Stress Relaxation in Entangled Melts of Unlinked Ring Polymers

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Stress relaxation in unlinked ring polymer melts poses an important challenge to our theoretical understanding of entangled polymer dynamics. Recent experiments on entangled unlinked ring melts show power-law stress relaxation with no hint of a rubbery plateau, usually the hallmark of entangled polymers. Here we present a theory for stress relaxation in rings analogous to the successful approach for star polymers. We augment our theory with mesoscale Monte Carlo dynamics simulations of equivalent "lattice animal" configurations. We find a stress relaxation function $G(t) \sim t^{-\alpha}$ with $\alpha \approx 1/2$ consistent with experiment, emerging ultimately from the disparate relaxation times of more- and less-central portions of ring conformations.

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Over the past three decades, the concept of the tube as a single-chain approximation to uncrossability constraints [1,2], coupled with mechanisms of reptation, contour-length fluctuations, and arm retraction for chain segments to explore new paths, have led to quantitatively accurate theories of stress relaxation in linear and branched polymers. By coming to grips with the progression of experimental systems from entangled melts of monodisperse linear chains [3,4], to polydisperse linear chains, star polymers [5], star-linear blends [6], and more complex branched architectures [7], we greatly increased our understanding of how entangled polymers move.

In the context of that success, entangled melts of unlinked ring polymers present a vexing challenge, testing the depth of our understanding of entanglement. How do such ring polymers move, and even what conformations they adopt, have been longstanding theoretical challenges. These systems present formidable experimental challenges as well, because heroic measures are required to make reliably closed rings, with synthesis carried out in very dilute solution to avoid links. Such materials are not likely ever to be commercially relevant.

However, recent careful measurements of dynamical response $G(\omega)$ have been performed on polystyrene (PS) rings of molecular weight 198 kg/mol, corresponding to about 15 times the entanglement mass M_e [8]. The sample shows a power-law behavior with $G'(\omega)$ and $G''(\omega)$ both scaling as $\omega^{1/2}$, corresponding to a power-law stress relaxation function $G(t)$ scaling as $t^{-1/2}$.

The frequency-dependent elastic modulus $G'(\omega)$ showed no hint of a plateau, which ordinarily is a hallmark of well-entangled chains for both linear and branched polymers, because of the near-absence of stress relaxation mechanisms over a broad frequency range, between the time scale τ_e at which chain segments first explore the local tube, and the much longer relaxation time scales for reptation or arm retraction.

Multiple attempts have been made to construct a theory for stress relaxation in unlinked rings [9,10]. Even the static conformations of a melt of rings are not completely resolved [11]. It is relatively unambiguous that a single unlinked ring in network of obstacles (e.g., a lightly cross-linked gel, without dangling chain ends) should adopt "lattice animal" configurations, in which each "bond" in the animal represents a doubled polymer strand, of length the tube diameter a, and total mass $2N_e$. (See Fig. 1.) The ultimate scaling of R_g for large molecular weight unlinked rings in a melt is most likely compact collapsed chains; however, there exists a broad crossover region where conformations something like lattice animals are observed in molecular dynamics simulation. In this work we assume rings in a melt adopt lattice animal configurations (discussed further, below).

The most recent theoretical account of stress relaxation in rings gives exponents in reasonable agreement with experiment [8,10]. However, the treatment is unsatisfying in that the argument is of a completely different form than those used successfully to describe stress relaxation in

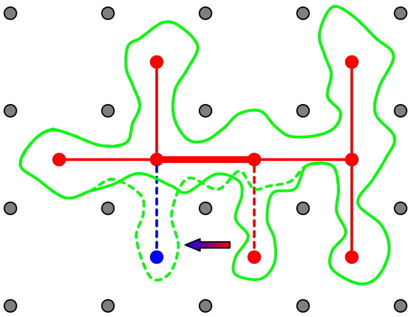

FIG. 1 (color online). A ring polymer in a network of fixed obstacles, abstracted as a lattice animal. Ring moves by retracting a loop (dashed) and extending it nearby (dashed), changing centrality of neighboring bond (thick).

linear and branched polymers. The object of this Letter is to describe stress relaxation in a melt of unlinked rings in the same manner as for linear and branched polymers.

