Topological Contributions to Nonlinear Elasticity in Branched Polymers

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The dynamics and rheology of entangled polymer fluids are dominated at long times by topological constraints. The topological structure of the molecules themselves is known to control the linear stress relaxation function in a way that agrees well with the "tube" model. Here we extend the model to calculate the nonlinear elastic response of highly branched polymers under large shear strains. The nonlinear strain dependence is strongly sensitive to the distribution of free ends in the molecules, in contrast to the linear stress relaxation. Calculations for combs, monodisperse trees, and the classical gelation ensemble are compared to experimental results on the unknown structure of branched polyethylene, and point strongly to a treelike structure.

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The dynamics of entangled polymeric liquids exhibit a high degree of universality because of the dominance of topological constraints for many physical properties [1]. The most successful theoretical approach has developed the "tube" model of de Gennes [2] to increasingly complex but well-defined systems, which have also been the subject of extensive experimental study [1–12].

In the tube model the constraints imposed on a single polymer chain by its neighbors are represented by placing the chain within a tube, the axis of which follows the topological constraints on the chain. The chain is generally free to move along the axis of the tube, but motion perpendicular to the axis is inhibited beyond the tube width.

For linear polymers this results in a relaxation mechanism known as reptation [2], in which the chain "snakes" its way backwards and forwards out of an imposed orientation. Star polymers (polymers in which three or more chains are joined at a central branch point) find reptation impossible since one end of each chain is anchored. Instead each arm must retrace itself back along its tube whereupon it can spring out into a new configuration [4–7].

The qualitatively new feature in entangled star polymers is that modes with well-defined (exponential) relaxation kinetics are spatially localized within entanglement segments. The relaxation times of an entanglement segment depend exponentially on the molecular distance to the nearest effective free end (called its "seniority" [12]). This localization is generic for all entangled branched polymers, as has been shown experimentally and theoretically for various topologies [8–12]. The distribution of seniorities within a branched polymer melt completely determines the linear stress relaxation function at the level of the tube model [12]. This is because the orientational relaxation of segments of equal seniority occurs simultaneously. In this way branched polymers furnish examples of systems with hierarchically controlled dynamics [13].

A significant success of the tube model was its successful prediction of the stress-strain dependence in nonlinear shear deformation of monodisperse linear polymers [14] and surfactant micelles [15]. The deviation of the stress from ideal-rubber response following the imposed shear is described by a "damping function" of strain $h(\gamma)$. This is well defined since at long times it is observed that the relaxation modulus $G(t, \gamma)$ is separable [16] such that

$$G(t, \gamma) = h(\gamma)G(t). \qquad (1)$$

The tube model accounts for this observation by the natural separation in time scale of a fast "retraction" process and a slow "reptation" process.

For small deformations the stress arising is seen to come predominantly from the orientation of the entangled polymer chain. At higher strains the chain can become significantly extended, and the elastic stress contribution from the increase in contour length must be considered. For linear polymers (and, in fact, star polymers) this contribution relaxes in a time τ_R, the Rouse time for the linear polymer or star arm, during which the polymer retracts into its tube and regains its equilibrium contour length [Fig. 1(a)].

The amount of stress lost in the retraction process comes from both (i) the reequilibrium of the entropic tension in the polymer chain to its equilibrium value and (ii) the loss of topological constraints represented by the vacated tube. The Doi-Edwards (DE) damping function is known to fit well the experimentally observed results for linear polymers above the entanglement molecular weight [14]. However, polymers with substantial long-chain branching (LCB) consistently have much weaker damping [14], suggesting that the retraction is inhibited in some way.

