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Reptation and Contour-Length Fluctuations in Melts of Linear Polymers

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We present an analytical theory of stress relaxation in monodisperse linear polymer melts that contains contributions from both reptation and contour-length fluctuations, modeled as in our previous work on arm retraction in star polymers. Our approach resolves two long-standing problems with reptation theory: it predicts a zero-shear viscosity η scaling as $\eta \sim N^{3.4}$ over a broad range in chain length N before reaching an asymptotic N^3 dependence, and a power law $\omega^{-\alpha}$ in the dynamic loss modulus $G''(\omega)$ with $0 < \alpha < 1/4$ depending on chain length, in agreement with experiment. [S0031-9007(98)06599-5]

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The reptation theory of stress relaxation in monodisperse linear polymers, originated by de Gennes [1] and developed by Doi and Edwards [2] into a full description of the linear and nonlinear rheology of monodisperse entangled melts, is a remarkably successful theory. The many-body problem of motion of a chain entangled with a melt of others is replaced by a single chain in a “tube” that represents the constraints from entanglement with other chains. The reptation theory explains the origin of shear thinning due to alignment in flow of the tubes, the origin of a plateau region in the dynamic elastic modulus $G'(\omega)$ above the terminal time, and the approximate scaling of the reptation time τ_d with chain length N .

However, there are several notable shortcomings of the reptation theory, in both the linear and the nonlinear regimes. In the linear regime, the shortcomings are (1) reptation predicts that τ_d scales with N as N^3 , while numerous experiments give $\tau_d \sim N^{3.4}$ [3], and (2) for frequencies above τ_d^{-1} , Doi-Edwards (DE) theory predicts a dynamic loss modulus $G''(\omega)$ going as $\omega^{-1/2}$, where experiment finds a much weaker power law, between zero and $-1/4$ depending on chain length [4].

It has been understood for some time that the physical origin of the 3.4 scaling is the relaxation of some portion of the stress by a faster process than reptation, which would decrease the viscosity relative to the asymptotic result [5]. The fast process becomes less important as N becomes large, so the viscosity increases faster than the asymptotic N^3 result, meeting it from below.

Doi identified this faster process with “contour-length fluctuations,” i.e., the fluctuation-driven stretchings and contractions of the chain along the tube [6]. When the chain contracts within the tube and then stretches out again, the orientation of the ends of the tube is forgotten, and stress associated with alignment of those portions of the tube is relaxed. Doi argued that the fraction of tube relaxed in this way should scale as $N^{-1/2}$.

Simulations by O’Connor and Ball [7] and Rubinstein [8] of the combined reptation and contour-length dynamics of a single chain within a tube, equating the time when the chain ends first visit a given portion of the tube to the relaxation time for stress held there, give a result for $\eta(N)$ consistent with the experimental 3.4 scaling. Rubinstein, Helfand, and Pearson [9] proposed the Rouse-like path-length fluctuations at the chain ends as the source for the near- $\omega^{-1/4}$ form of $G''(\omega)$ at high frequencies. However, they were unable to treat the crossover quantitatively.

Recently, we have developed a powerful tube-based theory of stress relaxation in an apparently unrelated system, melts of entangled *f*-arm star polymers (*f* “arms” attached by their ends to a single branch point) [10]. Reptation is impossible for stars, because the arms have no single tube down which to slither. Stress relaxes in star melts by arm retraction [11], in which the free end of a star arm fluctuates down its tube some distance toward the branch point and pops out again, thus “forgetting” the section of tube near the free end.

This arm retraction is entropically unfavorable and hence “activated,” with retraction time scales depending exponentially on the length of the arm and on the fractional distance retracted. Our development of this idea gives an analytical theory for $G(\omega)$ in star melts that agrees remarkably well with a wide range of experimental data on stars with various number and length of arms. The only parameters in the theory, the entanglement length N_e and a microscopic time scale, are accessible from experiment on linear chains.

