which takes into account the characteristic shape of the monomers. Rheological experiments on BPA-PC typically report values for $N_e$ between 5 and 8 repeat units. The other data are from simulations of fully flexible bead-spring chains. This
Table 1

<table>
<thead>
<tr>
<th>$N_e$</th>
<th>$N_e$</th>
<th>$N_e$</th>
</tr>
</thead>
<tbody>
<tr>
<td>BPA-PC</td>
<td>12</td>
<td>70</td>
</tr>
<tr>
<td>$S(q,t)$</td>
<td>10</td>
<td>55</td>
</tr>
<tr>
<td>$G_N^{0}$</td>
<td>5</td>
<td>72</td>
</tr>
<tr>
<td>$N_{\text{max}}$</td>
<td>120</td>
<td>2000</td>
</tr>
</tbody>
</table>

is one of the most studied models available in the literature. In both cases different “experiments” give rather different results for $N_e$. This in principle is not a severe problem, as different experiments measure different quantities and the underlying theoretical expressions are not exact. However what it is more problematic is that not only are the values different, but also their ratios vary and in some cases even the trend is not the same. While $N_e$ from the modulus is smaller for BPA-PC than from the other two measurements it is just the opposite for the fully flexible bead-spring chains. That means that there is a clear need for a direct determination of the topological state of a polymer melt and to determine whether the knowledge of this state is sufficient to give a definite answer to the question of what $N_e$ is.

### 3. Primitive path analysis

To do this, we go back to the original idea of Edwards [23] who identified the random walk-like axis of the tube with what he called the “primitive” path: the shortest path between the endpoints of the original chain into which its contour can be contracted without crossing any obstacle. Similar to the tube, the primitive path is usually discussed without specifying the relation between the obstacles and the melt structure. In Refs. [24,25] we argued that the obstacles encountered by a test chain are themselves polymers with identical properties and introduced a primitive path analysis (PPA) where all polymers in the system are contracted simultaneously. This allows us to establish the microscopic foundations of the tube model and to endow a highly successful phenomenological model with predictive power for structure-property relations.

### 3.1. Model and method

In order to study generic properties of entangled polymers in computer simulations one can choose a coarse-grained model which combines numerical efficiency with the characteristic features of (synthetic) polymers: connectivity, flexibility, local liquid-like monomer packing and mutual uncrossability of the chain backbones. We mainly study dense melts of bead-spring polymers [26] with variable intrinsic stiffness [27] and semi-dilute solutions [28].

Chain monomeric units are represented as spheres of diameter $\sigma$ and mass $m$. All monomeric units interact via a purely repulsive Lennard–Jones (LJ) potential (excluded volume (EV) interaction),

$$U_{\text{LJ}}(r) = \begin{cases} 
4\epsilon \left( \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^{6} + \frac{1}{4} \right) & \text{for } r < r_c, \\
0 & \text{for } r \geq r_c.
\end{cases}$$

where $\epsilon$ is the energy scale of the potential, $r$ is the distance between two interacting monomers and $r_c = 2^{1/6} \sigma$. The polymers are formed by connecting the monomers with an additional non-linear spring potential given by,

$$U_{\text{FENE}} = -(kR_0^2/2) \log(1 - r^2/R_0^2),$$

where $k$ is the spring constant and $R_0$ is the maximum extension of the FENE bond. The equations of motion are integrated using a velocity-Verlet algorithm in which all monomers are weakly coupled to a Langevin heat bath with coupling $\Gamma = 0.5 \tau^{-1}$, where $\tau = \sigma (m/\epsilon)^{1/2}$ [26]. The time step for the integration is $\Delta t = 0.012 \tau$. For the FENE potential, we use $k = 30 \epsilon / \sigma^2$ and $R_0 = 1.5 \sigma$ [27]. The parameter choice yields an average bond length $b_{\text{avg}} = 0.97 \sigma$ and guarantees sufficiently close contact between connected monomers to prevent chain crossings. The parameters used for the PPA are given in [25].

Monodisperse polymer melts of $M = 200$–500 chains of length $50 < N < 700$ at a bead density of $\rho = 0.85 \sigma^{-3}$ are studied. By introducing a small intrinsic bond bending potential, the Kuhn length, $l_K = \langle R^2 \rangle / L$, is varied between 1.80$\sigma$ and 3.34$\sigma$, where the lower value corresponds to the fully flexible case. Here, $\langle R^2 \rangle$ is the mean square end-to-end distance of the chain and $L$ is the chain contour length. For details see Ref. [27]. In addition, we present results for a coarse-grained model for polycarbonate.
In this case, we analyzed melt configurations for $M = 100$ chains of $N = 60$ chemical repeat units which are represented by four beads each. All the melt samples studied are tabulated in [25]. For semi-dilute and dense solutions we only studied fully flexible chains swollen in an athermal (vacuum) solvent [28]. Each solution consists of $M = 50$ chains of length $N = 1000$.

