Mesoscopic Simulations of Crosslinked Polymer Networks

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Abstract. A new methodology and the corresponding C++ code for mesoscopic simulations of elastomers are presented. The test system, crosslinked cis-1,4-polyisoprene, is simulated with a Brownian Dynamics/kinetic Monte Carlo algorithm as a dense liquid of soft, coarse-grained beads, each representing 5-10 Kuhn segments. From the thermodynamic point of view, the system is described by a Helmholtz free-energy containing contributions from entropic springs between successive beads along a chain, slip-springs representing entanglements between beads on different chains, and non-bonded interactions. The methodology is employed for the calculation of the stress relaxation function from simulations of several microseconds at equilibrium, as well as for the prediction of stress-strain curves of crosslinked polymer networks under deformation.

1. Introduction

Atomistic and mesoscopic simulations are widely employed for the study of polymer systems, since they provide insights that are complementary to the information derived from experiments. Although the full-atom or united-atom representations provide an accurate description of polymers, their long relaxation time constitutes a severe obstacle to such approaches, and thus the development of mesoscopic (or coarse-grained) models is needed to cover longer time and length scales. One of the main characteristics of polymer melts and polymer networks is the entanglement effect, arising due to the uncrossability of polymer chains, which gives rise to complicated topological constraints [1]-[4]. The tube model, which considers a single chain in a mean field, is one of the most significant models for the description of entangled polymers [5], [6]. The model in question has been refined by introducing additional relaxation mechanisms such as contour length fluctuation and constraint release [7]-[9]. Also, slip-link and slip-spring models [10]-[22] have been introduced for the description of entanglement effects. In slip-link models a number of discrete points restrict the lateral motion of the chains, whereas the chain can slide through them [10]-[12]. Likhtman introduced a single-chain slip-link model [15]. Alternatively the lateral motion of the chain is restricted by slip-springs connecting pairs of beads [21], with slip-springs being created or destroyed at chain ends. The additional attraction in melts or solutions that is induced by slip-springs can be exactly compensated by a pairwise repulsive potential. Both concepts, of slip-links and slip-springs, have been widely employed in mesoscopic multi-chain simulations for the computation of viscoelastic properties of polymer systems [16]-[22].

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Polymer networks are created by interconnection of polymer chains, with the connection points being named crosslinks. If the crosslinked polymer chains are highly flexible and mobile, the material exhibits very high deformability and practically complete recovery [23]. Materials exhibiting such properties are known as elastomers (or rubber-like materials), whereas their elastic behaviour is called rubber-like elasticity. Its interpretation may be achieved by a number of molecular theories [23], [24]. The concept of slip-links has also been successfully introduced in mesoscopic multi-chain simulations of crosslinked polymer networks [23]-[25]. Atomistic simulations are also possible; however, the time and length scales are rather limited in this approach [3], [28]-[31].

2. Models and Methods

A full description of the methodology and the corresponding C++ code will be provided in two upcoming studies; the first study refers to polymer melts [22], while the second one is focused on crosslinked polymer networks [32]. The polymer chains are considered as sequences of beads, which are connected via (entropic) springs, with each coarse-grained bead encompassing a large number of Kuhn segments (e.g 5-10). In the context of our methodology, a polymer network consists of three kinds of beads, i.e., end-points, internal nodal points and crosslinks. The temporal evolution of our polymer network configurations is generated by Brownian dynamics (BD) simulation in the high friction limit, while the entanglement effect is introduced through slip-springs connecting neighbouring polymer chains. A slip-spring is a spring whose ends change as the simulation time elapses. These springs may hop between neighbouring beads along the polymer chains and may also be created and destroyed at the end-points, with the total number of slips-springs remaining constant. All the aforementioned mechanisms are governed by a kinetic Monte Carlo scheme, with only one adjustable parameter ($v_{diff}$), obeying the condition of microscopic reversibility [22]. This adjustable parameter can be regarded as a rate constant for a slip-spring to overcome the free-energy barrier of its hopping along the polymer chain. Initial configurations of monodisperse polymer melts are obtained by a field-theory inspired Monte Carlo simulation of a soft, coarse-grained model, wherein chains are represented as freely jointed sequences of Kuhn segments subject to a coarse-grained Helfand Hamiltonian [33] which restrains the density from departing from its mean value anywhere in the system [34], [35]. Crosslinked polymer networks are created by applying crosslinking in the coarse-grained representation of the polymer melts. In particular, two algorithms for crosslinking are available in our C++ code, i.e., end-grafting and random-crosslinking. In the former procedure, all end-points of the polymer chains are connected with internal nodal points of other neighbouring polymer chains. When an internal nodal point is connected with an end-point, a trifunctional crosslink is created and the end is no longer available for interconnection with other polymer chains. The resultant polymer network is free of dangling chains, since there are no end-points. A graphical representation of end-grafting is provided in figure 1a. As far as the random-crosslinking is concerned, a number of prescribed points ($N_c$) are randomly dispersed in the simulation box. These points serve as the crosslinks for the polymer network and are always tetrafunctional, i.e., four strands emanate from each. In more detail, the procedure follows the scheme:

- A number of pairs of internal nodal points belonging to two neighboring chains are selected by a sorted list. The sorting criterion is the distance from the considered crosslink. Among these pairs the closest pair is chosen.
- The aforementioned pair is deleted, along with the four strands emanating from it.
- The two polymer chains are connected at the considered crosslink by creating four new strands.