Based on this theory, we have returned to consider the shortcomings of reptation theory applied to *linear* chains. The idea is simple: treat linear chains as two-armed stars. That is, the motion of star arms retracting is nearly the same as the contour-length fluctuation motion of the end of a linear chain. However, stress relaxation by retraction in linear chains is “cut off” by reptation: tube segments

not visited by a retracting end on a time scale τ_d will be relaxed by reptation. Thus for a linear chain, the fast (and thus relevant) retractions will tend to involve motion near the chain ends; because of this, modeling the retraction as if the center of the chain were fixed is a reasonable approximation. If the full DE spectrum is used for the central position of the chain, the crossover is smooth: the relaxation time $\tau(s)$ of a tube segment a distance s from the free end varies from control by retraction from its nearest free end [$\tau(s) \sim s^4$, see below] to control by reptative diffusion [$\tau(s) \sim s^2$].

The stress relaxation function $G(t)$ then becomes a sum of two terms, one corresponding to loss of memory of the ends of the tube due to contour-length fluctuations, and one corresponding to escaping the remainder of the tube by reptation. The portion of the stress relaxing by arm retraction takes a form identical to the star theory,

$$G_{\text{retract}}(t) = \int_0^{s_d} ds \frac{dG(\phi(s))}{ds} \exp[-t/\tau(s)]. \quad (1)$$

Here s ($0 \leq s \leq 1$) denotes the fractional distance from the free end of a chain to the middle (the “joint” of the two-arm star), and s_d the value of s for which reptation becomes faster than arm retraction.

Equation (1) expresses the relaxation of the time-dependent modulus after a step strain, by progressive removal of relaxed chain material from the entanglement network. Before reptation has occurred, the volume fraction ϕ of still-entangled material is given simply by $\phi(s) = 1 - s$.

To use Eq. (1) we must specify how the modulus of an entanglement network dilutes, i.e., the function $G(\phi)$. A simple argument based on entanglements in the melt as “binary events” between Gaussian chains in the melt, either of which may be “inactive” as a result of having relaxed on some faster time scale, suggests $G(\phi) = G\phi^2$, where G is the melt plateau modulus. Measurements of the plateau modulus of well-entangled theta solutions [12], as well as a subtle scaling argument [13], suggest instead $G(\phi) = G\phi^{7/3}$. This is a significant difference for star melts; here, since the value of s_d in the crossover region is becoming small [of order $(N_e/N)^{-1/2}$], the difference is not serious, and for simplicity we take $G(\phi) = G\phi^2$.

We have computed the relaxation time $\tau(s)$ for retracting star arms as part of the theory for star melts. There are two regimes: for sufficiently large s , the entropic barrier to retraction is large compared to $k_B T$ and retraction is well described by diffusion of a single coordinate (the free end location) uphill in an effective potential. This regime is described in Refs. [14] and [10], but is not so relevant for contour-length fluctuations of linear chains.

For small s , the barrier is irrelevant, and the motion of the free end in the tube is described in terms of the Rouse modes of a semi-infinite chain in a tube [10]. The mean-square fluctuations of the end location grow with time, as lower Rouse modes with longer relaxation times contribute. At the Rouse time τ_R , the mean-square

displacement along the tube $z^2(t)$ is of order the chain end-to-end radius $R^2 = Nb^2$ (b the Kuhn step size for the chain), and the chain free end “discovers” that it is not infinite; before this, $z^2(t)$ is independent of chain length.

We expose the length dependence of the Rouse time for a chain $\tau_R(N)$ by writing it in terms of τ_e , the Rouse time for an entanglement segment (of length N_e), as $\tau_R = \tau_e(N/N_e)^2$. Requiring $z^2(t)$ to be independent of N then leads to a scaling result $z^2(t) \sim R^2(t/\tau_R)^{1/2}$.