The implementation of the PPA is straightforward: First the chain-ends are fixed in space. Then, all intrachain interactions other than the FENE bond interaction, which has its minimum at $r = 0$, are switched off. Finally the total energy is minimized by cooling the system to $T \approx 0$. Without thermal fluctuations and intrachain EV interactions, the bond springs try to reduce the bond length to zero and pull the chains taut. The intrachain EV interactions provide an energy barrier to prevent chain crossings. We are assured that the chains do not cross by ensuring that the maximum bond length in the system remains below a chosen value [25].

The algorithm introduced so far does not account for self-entanglements. In a recent variant of the approach this is included in the PPA [25]. One way to preserve self-entanglements on different length scales is to disable the intrachain EV interactions all the monomers that are at a chemical distance of $(n_{\text{seg}} - 1)$ or less from each other. The two extreme cases $n_{\text{seg}} = N$ and $n_{\text{seg}} = 1$ correspond to the original algorithm and a (useless) path analysis with conserved chain contour length, respectively. A sensible lower limit is given by $n_{\text{seg}} = (b/b_{\text{pp}})$ where $b_{\text{pp}}$ is the primitive path bond length to which the original algorithm converges.

4. Results—comparison to experiments

We are interested in understanding the relationship between the melt structure and properties like the plateau modulus. In order to accomplish this we need a dimensionless way to compare the experimental data from many different chemical species to the simulation data from the bead spring polymer models. To render the $G_0^N$ values dimensionless, we need an energy scale and a length scale. As the dominant contribution to $G_0^N$ in these systems is believed to be entropic in origin, the choice of $k_B T$ as the energy scale suggests itself. However, there are essentially two independent length scales that characterize the local structure of the polymer melts. One of these length scales, the Kuhn length, $l_K$ [1] is a characteristic of single polymer chains and can be defined as the length of an individual step of a freely jointed chain with the same mean-square end-to-end distance $\langle R^2 \rangle = l_K L$ and contour length $L$ as the polymer chain under consideration. Polymer chains in melts obey random walk statistics between the maximum length given by the square root of the mean-square end-to-end distance $\langle R^2 \rangle$ and a characteristic minimum length scale given by $l_K$. Random walks do not densely fill space and so to reach melt density the polymer chains have to interpenetrate at large length scales. Locally however, due to the chain connectivity, most monomers will belong to the same chain. The length at which the polymers start to interpenetrate is given by the packing length, $p = (\rho_{\text{chain}} \langle R^2 \rangle)^{-1}$. The packing length can be visualized as the average distance one needs to traverse from any monomer before one reaches another monomer which belongs to a different chain. It is relevant to note that the product of the number density of chains, $\rho_{\text{chain}}$, and of $\langle R^2 \rangle$ is independent of chain length for a fixed monomer number density, $\rho$. Following the standard convention [29] based on the chemical structure of the polymers, we choose $l_K^p$ as the unit of length. With this choice, instead of $G_0^N$ we can consider the dimensionless quantity $G_0^N l_K^p / k_B T$. This quantity has to be a function of the only remaining dimensionless parameter: the ratio of Kuhn and packing length $l_K / p$. Analyzing data in this reduced manner provides the easiest way to compare rather different systems, at least in the case of the melts.

The available experimental data for dense melts are the result of a long term substantial effort [30,31] to synthesize monodisperse high-molecular weight samples for a wide variety of polymer species. Rheological measurements were performed on these samples and in many cases the $\langle R^2 \rangle$ values were determined using small angle neutron scattering. Refs. [30,31] provide the values for the plateau modulus, $G_0^N$, the mass density, $\rho_m$, the ratio of the mean-square end-to-end distance to the molecular weight of the polymer, $\langle R^2 \rangle / M$, and the packing length, $p = M / (\langle R^2 \rangle / \rho_m N_A)$, where $N_A$ is the Avogadro number. All the melt data points
obey the empirical relation \( G_N^0 = 0.00226 k_B T / p^3 \), indicated as the dashed line in Fig. 1. Before we discuss the method to calculate \( l_K \), it is worthwhile to note if the empirical relation is valid, then any choice for \( l_K \) will preserve the scaling relationship between \( G_N^0 \) and \( p \). The actual choice for \( l_K \) will determine the position of the data points in Fig. 1 but will just move them along the dashed line in the figure. To calculate \( l_K \) from the experimental data using \( l_K = (R^2)/(M/m_o)l_o \), we need a choice for the monomer mass, \( m_o \), and the monomer length, \( l_o \). In this work, we choose \( m_o \) and \( l_o \) corresponding to one average bond. For the average bond, \( m_o \) is calculated from the chemical structure, while \( l_o \) is taken to be the average of the lengths of all the backbone bonds in a repeat unit. The bond lengths for several chemical species are available in [19]. The procedure for the calculation of \( l_o \) implies that we have assumed the contour length of the polymer as the sum of all the bond lengths in the chain backbone and not the distance between the end points of the polymer chain in a fully trans zig-zag configuration. The procedure, however, can be ambiguous for some chemical species. For, e.g., BPA-PC has 1,4 disubstituted benzene rings in the backbone which raises the question of the value of the bond length that one should use to calculate \( l_K \). Here, we just use the distance between the two carbon atoms of the benzene ring that connect to the rest of the chain backbone as the corresponding bond length although any other reasonable alternative should suffice. All the melt data shown in the figure are tabulated in [25]. In the case of simulations, the characteristic lengths \( l_K \) and \( p \) can be determined directly from the polymer conformations in the equilibrated melt. Using the definition of the \( l_K \) in combination with \( L = (N - 1) b \) yields, \( l_K = (R^2)/(N - 1) b \). Similarly, the calculation of \( p \) follows directly from the definition. A more detailed discussion of the length scales, and the mapping can be found in [25].

