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The dynamic response of isolated polybutadiene chains undergoing thermal retraction from extended conformations

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ABSTRACT

All-atom molecular dynamic simulations were performed on isolated polybutadiene chains to study the retraction velocity of a free end of an idealized network chain from extended conformations due to thermal collisions. We compare the snap-back velocity calculated from these simulations with experimental measurements on bulk rubber samples. Over a range of chain lengths, extension ratios and temperatures, we find that the average retraction velocity of a free end seen in the simulations is about two orders of magnitude less than the experimental value.

1. Introduction

Rubber elasticity has been a topic of enduring scientific fascination since the late eighteenth century when natural rubber was introduced to Europe. Classical rubber elasticity theory, which we shall refer to simply as "the theory", had its origins in the 1930s and it has remained an area of active research. It relates the retractive force in elastomers to the change in conformational entropy of the individual polymer chains that comprise the cross-linked network. As a piece of rubber is subjected to a tensile strain, the connecting polymer chains are uncoiled (or straightened) and their conformational entropy decreases. This leads to a change in the free energy given by $\Delta W = -T\Delta S$, where T is the absolute temperature and ΔS is the change in entropy due to extension. At constant temperature, the force required to stretch a chain (or a sample of bulk rubber) is the partial derivative of ΔW with respect to the strain axis (z), $f_z = -T\partial\Delta S/\partial z$. Derivations of elasticity relations based on this formula, as applied to various ideal network models, abound in the polymer physics literature [1–4]. They usually begin with a statistical analysis of a Markov walk in three dimensions. From this, a probability distribution of the number of possible (isolated) chain conformations, as a function of the end-to-end distance, R_e, is obtained. The entropy of the chain is then defined as the logarithm of the number of conformational states, as a function of R_e, multiplied by Boltzmann's constant. The putative mechanism that produces the retractive force is the tendency for the polymer chains to seek conformations with more probable (higher entropy) end-to-end distances in response to random thermal collisions. We shall refer to this process as 'thermal retraction'. In the derivation, the chain is assumed to be isolated but the theory is thought to apply to melt systems as well. Although predictions of the theory are considered to be in reasonable agreement with stress/strain measurements for some elastomers [2,5], discrepancies with experiment are also acknowledged [2]. Devising modifications to the theory (within the paradigm of conformational entropy changes) to resolve these disagreements continues to be an active area of investigation.

Because the theory is formulated from within the framework of thermodynamics, it does not explicitly include time, and it is not possible to apply it to kinetic processes. For example, the theory says nothing about how fast a polymer chain should retract from an extended conformation when one end is released, a situation that occurs when a stretched elastomer is suddenly released from tension. It is obvious that the retraction velocity of the network chains is a consequence of the elasticity and must be at least as fast as the bulk material. Experiments performed as early as 1944 [6–10,38] show that the retraction velocity of a rubber sample, abruptly released from tension, can be as high as 100 m/s. Furthermore, these experiments clearly establish that the retraction propagates as a wave along the sample, starting at the tip, with points along the sample remaining at rest until the retraction wave has passed. Several papers have presented models to describe this process [7,9–12]. Stevenson and Thomas [12] studied the crack (or tear) propagation in a rubber sheet under bi-axial strain by

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observing a balloon as it popped. Using the conservation of volume and the relationship between the local true stress and momentum change across the relaxation region, they derived expressions for the velocity of the relaxation wave v, and the tip velocity u, as a function of the extension ratio, λ. Since they were concerned principally with crack propagation, their model assumed that the relaxation occurred only along the direction normal to the tear axis, but the derivation is easily modified for the case of pure tensile strain. The relationship between the retraction wave velocity and the tip velocity is then:

$$v = \frac{u}{(1 - 1/\lambda)}. \tag{1}$$

This relationship can also be obtained from the following observation: in the same time that the tip moves a distance $(\lambda-1)L_o$, the retraction wave propagates a distance λL_o, where L_o is the unstrained length of the sample. The expression diverges at an extension ratio of one, i.e., no extension, and approaches unity for large extensions. At an extension ratio of 2.0 (100% strain), the unloading wave velocity is about 1.5 times the tip velocity; for a strain of 40%, the factor is about 4. An obvious question is: can the random thermal motions of a polymer chain produce thermal retraction on a timescale comparable to what is observed in the experiments, i.e., is thermal retraction a viable mechanism for elasticity? Answering this question is the motivation for the present study.