We convert distance down the tube z to fractional distance s using $z = sL$, where L is the tube length. The chain may be thought of as a random walk of (L/a) steps of size the tube diameter a , so $La = R^2$. The tube diameter is the radius of an entanglement segment, so a is related to N_e by $a^2 = (4/5)N_e b^2$ (the coefficient being a matter of convention [2]). Inverting the scaling relation above, with an explicit Rouse model calculation to fix the coefficient, we find [10]

$$\tau(s) = (225\pi^3/256)\tau_e s^4 (N/N_e)^4, \quad (2)$$

which is valid up to $s = s_d$ of order $(N_e/N)^{1/2}$, where $\tau(s)$ is of order τ_R and we cross over to the activated form for $\tau(s)$ (from Ref. [10]).

Beyond s_d , retraction becomes increasingly slow [10], and most of the remaining chain segments will relax their stress by reptation at time τ_d . Note that the contour-length fluctuations have the effect of shortening by a factor $1 - s$ the distance a chain segment must diffuse along the tube to reach a relaxed tube segment, which shortens the reptation time itself. We thus have

$$\tau_d = \tau_e(N/N_e)^3(1 - s_d)^2 = \tau(s_d), \quad (3)$$

which with Eq. (2) (and the result for larger s from Ref. [10]) define τ_d and give an implicit equation for s_d .

Given a value for τ_d , we take the DE expression for the reptation contribution to stress relaxation [2], with the modification that only a fraction $G(\phi(s_d))/G$ of the stress remains to be relaxed:

$$G_{\text{reptate}}(t) = G(\phi(s_d)) \sum_{p \text{ odd}} (8/\pi^2)p^{-2} \exp[-p^2 t/\tau_d]. \quad (4)$$

Finally, we add a Rouse stress relaxation function with modes down to τ_R , which is meant to account for (1) the stress relaxation on time scales shorter than τ_e for which the tube constraint has not yet been explored, and (2) the longitudinal Rouse modes inside the tube that leave the free end fixed but relax stress by redistributing chain segments inside the tube. The Rouse stress relaxation function takes the form

$$G_{\text{Rouse}}(t) = G(N_e/N) \sum_{p=1}^N \exp[-p^2 t/\tau_R]. \quad (5)$$

Transverse Rouse modes on time scales longer than τ_e are forbidden by the tube. To include in an approximate

way only longitudinal Rouse modes on time scales longer than τ_e , we break the sum in Eq. (5) into two parts ($1 \leq p \leq N/N_e$ and $N/N_e < p < N$) and multiply the low-frequency contribution by 1/3, as only one of the three vector components of the Rouse modes remains free.

The full stress relaxation function is then simply

$$G(t) = G_{\text{retract}}(t) + G_{\text{reptate}}(t) + G_{\text{Rouse}}(t). \quad (6)$$

The dynamical modulus $G(\omega)$ (ratio of frequency-dependent stress to strain) is given in terms of the Fourier transform of $G(t)$ by $G(\omega) = i\omega \mathcal{F}[G(t)](\omega)$; the zero-shear viscosity η is $\lim_{\omega \rightarrow 0} G(\omega)/(i\omega)$.

Calculated results for η are shown in Fig. 1, plotted log-log versus M/M_e . Note the effective exponent for η of 3.4 over an extremely wide range of M/M_e before crossing over to the asymptotic exponent of 3, which arises from our theory with no adjustable parameters.

Deviations from the effective exponent can be made more evident by plotting $\log_{10} \eta/(M/M_e)^3$ versus $\log_{10}(M/M_e)$, shown in the inset of Fig. 1. Plotted in this way [7], deviations from the 0.4 slope begin at about $10^{2.5} \approx 300$; this behavior is quite consistent with that reported by Colby *et al.* in Ref. [15]. So the present theory also gives a reasonable location for the crossover, again without adjustable parameters.