The aforementioned mapping can be used to identify bead spring polymer models to individual chemical species. The standard model [26] with fully flexible polymer chains used in molecular dynamics simulations corresponds to \( l_K / p = 2.68 \). Among the available experimental data, the chemical species with the closest \( l_K / p \) value is natural rubber (cis-Polyisoprene) with \( l_K / p = 2.72 \). This suggests that the elastic properties of the usually studied bead spring polymer model corresponds most closely to that of natural rubber, the prototypical experimental system for elastic behavior, further validating the simulation model as an excellent choice for these studies.

5. Discussion

Having provided a method to determine the primitive paths for melt configurations of entangled bead-spring model polymers, we can now test the predictive power of the tube model. To this end, we use the standard expression [1,24]

\[
G_N^0 = \frac{4 k_B T}{5 pd_T} = \frac{4 \rho k_B T}{5 N_c},
\]

which relates the plateau modulus to the Kuhn length of the primitive path. The \( d_T \) values can be obtained from the contour length of the primitive path, \( L_{pp} \) (which is the sum of the lengths of all the backbone bonds of a chain averaged over all the chains in the melt) using \( d_T = (R^2)/L_{pp} \). For details see [24,25].
The results are listed in Table 2 and we already note excellent agreement in those cases, where we also determined the plateau modulus in simulations of stretched melts. Fig. 1 shows an explicit comparison of the dimensionless plateau moduli \( G_{\text{c}}^{(0)} \sigma^3 / k_B T \) of experimental systems and bead-spring model polymers with identical ratios \( I_K / p \). The good agreement of the two data sets confirms the insensitivity of entanglement effects to atomistic details and provides the necessary validation of our generic bead-spring models.

Besides assisting in the systematic development of rheological theories our results also open up new practical opportunities: While new algorithms allow the equilibration of the static structure of polymeric melts in (atomic) simulations [27,32,33], the determination of the time-dependent viscoelastic properties from atomistic molecular dynamics simulations is still out of question. However, using our approach it should also be possible to systematically link the atomic structure to dynamic simulations on primitive path level [3,10–14]. Since these ideas are neither restricted to monodisperse samples, nor to linear chain architectures, small deformations or equilibrium systems, they may help pave the way to the computer assisted development of materials with customized rheological properties.

Acknowledgements

Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy’s National Nuclear Security Administration under contract DE-AC04-94AL85000.

References


Table 2

<table>
<thead>
<tr>
<th>Structure</th>
<th>Melts</th>
<th>Solutions</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \rho/\sigma^3 )</td>
<td>I</td>
<td>II</td>
</tr>
<tr>
<td>0.85</td>
<td>0.85</td>
<td>0.85</td>
</tr>
<tr>
<td>( I_K/\sigma )</td>
<td>1.80</td>
<td>2.16</td>
</tr>
<tr>
<td>( p/\sigma )</td>
<td>0.68</td>
<td>0.56</td>
</tr>
</tbody>
</table>

Rheological simulations

| \( 10^3 G_{\text{c}}^{(0)} \sigma^3 / k_B T \) | 9.7 ± 1.4 | 23 ± 3 | 34 ± 14 | – | – |
| \( \rho/\sigma^3 \) | 0.85 | 0.85 | 0.85 | 0.85 | 0.85 | 0.231 |
| \( p/\sigma \) | 0.68 | 0.56 | 0.43 | 0.36 | 0.37 | 2.28 | 1.38 |

Path analysis

| \( \rho/\sigma^3 \) | 10.5 ± 0.1 | 9.7 ± 0.3 | 8.7 ± 0.1 | 8.46 ± 0.02 | 8.9 ± 0.7 | 33.8 ± 0.3 | 21.7 ± 2.7 |
| \( \rho/\sigma^3 \) | 10.5 ± 0.1 | 9.7 ± 0.3 | 8.7 ± 0.1 | 8.46 ± 0.02 | 8.9 ± 0.7 | 33.8 ± 0.3 | 21.7 ± 2.7 |
| \( \rho/\sigma^3 \) | 10.5 ± 0.1 | 9.7 ± 0.3 | 8.7 ± 0.1 | 8.46 ± 0.02 | 8.9 ± 0.7 | 33.8 ± 0.3 | 21.7 ± 2.7 |