2. Molecular dynamics simulation background and methodology

Molecular dynamic (MD) simulations have proven to be a valuable tool in the study of polymer melts and networks [13–31]. A number of inter-atomic potentials have been used that offer varying compromises between physical fidelity and numerical efficiency to allow the simulation of ever larger polymer systems. One of the earliest and simplest potentials is the bead and spring (freely-jointed-chain) model combined with a Lennard–Jones term to mimic an inter-atomic Van der Waals' interaction. Together, these enforce a finite chain extensibility and a robust excluded volume constraint. The system is coupled to a heat bath to maintain constant temperature with a velocity dependent friction term and a random force. Although the method is computationally efficient, it contains very little molecular specificity, making comparison with experiment difficult. It has been used to study the effect of entanglements [15,20,27], the kinetics and relaxation of melts and networks [14,16,25,28], the role of ambient pressure on tensile stress [13], the effect of strain history and cross-linking on permanent set [24,26] and used to sample the single-chain form factor to compute a scattering function [28]. Better accuracy is obtained with united-atom potentials, that lump the hydrogen atoms and methyl groups with polymer backbone units but still contain realistic harmonic functions for bond stretches, bends and torsional rotations. While providing more molecular specificity than bead and spring models, they are not as faithful as all-atom potentials. United-atom potentials have been used to study the structure and relaxation of polydimethylsiloxane networks [22] and polybutadiene [29]. MD simulations using united-atom potentials have also been used by Gao and Weiner [17] to study the effect of non-bond interactions on the tensile stress of a generic polymer network and by Yang et al. [30,31] to model the glass transition in polyethylene melts. A network model that coarse-grains at the level of chain segments has been used to study the effect of cross-linking on the tensile stress [23]. Dimitrakopoulos [32] studied the configuration relaxation of freely rotating chains subject to Brownian dynamics using a discretized version of the flexible wormlike chain model. Starting with initially straight chain configurations, the relaxation of the stress tensor was computed as a function of a dimensionless time.

This work differs from previous studies in several important aspects. (1) We have used MD simulations to study the retraction of polybutadiene chains from highly extended conformations and (2) we used an all-atom potential. To our knowledge, these are the first simulations that elucidate the retraction velocity of a polymer chain in response to abrupt release of one end. The details of our simulation are as follows. Isolated (1,4)polybutadiene chains containing 96, 148 and 200 carbon atoms were constructed with random (0° or 180°) torsion angles. To facilitate locating the chain ends visually and computationally, the chains were terminated with amine groups (NH_2). Since the theory explicitly assumes that the network chains are functionally isolated when the conformational probability distribution is computed, we believe that studying an isolated chain is the most relevant test of that theory. The butene backbone units were isotactic, with either all *cis* (denoted by the suffix 'c') or all *trans* conformations (denoted by the suffix 't'). This procedure yielded initial end-to-end distances of ~84% and 69%, of full extension for the chains composed of all *trans* and all *cis* butene units, respectively. Simulations were performed with a commercial software package, Accelrys/Materials Studio [33] with the compass [34] all-atom force field, using group-based summations for the non-bond interactions. The simulations were run out to 20 ns, with 1 fs time steps, at three temperatures: 150 K, 298 K and 600 K. As suggested by the experiments, we simulated the retraction of a network chain, in response to an unloading wave, by keeping one end fixed during the MD run. The specified temperature was maintained by employing an Andersen thermostat [35]. Five statistically independent simulations for each chain length/temperature combination were performed and the chain end-to-end distance (R_e), temperature, potential energy and the radius of gyration (R_g) were recorded every 0.1 ns. Each such simulation used the same starting chain conformation. Average values for the retraction trajectory (R_e) were computed for each set of simulations. This procedure yielded acceptably smooth trajectories of R_e.