The cause of this behavior is apparent if we consider the generalization of the tube model to a branched polymer. In the following the term "chain segment" will refer to the length of polymer chain between branch points, whereas
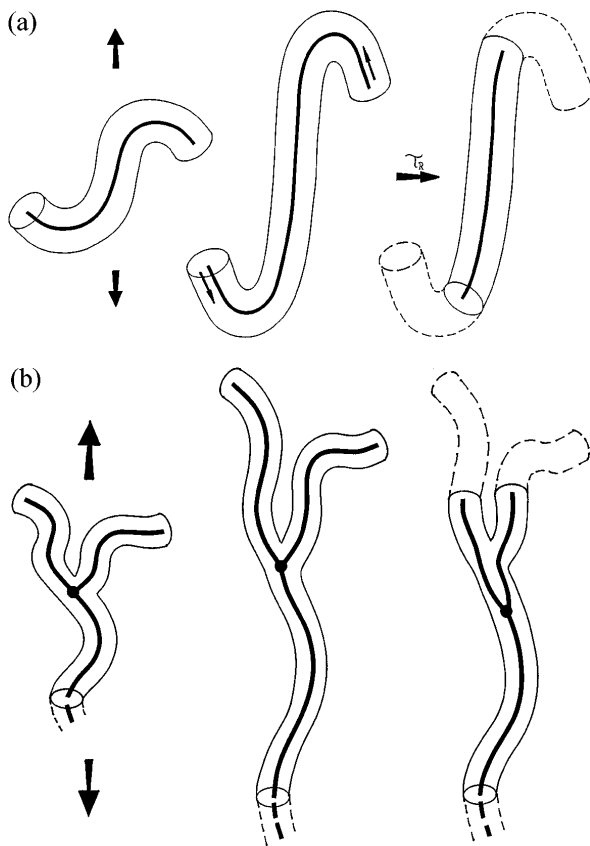
FIG. 1. A polymer subject to a nonlinear strain will experience an increase in contour length. For a linear polymer this contribution to stress relaxes in a time τ_R, during which time the polymer retracts back to its equilibrium contour length (a). A branched polymer finds this process inhibited for all but its free ends, since inner chain segments must contend with the entropic tension in all of the free ends to which they are attached (b).

"tube segment" will mean a length a of the tube, where a is the tube diameter. The outermost chain segments of a branched polymer may retract normally, as for the arms of a star polymer. A subsequent chain segment, attached to two such outer segments, finds that as it tries to retract it withdraws the branch point and two outer segments into its own tube, aligning them with each other [Fig. 1(b)]. However, this will not occur at all strains for the following reason: Both outer chain segments are subject to the entropic tension $f_0 = k_B T/a$ when trapped in tubes of diameter a. (This tension arises physically from the unrestricted motion of their free ends compared with their confined central portions [1].) The next chain segment into the polymer must be supporting a tension of twice the equilibrium tension in order to withdraw the branch point into its tube. This will only occur at deformations greater than a critical deformation at which this force balance is first achieved. At all greater deformations the stretched chain segment maintains twice its original contour length and tension. If the initial deformation is insufficient to

produce this twofold increase in contour length then branch point withdrawal will not occur.

This reasoning can be applied recursively to every chain segment in the polymer. We will refer to the ratio of the maximum permissible tension (after retraction) to the equilibrium tension as the *priority* of the chain. Any chain segment of a branched polymer is attached on either side to a tree, and each of these two trees will contain a number of free ends. Noting that each free end transmits an entropic tension f_0 to the interior chain segments of the tree, we deduce that the priority of a segment is just the lesser of the totals of free ends in the two trees to which it is attached (cf. *seniority* [12]).

The stress tensor for a given polymer can be calculated by summing over the outer product of tension and displacement of occupied tube segments

$$\boldsymbol{\sigma} = \frac{1}{V} \sum_{\text{tube segs}} \boldsymbol{f}\boldsymbol{r}, \tag{2}$$

where $\boldsymbol{r}$ is the displacement along the segment, $\boldsymbol{f}$ the tension of the chain segment it contains (or sum of tensions for multiply occupied tube segments), and V the volume chosen to calculate the coarse-grained stress. If a polymer is subject to a strain $\boldsymbol{E}$ such that a vector $\boldsymbol{u}$ of initially unit length transforms as

$$\boldsymbol{u}' = \boldsymbol{E} \cdot \boldsymbol{u}, \tag{3}$$

then the average tension along the tube segment whose initial orientation is $\boldsymbol{u}$ can be written as