Stress relaxation in entangled polymers, whether linear or branched, has been described in terms of the survival probability for tube segments [12]. The linear viscoelastic response is determined by the time-dependent stress relaxation $G(t)$ following a small step strain. At time t after a step strain, a fraction $\psi(t)$ of tube segments survive, some having been vacated by whatever random motions of the chain its architecture permits. For a polymer in a network of fixed obstacles, $\psi(t)$ is also the fraction of the initial stress that survives at time t. For an entangled melt of identical polymers, the dynamic dilution approximation [13] (equivalent to double reptation for entangled linear polymers) [14,15] posits that the stress relaxation behaves as a progressively diluted network, which leads to reasonable quantitative predictions for stress relaxation.

For a linear polymer, $\psi(t)$ is determined mainly by reptation, with segments in the center of the chain surviving longer because the chain must reptate farther to vacate these segments. For star polymers, which cannot reptate, $\psi(t)$ is controlled by arm retraction, with segments far from the free end surviving much longer because deep retractions face an entropic barrier. We seek to describe the dynamics of ring polymers in terms of $\psi(t)$ as well.

Note that the local motion of ring polymers in a network of obstacles is again very different from either linear or star polymers. The ring polymer, represented as a lattice animal, consists of a treelike structure of nodes connected by bonds. The fundamental random motions available to ring polymers are events in which a "leaf" bond (bond terminating in a leaf node) retracts from one portion of tube, and reemerges from a neighboring node. (See Fig. 1). By a succession of such moves, eventually a lattice animal can completely renew its configuration.

To analyze the survival probability for bonds in a lattice animal, consider a particular given bond (e.g., the thick red bond in Fig. 1). Every bond divides the animal into left and right subtrees, of mass m and $N - m$, where N is the total mass (number of nodes) of the animal. For this bond to be vacated by the polymer, the smaller of the two subtrees must completely "evaporate" across the given bond, into the larger subtree on the other side of the bond. This evaporation takes place as leaves from the smaller subtree diffuse randomly across the given bond.

This motivates the definition of "centrality" c of a bond, defined as $c = \mathrm{Min}(m, N - m)$. If c is small, we expect relaxation to be rapid. We can find the probability distribution $P(c)$ analytically for randomly constructed lattice animals, representing the animals on a Bethe lattice for simplicity (to preclude "collisions" between segments). From simple counting arguments [16], the number of possible subtrees $s(m)$ of m nodes is

$$s(m) = \frac{[(f-1)m]!}{m![(f-2)m+1]!}, \tag{1}$$

where f is the coordination number of the lattice.

Then, the probability $P(c)$ of a bond having centrality c is equal to the probability that the left subtree has c nodes and the right subtree $N - c$ nodes:

$$P(c) = \frac{s(c)s(N-c)}{\sum s(c)s(N-c)} \approx \sqrt{\frac{(f-1)}{8\pi(f-2)}}\left(\frac{N}{c(N-c)}\right)^{3/2}. \tag{2}$$

Most bonds are of low centrality, and relax quickly.

To find the typical relaxation time $\tau(c)$ for bonds of centrality c, we analyze the dynamics of a given bond, following the (left) subtree mass m as a "reaction coordinate." Roughly speaking, m diffuses randomly as leaves from the two subtrees diffuse back and forth across the given bond. When m reaches either zero or N, the bond is vacated and its stress contribution relaxed. The situation is similar to a random walk on a $1d$ mesa, in which the walker (a sunstruck tourist?) meets his demise if he reaches either end of the mesa.