With regard to the chain lengths that we chose, we are not aware of any experimental determinations of the average chain length between network cross-links in rubber. Although the molecular weight of the rubber molecules is typically quite large (300,000 Da, or more), it is only the chain length between network cross-links that the theory considers. Fits of the classical theory to experimental tensile stress/strain data [2], for extensions up to ~7, imply that the chains must contain over 400 backbone carbon atoms. As will be shown below, the retraction velocities observed were essentially independent of chain length; if anything, the trend was for longer chains to exhibit slightly lower retraction velocities. We believe that the chain lengths and starting conformations chosen for this study are relevant to the experiments to which we compare.

Fig. 1 shows three conformations over the course of a simulation showing that retraction progresses locally (starting at the free end), rather than continuously all along the chain. Fig. 2 shows five statistically independent R_e trajectories and their average as a function of simulation time for a polybutadiene(t) chain containing 148-carbon atoms, 84% extended at 298 K. Also shown is the calculated radius of gyration, R_g, for the 84% case and the R_e trajectory for 50% initial extension. Complete retraction is most evident in the radius of gyration which approaches a constant value at $t \sim 12$ ns. Fig. 3 shows the velocity of the free end, computed as the numerical derivative of R_e with respect to time. As a viewing aid, the figure also shows the data after being smoothed with a Stineman function using a commercial software-plotting package

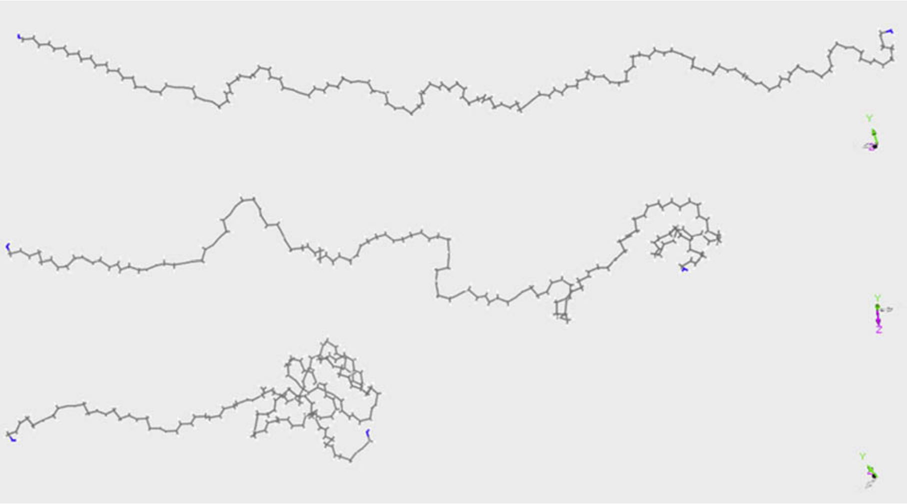

Fig. 1. Three retraction conformations for 148-carbon chain (starting at 84% extension, $T = 298$ K) at times 0 (top), 2 ns (middle) and 10 ns (bottom). Note that the thermal retraction proceeds from the free end.

[36]. There is an initial velocity spike of ~5 m/s but after 5 ns, the velocity falls below 1 m/s. The average velocity computed over the time interval 0 to12 ns is 1.03 m/s. Because the chain was isolated, the Van der Waals' and electrostatic forces between proximate atoms along the chain were not shielded.