We have compared our predictions for $G(\omega)$ to data of Schausberger *et al.* [16] on reasonably monodisperse polystyrene (PS) chains of three different lengths, $M = 292K, 757K, 2540K$ g/mol corresponding to $N/N_e = 22, 57, 191$ ($M_e = 13300$ g/mol). In our comparison we have chosen a single value of τ_e and plateau modulus G (i.e., a single common horizontal and vertical shift on a log-log plot) to compare theory to data. The resulting plots of $G''(\omega)$ are shown in Fig. 2.

The terminal behaviors of all three curves are well matched by the theory without any adjustment to achieve the 3.4 effective scaling. Since the value of N/N_e changes

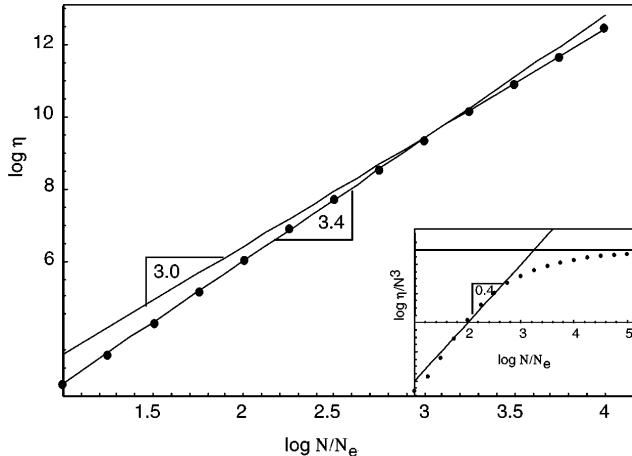


FIG. 1. Predicted viscosity η as a function of chain length N/N_e shows without adjustable parameters an effective exponent of 3.4. Plotted as η/N^3 versus N/N_e , crossover occurs at around $N/N_e = 200$, as in experiment [15].

by a factor of 10, the difference between terminal behavior scaling as N^3 and $N^{3.4}$ is $10^{0.4} = 2.5$; a discrepancy of this size would be evident in the figure.

The theory also shows the same evolution with chain length of the slope of $G''(\omega)$ as the data, in the intermediate frequency range between the terminal peak and the minimum. This behavior results directly from the contour-length fluctuations, as we now show.

The reptation contribution $G_{\text{reptate}}(\omega)$ dominates at low frequencies ($\omega \tau_d < 1$), and leads to a plateau in $G'(\omega)$ for high frequencies ($\omega \tau_d \gg 1$), but by itself would only contribute a power law in $G''(\omega)$ of $\omega^{-1/2}$ for $\omega \tau_d > 1$. The Rouse contribution $G_{\text{Rouse}}(\omega)$ dominates at high frequencies, resulting in $G'(\omega)$ and $G''(\omega)$ both going as $\omega^{1/2}$. The Rouse and reptation contributions to $G'(\omega)$ become comparable at $\omega \tau_e \sim 1$.

Without the contribution of $G_{\text{retract}}(\omega)$, the frequency range $\tau_d^{-1} < \omega < \tau_e^{-1}$ would have a power law in $G''(\omega)$ of $\omega^{-1/2}$; this is much steeper than experimental data, which show a power law in this region depending on chain length and never steeper than $-1/4$.

In fact, the fast-relaxing contour-length fluctuations $G_{\text{retract}}(\omega)$ contribute in this intermediate frequency range, and give rise to a power law in $G''(\omega)$ of $\omega^{-1/4}$. This can be shown easily from Eqs. (1) and (2), the result being that a power law $\tau(s) \sim s^\beta$ leads to a power law in $G''(\omega)$ of $\omega^{-1/\beta}$. The relaxation processes in this intermediate frequency range are a direct signature of contour-length fluctuations, which relax stress at the ends of the tube by retracting the chain end inwards and popping it out again into a new tube.