$$\boldsymbol{f} = f_0 \langle |\boldsymbol{u}'| \rangle \frac{\boldsymbol{u}'}{|\boldsymbol{u}'|}, \tag{4}$$

where f_0 is the equilibrium tension of a chain segment. The average is taken over the isotropic distribution which assumes that the tubes are sufficiently long to permit their segments to effectively self-average over all orientations in $\boldsymbol{u}$. Equation (4) describes the tension only after it has equilibrated along the length of the occupying chain segment, a process that happens in the rapid time τ_e, the Rouse time for an entanglement length. Similarly the end-to-end displacement of a tube segment $\boldsymbol{r}$ transforms to

$$\boldsymbol{r}' = a\boldsymbol{u}'. \tag{5}$$

At very early times following the deformation, before τ_R, the stress contribution from all the tube segments occupied by unretracted chains of priority i is therefore

$$\boldsymbol{\sigma}_i = c_i n_{0i} \left\langle f_0 \langle |\boldsymbol{u}'| \rangle \frac{\boldsymbol{u}'}{|\boldsymbol{u}'|} a\boldsymbol{u}' \right\rangle, \tag{6}$$

where c_i is the concentration of *chain* segments of priority i and n_{0i} is the number of entanglements (tube segments) per chain segment of priority i at equilibrium.

For longer times, after all permitted retractions and branch point withdrawal processes have taken place, we can recalculate the stress from the consequent changes to the tension f_i, and number of entanglements n_i, for chain

segments of priority i. These quantities transform after retraction such that

$$f_i \rightarrow \begin{cases} f_0 i, & i < \langle |\mathbf{u}'| \rangle, \\ f_0 \langle |\mathbf{u}'| \rangle, & i \geq \langle |\mathbf{u}'| \rangle, \end{cases} \quad (7a)$$

$$n_i \rightarrow \begin{cases} n_{0i} i / \langle |\mathbf{u}'| \rangle, & i < \langle |\mathbf{u}'| \rangle, \\ n_{0i}, & i \geq \langle |\mathbf{u}'| \rangle. \end{cases} \quad (7b)$$

The transformations are the result of the branch point withdrawal mechanism: If the deformation has induced a sufficient tension then the branch point is withdrawn, the tension being limited by the priority i of the chain segment to $f_0 i$. If the tension is insufficient for branch point withdrawal to occur, then the tension remains unchanged from its value following the original deformation (7a). Similarly, if branch point withdrawal occurs, then the reduction in contour length of the chain segment will cause some tube segments to become vacated, reducing n_i (7b). If branch point withdrawal has not occurred, the number of tube segments is taken to be unchanged.

The stress sum (2) may then be rewritten for an arbitrary system of branched polymers as a sum over *chain* segments of priority i in their deformed tubes. The sum divides into those segments (of low priority) for which branch point withdrawal has occurred and those (of higher priority) for which it has not,

$$\sigma = f_0 r_0 \left\langle \frac{\mathbf{u}'\mathbf{u}'}{|\mathbf{u}'|} \right\rangle$$

$$\times \left[\sum_{i=1}^{i < \langle |\mathbf{u}'| \rangle} n_{0i} c_i \frac{i^2}{\langle |\mathbf{u}'| \rangle} + \sum_{i > \langle |\mathbf{u}'| \rangle}^{i_{max}} n_{0i} c_i \langle |\mathbf{u}'| \rangle \right]. \quad (8)$$

This shows by demonstration that the priority distribution (given by n_{0i} and c_i) is sufficient information to calculate the damping function, which may then be simply written as

$$h(\gamma) = \sigma(\gamma)/\gamma. \quad (9)$$

This method has been applied to three different topologies of LCB: trees, combs, and the gelation ensemble, then compared with experimental data for randomly branched low-density polyethylene (LDPE), in shear [14].

The first model is the Cayley tree, in which all chain segments are the same length and end in branch points of fixed functionality. Taking a functionality of three, the relative concentration of segments with priority i is

$$c_i = 2^{N-i}/(2^N - 1), \quad i = 2^n, \; n \in \mathbb{N}, \quad (10)$$

where N is the maximum generation number in the tree. The damping function for shear was calculated and is shown in Fig. 2(a). A limiting curve of many levels of branching is shown (providing an envelope for all possible damping functions for the tree) along with a curve that best fits the experimental results on LDPE.