The R_e trajectory for a 148-carbon chain (averaged over 5 independent runs) at three temperatures, 150 K, 298 K and 600 K, is shown in Fig. 4. For each MD run, the same starting conformation was used. Since the differences between the three cases are within the statistical variation of the 5 independent runs at each temperature, we conclude that the retraction rate is not strongly influenced by temperature. The average velocity between $t = 0$ and 12 ns is 1.03 m/s. We also performed MD simulations at 298 K for chains constructed from *trans* butadiene units containing 96 and 200 carbon atoms. The end-to-end distance vs. time for these cases is shown in Fig. 5. The 148-carbon chain results are also included for comparison. The averaging times and velocities were (7 ns, 1.04 m/s) for the 96-carbon chain and (18 ns, 0.93 m/s) for the 200-carbon chain. We also performed MD simulations for two other cases (not shown) at 298 K: (1) a 148-carbon chain constructed from butadiene units in the *cis* conformation and (2), a linear 148-carbon chain constructed with *trans* butadiene units. The conformation for the second case was fully extended commensurate with all bond lengths and angles nominally at equilibrium values. For both of these cases, we observed essentially the same retraction behavior. The averaging times and velocities were 8 ns, 1.29 m/s and 18 ns, 0.80 m/s, respectively, for these cases.

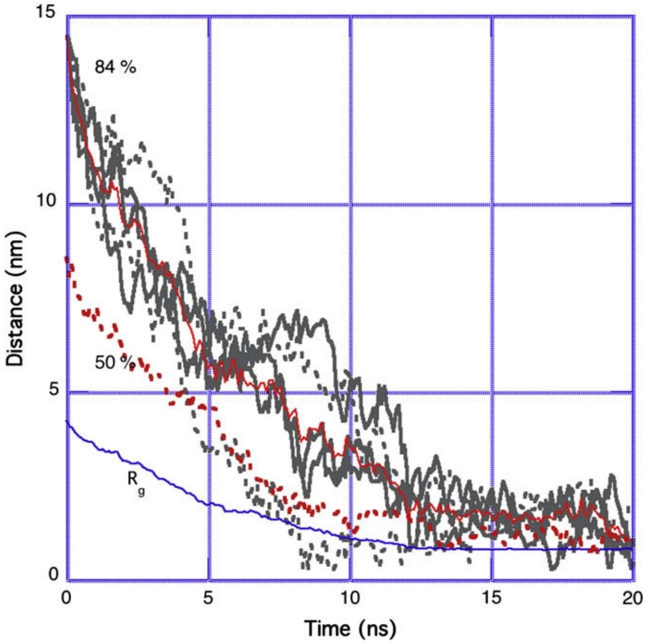

Fig. 2. End-to-end distance (R_e) vs. time for 148-carbon chain (84% extension) for 5 statistically independent MD runs (gray) and average over 5 runs (solid red). The averaged radius of gyration (R_g) for 84% extension is shown as solid blue and the R_e trajectory for 50% extension as dotted red. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.).

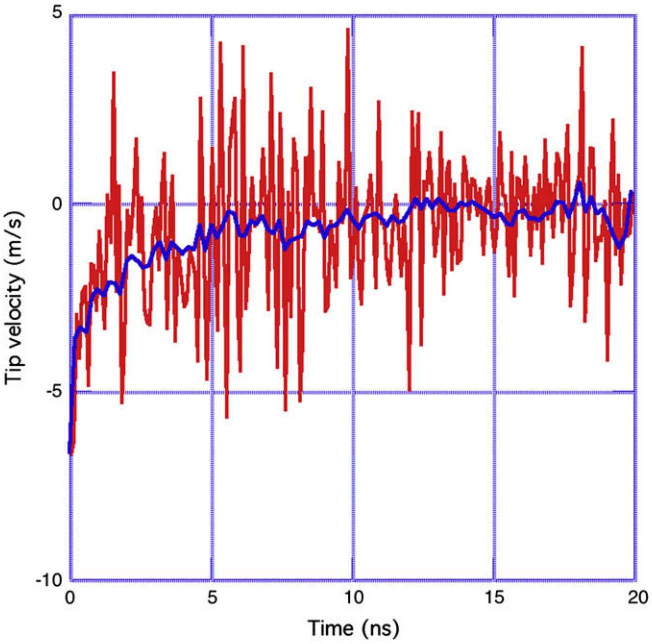

Fig. 3. Radial velocity of the free end with respect to fixed end computed as the numerical derivative of the end-to-end distance averaged over 5 MD runs (solid red), and numerically smoothed data (solid blue). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.).