This random crosslinking procedure is schematically presented in the figure 1b. In the context of our methodology, the system is fully described from a thermodynamic point of view by a Helmholtz free-energy containing three explicit terms:

$$ A = A_{\text{entropy springs}} + A_{\text{slip springs}} + A_{\text{lab}} $$

(1)
The first term is the contribution from the entropic springs, which connect successive beads along polymer chains, whereas the second term is included to account for the entanglement effect. In particular, the following equations are employed:

\begin{align}
    A_{\text{entropy springs}} &= \sum_{ij}^N \frac{3}{2} k_B T \frac{R^2_{ij}}{n_{ij} b^2} \\
    A_{\text{slip springs}} &= \sum_{kl}^N \frac{3k_B T}{2b^2_{kl}} (R_k - R_l)^2
\end{align}

The sum in eq. 2 is over all strands (or subchains) of the polymer melt or crosslinked polymer network whereas \( b \) and \( n_{ij} \) stand for the Kuhn length and the number of Kuhn segments in the strand, respectively. As far as the second contribution to the Helmholtz free-energy is concerned, it is computed as a sum over all slip-springs connecting two beads belonging to different neighbouring polymer chains. There is an additional parameter \( b_{sl} \) controlling the stiffness of the slip-spring, which can be set equal to the entanglement tube diameter of the considered polymer system. To deal with non-bonded interactions in the polymer network representation, an additional free energy contribution is included:

\[ A_{\text{non-bonded}} = \int d^3 r \ a_{\text{vol}}(\rho(r)) = \sum_{\text{cells}} V_{cell} a_{\text{vol}}(\rho_{\text{cell}}) \]

In Eq. (4), \( \rho(r) \) is the local density at a position \( r \) and \( a_{\text{vol}}(\rho) \) is a free energy density, which is obtained from the local density using an equation of state (EOS). In this study, we make use of the Sanchez-Lacombe EOS [36]. In the above equation, the volume integral is approximated as a sum over all cells of an orthogonal grid introduced in the primary simulation box. \( V_{\text{cell}} = L_x^\text{grid} L_y^\text{grid} L_z^\text{grid} \) is the volume of the rectangular parallelepiped defining the cell.

Figure 1. (a) Schematic representation of random crosslinking with all crosslinks being tetrafunctional. (b) End-grafting: all end-points are connected with internal beads of neighbouring polymer chains. The resultant polymer network is free of end-points and all crosslinks are trifunctional by construction.

3. Results
A polymer network of cis-PI is created by random-crosslinking which is applied on a monodisperse polymer melt containing 172 linear polymer chains. A chain consists of 53 beads with each bead corresponding to 10.21 Kuhn segments. This polymer network contains 300 crosslinks, with their initial spatial distribution being visualized in figure 2a, while the whole polymer network is depicted in figure 2b. The entanglement effect is introduced by 496 slip-springs and the adjustable parameter \( (v_{\text{diff}}) \) is chosen equal to 10.0s\(^{-1}\). Furthermore, an end-grafted polymer network was created from a cis-PI polymer melt containing 178 polymer chains. Each chain consists of 513 Kuhn segments. All BD simulations are conducted at constant temperature (\( T=400\text{K} \)) and volume with the integration time step
The undeformed polymer network is simulated in a cubic simulation box of edge length \( L = 30\text{nm} \) (\( L_x = L_y = L_z \)) and a cubic grid of \( 5^3 \) cells of the same size (\( N_{\text{cell/dim}} = 5 \)) is introduced for the computation of non-bonded interactions. Our analysis begins with the computation of some conformational properties. First, we want to check whether the unperturbed chain conformation of the initial configuration is retained during the BD simulations. To this end, the strand length distribution and the end-to-end distance distribution of the originally linear chains, which formed the network, are presented and compared with the corresponding theoretical predictions given by the following equations, respectively:

\[
P(r) = \left( \frac{3}{2 \pi n_{\text{Kuhn/strand}} b^2} \right)^{3/2} \exp \left( -\frac{3}{2} \frac{r^2}{n_{\text{Kuhn/strand}} b^2} \right) \quad (5)
\]

\[
P^{\text{end-to-end}}(r) = \left( \frac{3}{2 \pi n_{\text{Kuhn/strand}} n_{\text{strands/chain}} b^2} \right)^{3/2} \exp \left( -\frac{3}{2} \frac{r^2}{n_{\text{Kuhn/strand}} n_{\text{strands/chain}} b^2} \right) \quad (6)
\]