Extending the metaphor, if we put up guardrails at the ends of the mesa (to protect the tourists), the equilibrium distribution of the random walkers must reproduce $P(c)$. This implies the random walk is carried out in an effective entropic potential, $\beta U(c) = -\log P(c)$. The mesa, rather than being completely flat, is logarithmically sloping near the ends (more like Ayers' Rock than Devil's Tower). This entropic potential is strongly analogous to that governing arm retraction, except that in the present case, the potential actually favors relaxation, as it biases bonds towards low, quickly-relaxing centrality values.

It turns out that the stochastic dynamics of the centrality of a given bond is not quite simple diffusion. We have carried out Monte Carlo simulations of the dynamics of a lattice animal on a Bethe lattice, with moves corresponding to elementary hops of leaf bonds. The centrality is observed to undergo non-Fickian diffusion for short to intermediate displacements, with the variance growing as $t^{3/4}$, regardless of the initial centrality. (See Fig. 2.)

To investigate how the centrality diffuses, we gathered statistics on the rate $R(\Delta t, k)$ of "first crossings" at time delay Δt for leaves initially k generations removed from one end of a given high-centrality bond B. ("k generations removed" means "k steps away along the shortest path".) These results were obtained by "watching the movie backwards"; that is, by recording the time a particular bond-as-leaf B' hopped from the right side of the given bond B to the left (say), and noting how many generations removed the bond B' was from B while still in the left subtree, at later times.

By summing with respect to k, we obtain $R(\Delta t)$, the rate of first crossings of all leaf bonds over a given high-centrality bond. Summing $R(\Delta t)$ with respect to Δt gives $C(\Delta t)$, the total number of first crossings over a given

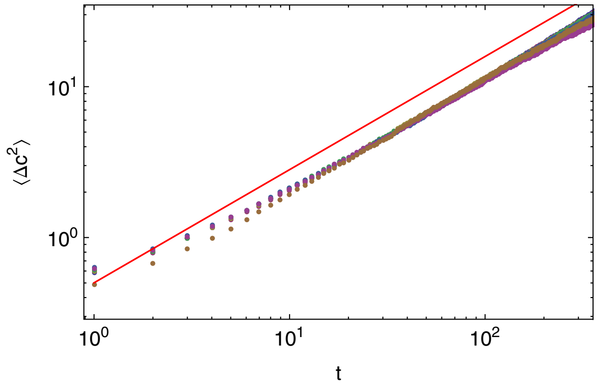

FIG. 2 (color online). Mean-square centrality displacement versus time, for starting centrality values $c = 20, 30, \ldots, 90$ on a lattice animal of 200 bonds. Line is slope 0.75.

high-centrality bond up to time delay Δt. $R(\Delta t)$ is found to be a power law, $\Delta t^{0.75\text{--}0.8}$. This is consistent with non-Fickian diffusion of centrality, because mass that is able to arrive at the given bond within time delay Δt will be found randomly on either side of the bond; thus $\langle\Delta c^2\rangle$ should scale the same way as $R(\Delta t)$.

We can understand the behavior more microscopically by finding out how much mass $M(k)$ there is within k generations of a given high-centrality bond. We then argue that the variance in centrality grows with time as the accessible mass $M(k(\tau))$, in which $\tau(k) \sim k^2$ is the typical diffusive arrival time for random walkers to traverse a generational distance of order k.

For this purpose, static Monte Carlo studies were performed in which lattice animals were randomly constructed [by means equivalent to the counting arguments leading to $P(m)$], and the mass $M(k)$ counted starting from high-centrality bonds. The results are well described by $M(k) \sim k^a$ with a ranging from 1.5 to 1.7 for lattice animals of 100–1600 bonds. (See Fig. 3.) (We do not have an analytical argument for this exponent, which evidently has not quite reached its asymptotic value even for animals as large as 1600 bonds.)