For sufficiently large chain length N , the experimentally observed power law in this region is indeed $-1/4$; for smaller N , as our computed curves for $G''(\omega)$ show, the Rouse relaxations contribute sufficiently in the

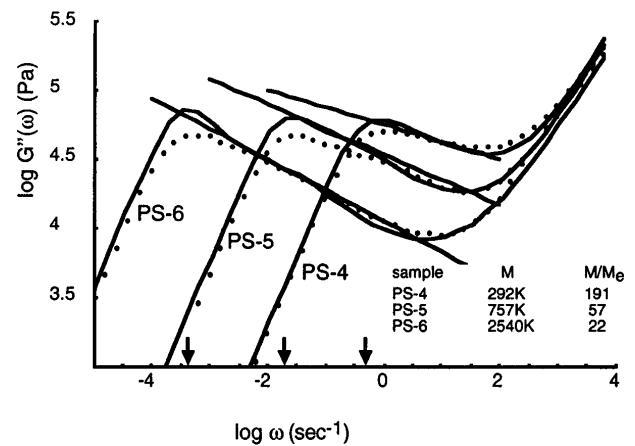


FIG. 2. Computed loss modulus $G''(\omega)$ compared to data of Ref. [16] for narrow-MWD polystyrene melts. A common value of τ_e and G has been taken for the three curves. The variation in slope above $\omega \tau_d = 1$ results from “contamination” of the $-1/4$ behavior by Rouse modes inside the tube. Arrows mark $\omega \tau_d = 1$. (Lines are guides to the eye of slope 1/8, 1/5.5, 1/4.5.)

intermediate region to flatten the curve, resulting in a progressively smaller slope for smaller N .

We have deliberately not included effects of polydispersity and constraint release modes arising from *reptation* of other chains, and suggest that these are jointly responsible for the differences between theory and data in the detailed peak shape at $\omega\tau_d \sim 1$. One approach to constraint release in entangled linear chains entails endowing the tube itself with Rouse motion, whose fastest mode is generated by the reptational release of entanglements [9]. It therefore affects the relaxation modulus at and to the left of $\omega\tau_d \sim 1$. The same is true of mild polydispersity, which generates a spread in τ_d , but will not alter the higher frequency response arising from fluctuations.

Our results have several clear consequences to be explored. First, contour-length fluctuations cannot contribute to stress relaxation at frequencies too far below $\omega\tau_R \sim 1$; because of the entropic barrier to arm retraction, Eq. (2) eventually crosses over to an exponential dependence on s [10], so that not many more chain segments relax by arm retraction between τ_R and τ_d .

Therefore, for sufficiently large N , enough separation between the reptation and Rouse time scales exists so that a $\omega^{-1/2}$ region of $G''(\omega)$, corresponding to the contributions of higher reptation modes only, opens up between the terminal peak and the $\omega^{-1/4}$ region. Unfortunately for experimenters, our calculations suggest that this region would only be visible for extremely large N/N_e , perhaps greater than 1000; still, we would encourage experiments on the rheology in the regime above $\omega\tau_d \sim 1$ of monodisperse, extremely high molecular weight polymers to investigate this behavior.

Second, our results suggest a new way to extract the “friction coefficient” from rheological data. In the past, it was not possible to infer a microscopic time scale (τ_e , for instance) or a friction coefficient ζ [from the relation $\tau_e = \zeta R^2/(3\pi^2 k_B T)$] by comparison to the reptation theory, because there was no quantitative explanation of the deviation from N^3 scaling of the stress relaxation.

Instead, ζ was inferred either (1) by measurements at very high frequencies [17], for which the motion of the chain inside the tube is Rouse-like, but so local that the flexible-chain assumptions leading to Eq. (5) are not necessarily valid, or (2) by measurements of stress relaxation for *unentangled* polymer melts [15], which is difficult because as chain length is varied for such short chains, the concentration of chain ends changes enough to affect the glass transition temperature T_g . Rouse scaling of η is never observed directly, but only after attempts to correct for the varying T_g [15]. Using our results, ζ can be extracted by comparing the computed $G(\omega)$ directly to experiments on entangled melts.