Similar curves were also calculated for comb structures [Fig. 2(b)]. The comb and the Cayley tree represent extremes of architecture that maximize and minimize, respectively, the relative concentration of chain segments with high priority. Once again a bounding curve and best fit are shown.
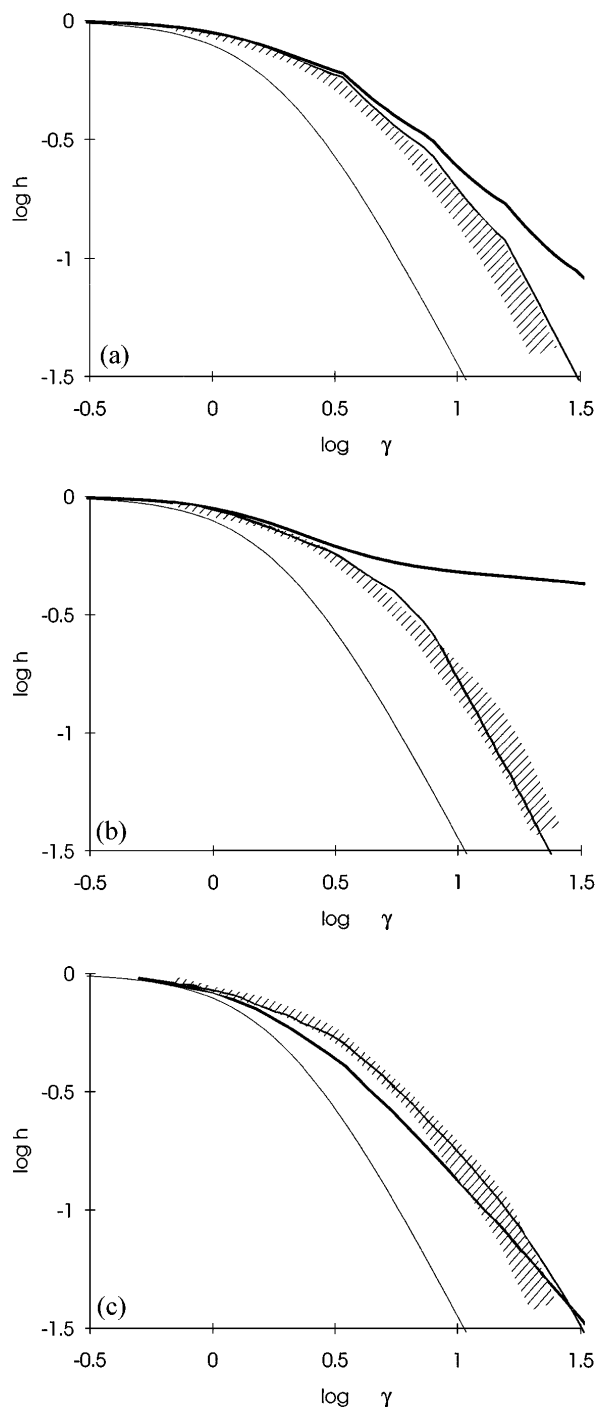

FIG. 2. The shear damping function plotted against shear strain. In all the graphs the thin line is the Doi-Edwards damping function and the hatched area the experimental results for LDPE [14]. (a) The Cayley tree, with a bounding curve for the limit of high branching (bold) and the result for four levels of branching. (b) The comb, with a bounding curve (bold) and the result for four levels of branching. (c) The Flory-Stockmayer, with the umodified curve (bold) and the result when starlike and linear material are removed.