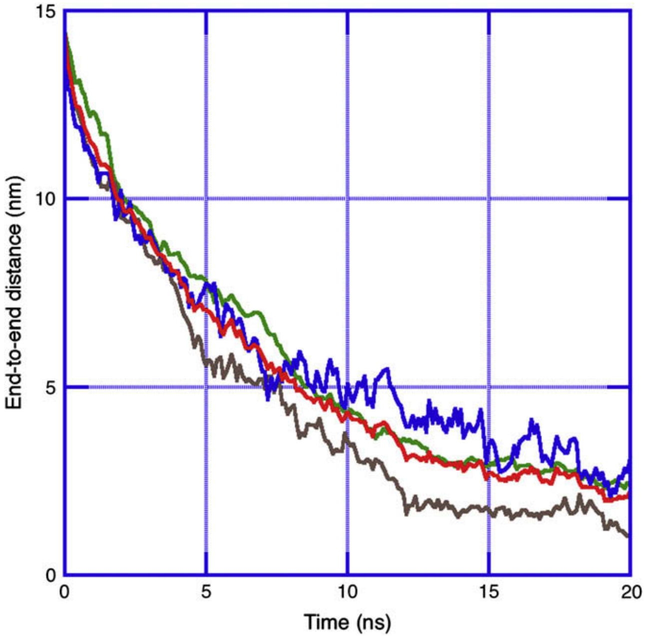

Fig. 4. End-to-end distance vs. time for 148-carbon chain at three temperatures, 150 K (blue), 298 K (tan), 600 K (green) and average (red). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.).

3. Discussion

Mrowca et al. [6,7,38] measured the retraction velocity of hevea and butyl gum rubber samples, for extension factors up to 4.5. Small styli, affixed to both the end and the midpoint of the samples, were maintained in contact with a rapidly rotating drum. The styli recorded the tip and midpoint positions of the sample during retraction with sub-millisecond resolution. Their data [7] show that the tip moves with approximately constant velocity and that the midpoint of the sample does not begin to move until the sample has contracted to ~ one half of its extended length. They repeated the experiment using a high-speed camera with stroboscopic illumination, confirming the stylus measurements. The velocities were found to be proportional to the maximum strain, with values up to 90 m/s. From Stevenson's model (as modified above), we know that the unloading wave must propagate faster than the tip velocity and it is the unloading wave velocity that is relevant to the polymer chain retraction velocity. For strains below 50%, the wave propagation model predicts unloading velocities several times greater.

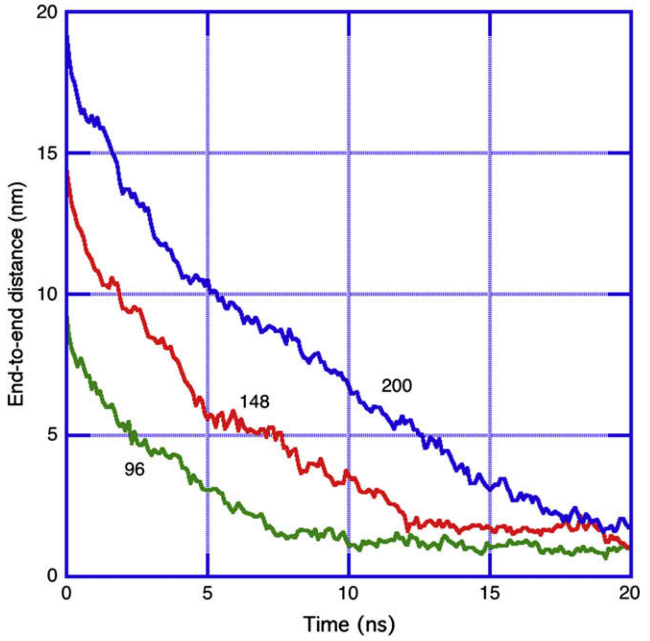

Fig. 5. End-to-end distance (averaged over 5 MD runs) vs. time for three chain lengths, 96-carbons (green), 148-carbons (red) and 200-carbons (blue). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.).