In the above sets of equations, \( b \) symbolizes the Kuhn length of the simulated polymer while \( n_{\text{Kuhn/strand}} \), \( n_{\text{strands/chain}} \) stand for the number of Kuhn segments per strand and the number of strands per polymer chain, respectively. Figures 3a and 3b show the strand-length and end-to-end-distance distributions, as computed from the simulation, along with the theoretical predictions of eqs 5 and 6. The excellent agreement demonstrates that the slip-spring-induced attraction is negligible for this choice of parameters. The non-bonded scheme adopted in the context of our methodology allows us to predict the isothermal compressibility of the polymer network. From the simulation point of view, the property in question is computed by the following fluctuation equation:

\[
\kappa_T = \frac{V \left\langle (\delta n_{\text{Kuhn/cell}})^2 \right\rangle}{k_B T \left\langle n_{\text{Kuhn/cell}} \right\rangle^2} \quad (7)
\]

The averages \( \left\langle \ldots \right\rangle \) are taken over all cells of the grid, which has been introduced in the primary simulation box due to the special nature of the non-bonded interactions. The averages in the numerator and denominator of eq 7 are the variance and the mean value of the number of Kuhn segments in each cell, respectively. The value calculated from eq 7 equals \( 1.278 \times 10^{-4} \text{ bar}^{-1} \) and is in very good agreement with the estimate from the Sanchez-Lacombe EOS (\( 1.270 \times 10^{-4} \)), which characterizes the long-wavelength behaviour. It is reminded that this is the underlying EOS of the non-bonded interactions (see also section 2). Regarding the computation of linear viscoelastic properties, the stress relaxation function, as defined in eq 8, is of great importance:

\[
G(t) = \frac{V}{3 k_B T} \left[ \left\langle \tau_{xy} (t_0 + t) \tau_{xy} (t_0) \right\rangle + \left\langle \tau_{xz} (t_0 + t) \tau_{xz} (t_0) \right\rangle + \left\langle \tau_{yz} (t_0 + t) \tau_{yz} (t_0) \right\rangle \right] \quad (8)
\]

\( V \) is the volume of the simulation box and the brackets indicate autocorrelation functions concerning the off-diagonal elements of the stress tensor \( \tau \). In the case of polymer melts, \( G(t) \) is employed for the computation of storage and loss moduli and the zero-shear-rate viscosity \([18],[19],[22],[37]\). The stress relaxation function of a crosslinked polymer network approaches a constant value at long times, and this value corresponds to the shear modulus of the rubbery material. A more accurate way of determining the shear modulus is through recording the stress-strain curve of a virtual elongation experiment at rather small deformations. The different rheological behavior between a polymer melt and a crosslinked polymer network is presented in figure 4a, in which the corresponding stress relaxation functions are provided. The black curve labelled \textit{Rouse} in the corresponding legend of the
figure refers to the stress relaxation function of the polymer melt, which was used for the end-grafting. Due to the absence of entanglements in our soft, coarse-grained model, the dynamics in a melt is well described by the well-known Rouse model [38]. In addition, the shear modulus \( G = (0.31 \pm 0.03) \text{bar} \) estimated by a virtual elongation experiment is also included. The stress relaxation function for the polymer network created by random-crosslinking is provided in figure 4b. The bigger noise, compared with that of the corresponding curve in figure 4a, is due to the presence of dangling chains, which is an inherent characteristic of this kind of crosslinking.

Figure 2. (a) Spatial distribution of 300 crosslinks in the simulation box after the implementation of random crosslinking. (b) Visualization of a polymer network created by random-crosslinking.

Figure 3. (a) Strand length distribution and (b) end-to-end distance distribution of the polymer chains comprising the polymer network created by random-crosslinking.
Figure 4. (a) Stress relaxation functions of a polymer network created by end-grafting (Rubber) and of a polymer melt without slip-springs (Rouse). (b) Stress relaxation function of a polymer network created by random-crosslinking.

4. Conclusions
A new methodology is presented in this study concerning the simulation of crosslinked polymer networks at the mesoscale. Such polymer systems are described from thermodynamic point of view by a Helmholtz free-energy including three terms: a term for entropic elasticity, another term for the entanglement effect, and a term for non-bonded interactions. The isothermal compressibility of the polymer network is predicted from equilibrium density fluctuations and is in very good agreement with the prediction estimated by the Sanchez-Lacombe EOS. Also, two conformational properties were investigated to establish that strands and chains are unperturbed by the presence of slip-springs and non-bonded interactions. Viscoelastic properties can be calculated through the computation of the stress relaxation function of undeformed polymer networks and through virtual elongation experiments.

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