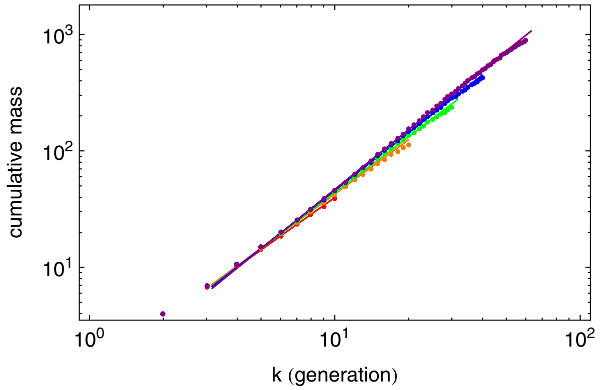

FIG. 3 (color online). Average total mass within k generations of a given high-centrality bond, for lattice animals with number of bonds $N = 100$ (lowest data), 200, 400, 800, 1600 (highest data). Corresponding slopes are 1.5, 1.55, 1.6, 1.65, 1.7.

By the arguments above, we then expect $\langle\Delta c^2\rangle$ to grow as $t^{a/2}$, Thus for lattice animals of 50–200 bonds for which Monte Carlo dynamical simulations were performed, we expect $\langle\Delta c^2\rangle \sim t^b$ with $b = 0.75\text{--}0.8$, as indeed we observed. The non-Fickian behavior for centrality diffusion then results from the expanding geometry of the lattice animal in the vicinity of high-centrality bonds, which controls the amount of accessible mass that can diffuse across a given bond. (Because a large lattice animal is self-similar, a scale-invariant power law is expected.)

Corresponding to this power-law behavior, we expect the maximum relaxation time $\tau(N)$ to scale as the time required for the centrality to diffuse a "distance" of order N, which implies $\tau(N) \sim N^{2/b\approx 8/3}$. This argument is consistent with our Monte Carlo results for the longest relaxation times as a function of lattice animal size.

Using the ingredients of a known entropic potential $U(c)$ and a known power-law short-time diffusive behavior for centrality, we can compute the mean first-passage time $\tau(c)$ for a bond of centrality c to relax, by applying the same methods we used for arm retraction in star polymers. To make this work, we temporarily redefine time as $t' = t^b$, so that centrality diffusion looks Fickian. Then we can compute the "mean first passage τ'", by standard methods, with the result

$$D\bar{\tau}'(c) = \frac{I_+}{I}\int_0^c dc' e^{-U(c')}\int_0^{c'} dc'' e^{U(c'')} + \frac{I_-}{I} \times \int_c^N dc' e^{-U(c')}\int_{c'}^N dc'' e^{U(c'')}, \tag{3}$$

with $I_- = \int_0^c dc' e^{U(c')}$, $I_+ = \int_c^N dc' e^{U(c')}$, and $I = I_- + I_+$. Finally, we invert the relationship $\bar{\tau}' = \bar{\tau}^b$, to obtain predictions for the desired mean first-passage time $\tau(c)$. Results are shown in Fig. 4 as the solid curve.

We can compare the above prediction to Monte Carlo simulation results for the average lifetime of bonds of

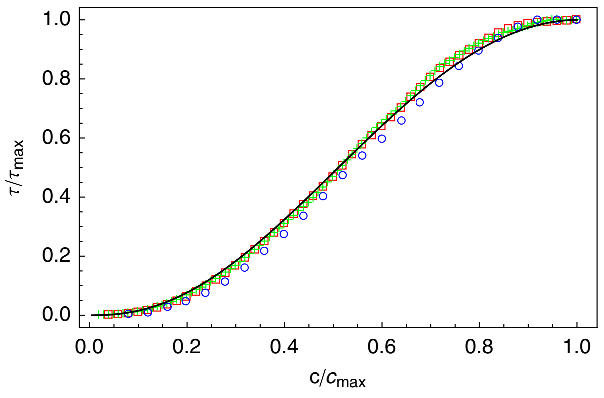

FIG. 4 (color online). Mean bond lifetime $\tau(c)$ vs centrality c, for animals with number of bonds $N = 50$ (circles), 100 (squares), 200 (stars), compared to theory (curve).

centrality c. These results were again obtained by time-reversing the simulation trajectory, recording the time when a given leaf bond B first becomes ''buried'' by some other bond, thus increasing its centrality, and noting the centrality of B at later times (interpreted as ''earlier'' times in the time-reversed trajectory). The results are shown in a master plot in Fig. 4 for animals of total mass 50, 100, and 200 bonds, in which lifetimes have been scaled by the maximum lifetime, and centralities by the maximum centrality.