Our approach differs conceptually from earlier attempts to include contour-length fluctuations [18], which represented the stress relaxation as simple reptation with a time-dependent curvilinear diffusion coefficient. That approach gave corrections to reptation of order $O(1/N)$ rather than

the expected $O(N^{-1/2})$, so that (1) unrealistically large values of N_e (13 times too large) were required for fits to data, and (2) the region of effective 3.4 exponent for viscosity was limited to $N/N_e < 20$.

Finally, we note that the contour-length fluctuations may also affect the chain self-diffusion, because the smallest uncorrelated spatial step for the chain center of mass becomes $R(1 - s_d)^{1/2}$ with a time step $t_d(1 - s_d)^2$. Corrections to scaling of the diffusion constant are then $D_{\text{self}}(N) \sim N^{-2}[1 - O(N^{-1/2})^{-1}]$, which would increase the apparent power law of $D_{\text{self}}(N)$. Larger power laws are indeed seen in concentrated solutions [19] but not in melts [20,21]. There are also theoretical issues [22] that are less well resolved in self-diffusion than for stress relaxation. We hope that the present approach will help in addressing these further challenges.

- [1] P. G. de Gennes, *Scaling Concepts in Polymer Physics* (Cornell University Press, Ithaca, NY, 1979).
- [2] M. Doi and S.F. Edwards, *The Theory of Polymer Dynamics* (Clarendon Press, Oxford, 1986).
- [3] J. D. Ferry, *Viscoelastic Properties of Polymers* (Wiley, New York, 1980), p. 244.
- [4] M. Baumgaertel, A. Schausberger, and H. H. Winter, *Rheol. Acta* **29**, 400 (1990).
- [5] W. W. Graessley, *J. Polym. Sci., Polym. Phys. Ed.* **18**, 27 (1980).
- [6] M. Doi, *J. Polym. Sci., Polym. Phys. Ed.* **21**, 667 (1983).
- [7] N. P. T. O'Connor and R. C. Ball, *Macromolecules* **25**, 5677 (1992).
- [8] M. Rubinstein, *Phys. Rev. Lett.* **59**, 1946 (1987).
- [9] M. Rubinstein, E. Helfand, and D. S. Pearson, *Macromolecules* **20**, 822 (1987).
- [10] S. T. Milner and T. C. B. McLeish, *Macromolecules* **30**, 2159 (1997).
- [11] D. S. Pearson and E. Helfand, *Macromolecules* **17**, 888 (1984).
- [12] M. Adam and M. Delsanti, *J. Phys. (Paris)* **45**, 1513 (1984).
- [13] R. H. Colby and M. Rubinstein, *Macromolecules* **23**, 2753 (1990).
- [14] R. C. Ball and T. C. B. McLeish, *Macromolecules* **22**, 1911 (1989).
- [15] R. H. Colby, L. J. Fetters, and W. W. Graessley, *Macromolecules* **20**, 2226 (1987).
- [16] A. Schausberger, G. Schindlauer, and H. Janeschitz-Kreigel, *Rheol. Acta* **24**, 222 (1985). We thank H. Henning Winter for supplying us with the data tables.
- [17] J. D. Ferry, *Viscoelastic Properties of Polymers* (Wiley, New York, 1980), pp. 328ff.
- [18] J. des Cloizeaux, *Macromolecules* **23**, 4678 (1990).
- [19] N. Nemoto, T. Kojima, T. Inohue, M. Kishine, T. Horayama, and M. Kurata, *Macromolecules* **22**, 308 (1989).
- [20] P. F. Green, P. J. Mills, C. J. Palmstrom, J. W. Mayer, and E. J. Kramer, *Phys. Rev. Lett.* **53**, 2145 (1984).
- [21] C. R. Bartels, B. Crist, and W. W. Graessley, *Macromolecules* **17**, 2702 (1984).
- [22] M. Rubinstein, in *Theoretical Challenges in the Dynamics of Complex Fluids*, edited by T. C. B. McLeish, NATO ASI Ser. E, Vol. 339 (Kluwer, Dordrecht, 1997), Chap. 2.