We acknowledge several issues and deficiencies with our simulations: Because we wished to study the thermal retraction of chains that are relevant to the assumptions of the theory, we focused on isolated chains. A more realistic system would include chains from the surrounding melt, and this would certainly affect the retraction process. But, including surrounding chains would tend to decrease the mobility of the chains and reduce their ability to assume more contracted conformations, i.e., reduce the retraction velocity. It would also tend to shield Van der Waals' and electrostatic interactions between the atoms on the same chain, further reducing the rate of retraction of the chain. The net result of neglecting surrounding material in the simulation leads to an overestimation of the tip velocity, probably by several orders of magnitude. Another deficiency in our simulation is that the end of the chain was free rather than being connected to other network chains via a cross-linking node. This would, too, would cause the observed retraction velocity to be artificially high, perhaps by another order of magnitude. One aspect of the simulations that could tend to reduce the contraction velocity is the energy barrier in the force field for transitions between different torsional conformations. If the barrier in the classical potentials were too large, then the retraction rate seen in the simulations would be artificially low. We examined the energy landscape in the force field for torsional transitions and found that the barrier for rotations about a carbon–carbon single bond, with adjacent single bonds, is about 2.9 kcal/mole. This is actually somewhat lower than the value obtained from quantum chemistry calculations [37] of 3.54 kcal/mole, and this error would also cause the retraction rate that we observed to be slightly high. We do not believe that there is much uncertainty in this barrier since the quantum chemistry calculations agree with values obtained from experiments to within about 10%.

We do not know the range or distribution of the chain extension ratios that were present in the samples reported in the snap-back experiments cited. Presumably, the samples were stretched near their breaking points so it is reasonable to assume that some if not most of the chains were highly extended and these would make the highest contribution to the stress and retraction behavior (according to the theory). Accordingly, we chose to concentrate on high extension ratios in our simulations. We do not claim that the initial chain extension ratios that we used in our simulations are related to the initial extension ratio in the experiments. We argue that comparisons between our results and these experiments are relevant to elasticity theory for the following reasons: (1) Elasticity theory assumes that the elastic force arises solely from the behavior of individual, non-interacting chains in response to random thermal interactions. The contraction of extended chains is assumed to be due to the tendency of the molecules to assume conformations with higher probability end-to-end distances. (2) The experiments clearly establish that the retraction propagates as a relaxation wave through the material, strongly suggesting that the relaxation process is local. It is not unreasonable to assume that it is operative at the individual chain level. (3) Points 1 and 2 suggest that a macroscopic rubber sample cannot contract faster than its constituent network chains.

4. Conclusions

Using all-atom molecular dynamics, we have simulated the thermal retraction of isolated polybutadiene chains with one end fixed, and compared the retraction velocity with experiment. To the extent that the inter-atomic potentials and the thermostat used in the molecular dynamic simulations accurately describe polybutadiene, our results show that the retraction velocity of a chain free end is between two and three orders of magnitude slower than what is observed experimentally in bulk rubber samples. The average velocity is essentially independent of chain length, extension ratio and temperature. Improving the simulation by including surrounding polymer chains would not only violate the strict assumptions of classical elasticity theory but also exacerbate the disagreement, probably by several orders of magnitude. Our simulations are relevant to classical elasticity theory because it is based on the conformational entropy of isolated chains. Comparisons to snap-back experiments are valid because: (1) the snap-back velocity is a consequence of the elasticity of the chains and, (2) experiments show that the relaxation occurs locally. Because the disagreement between simulation and experiment is so large, we conclude that the thermal retraction of network chains cannot be the sole mechanism for rubber elasticity; other mechanisms must also contribute. At this time, we do not know what these mechanisms might be. Further experimental and theoretical studies may provide additional insight, but speculation on possible mechanisms is not appropriate for this paper. In any case, a successful theory of rubber elasticity must also be able to account for the very high retraction velocities observed in experiments.

Acknowledgments

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