To this point, our discussion has treated the relaxation of a single ring in a fixed network of entanglements. Whereas, in a melt of unlinked rings, the entanglement network is itself relaxing by the same mechanisms that relax the conformations of a given ring. Melts of linear and branched polymers were also first treated by considering a single chain in a fixed network. For monodisperse linear polymers, which relax predominately by reptation, on approximately a single time scale, corrections to the fixed network picture are modest. For polydisperse linear melts or star polymers, both of which have a broad distribution of relaxation times, the effect is more severe.

Fortunately, a simple approach has been developed to describe the effects of a relaxing entanglement network, known as dynamic dilution (for branched polymers) or double reptation (for polydisperse linear chains). The residual stress a time t after a step strain is modeled as supported by a diluted entanglement network, diluted by removal of faster-relaxing material. The general result is

$$G(t) = -\int d\tau \left(\frac{\partial G}{\partial \Phi}\right)\left(\frac{\partial \Phi}{\partial \tau}\right) e^{-t/\tau}, \tag{4}$$

in which $\Phi(\tau)$ is the entanglement fraction or fraction of as-yet unrelaxed material a time τ after a step strain. Dilution of the transient network modulus is represented by taking $G(\Phi) = G_0\Phi^{\alpha}$, with α the ''dilution exponent'', given by various arguments as between 2 and 7/3 [17]. For ring polymers, we express Φ as $\Phi(c) = \int_c^{N/2} dc' P(c')$.

With $\tau(c)$ approximated as a power law $c^{\beta \approx 8/3}$ up to the maximum centrality, we can extract from Eq. (4) a power-law dependence for $G(t)$ of $t^{-\alpha/(2\beta)}$; carrying this result through to $G(\omega)$ results in $G'(\omega)$ and $G''(\omega)$ scaling as $\omega^{\alpha/(2\beta)\approx 7/16}$, consistent with recent experiments. Note that these rings are only about $15M_e$, which means about 7–8 bonds in the lattice animal, far from asymptotically large. However, the general result of power-law relaxation from the present theory resolves how an entangled system of ring polymers can nonetheless show no rubbery plateau, as a consequence of the power-law distribution of relaxation times $\tau(c)$ and power-law distribution of centrality values $P(c)$.

In conclusion, we have presented a theory of stress relaxation in melts of unlinked polymers that is strongly analogous to earlier successful descriptions of stress relaxation in linear and branched polymers. Our theory relies on local random motion of small unentangled loops, resulting in power-law diffusion of the centrality c of bonds in an entropic potential. From this, we compute the mean survival time $\tau(c)$ using first-passage time techniques, just as in the theory of stress relaxation in star polymers. We use dynamic dilution to connect predictions for a single unlinked ring in a network of obstacles to the behavior of a melt of unlinked rings. We find power-law stress relaxation consistent with recent experiments. (Exponent values are insensitive to coordination number f, but would likely change if the Bethe lattice approximation were relaxed.)

The present theory assumes that configurations of a melt of unlinked ring polymers are similar to those of a single ring in a network of obstacles. In fact, there are reasons to believe that a melt of sufficiently large unlinked rings would adopt collapsed conformations, because collapse is the most efficient way to minimize the entropy penalty in avoiding linked conformations with neighboring loops. But even for very large loops, there would be a surface layer of protrusions analogous to lattice animals, contributing to the stress relaxation. Analyzing the dynamics in this limit we leave to future work.

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