The last model considered here is based upon the Flory-Stockmayer ensemble below its gelation threshold: A given chain will branch with a probability p or

terminate with a probability $(1 - p)$. This generates a wide polydispersity of both topology and size, and so is a more realistic model for random branching than the two monodisperse models. The new parameter is the branching probability p. However, we note that the very broad polydispersity of industrial LDPE requires that one sets p close to (but less than) p_c, the critical probability for gelation. Finite values of $|p - p_c|$ then provide an upper exponential cutoff to the new distribution, but as this tail doe snot contribute significantly to the damping function we may work at $p = p_c$. Using a self-consistent equation in a generating function for the priorities [17] it can be shown that for a functionality of three the probability of a segment having a priority i is

$$c_i = q_i^2 + 2q_i \sum_{m>i} q_m, \qquad (11a)$$

where

$$q_i = \frac{[2(i - 1)]!}{i!(i - 1)!} (1 - p)^i p^{i-1}$$

are the probabilities of *one-sided* priorities—that the number of free ends of one tree connected to an arbitrarily chosen segment is i.

For large i and for p near p_c this is approximately a power law in i

$$c_i \approx \frac{1}{\pi i^2} + \mathcal{O}(i^{-3}). \qquad (11b)$$

The damping function is shown in Fig. 2(c) for $p \approx p_c = \frac{1}{2}$ and also for a modified Flory-Stockmayer model with the contributions from linear and starlike material removed.

As can be seen from a comparison of all three models the topology of each structure has a marked effect on its nonlinear properties, and each is very distinct from the DE damping function for linear polymers.

That the comb has the strongest elastic response can be understood thus: The quadratic weighting of the priority of a chain segment to its stress contribution means that those segments of high priority have by far the most important contribution to the stress at large strains. The comb has the highest relative concentration of such chain segments.

When these results are compared with the range of data available for LDPE the best fit is seen to be provided by the Cayley tree model. Industrial LDPE is produced by free-radical polymerization, for which the subgel Flory-Stockmayer ensemble might be expected to model the system since branching events are uncorrelated. This damping function, however, is generally seen to be too shear thinning. By artificially removing star and linear contributions from the ensemble the predictions can be made to lie within the experimental region, although the justification for introducing correlations in the long-chain branching in this way is somewhat pragmatic.

The sensitive dependence of nonlinear elasticity on topology with a tube approach is encouraging, as is the clear signature that all published data on LDPE fall into categories of treelike structures. However, the real test of this theory will be measurements on polymers of well-characterized topology more complex than simple stars.

As well as rheological response, the mechanism of branch point withdrawal makes direct predictions of molecular conformations on the scale of the tube diameter. These could be checked by neutron scattering from labeled branched polymers.

[1] M. Doi and S. F. Edwards, *The Theory of Polymer Dynamics* (Clarendon, Oxford, 1986).
[2] P. D. de Gennes, J. Chem. Phys. **55**, 572 (1971).
[3] M. Rubinstein, Phys. Rev. Lett. **57**, 3023 (1986).
[4] E. Helfand and D. S. Pearson, Macromolecules **17**, 888 (1984).
[5] R. C. Ball and T. C. B. McLeish, Macromolecules **22**, 1911 (1989).
[6] L. J. Fetters *et al.,* Macromolecules **26**, 647 (1993).
[7] N. Clarke and T. C. B. McLeish, J. Chem. Phys. **99**, 10 034 (1993).
[8] J. Roovers and W. W. Graessley, Macromolecules **14**, 766 (1981).
[9] T. A. Yurasova, T. C. B. McLeish, and A. N. Semenov, Macromolecules **27**, 7205 (1994).
[10] J. Roovers, J. Macromolecules **17**, 1196 (1984).
[11] T. C. B. McLeish, Macromolecules **21**, 1062 (1988).
[12] M. Rubinstein, S. Zurek, T. C. B. McLeish, and R. C. Ball, J. Phys. (Paris) **51**, 757 (1990).
[13] R. G. Palmer, D. L. Stein, E. Abrahams, and P. W. Anderson, Phys. Rev. Lett. **53**, 958 (1984).
[14] K. Osaki and M. Kurata, Macromolecules **13**, 671 (1980).
[15] N. A. Spenley, M. E. Cates, and T. C. B. McLeish, Phys. Rev. Lett. **71**, 939 (1993).
[16] J. D. Ferry, *Viscoelastic Properties of Polymers* (Wiley, New York, 1980), 3rd ed.
[17] D. K. Bick and T. C. B. McLeish (to be published).