Stress Relaxation of Star-Shaped Molecules in a Polymer Melt

Johan L. A. Dubbeldam*,[†] and J. Molenaar[‡]

[†]*Department of Electrical Engineering Computer Science and Applied Mathematics, (DIAM), Delft University of Technology, Mekelweg 4, 2628CD Delft, The Netherlands, and [‡]Department of Applied Mathematics and Statistics, Wageningen University, P.O. Box 100, 6700 AC Wageningen, The Netherlands*

ABSTRACT: We present a theoretical study of stress relaxation of star-shaped polymers starting from a Rouse model for a polymer in a tube. Instead of focusing on the potential in which the chain moves, we mathematically study the Rouse equation with a time-dependent boundary condition. This boundary condition arises as a consequence of tube dilution, which is implemented in the model through a tube diameter that increases with time, depending on position along the tube. We derive a Fokker−Planck equation for the probability distribution of the position of the chain end and find an analytical expression for the mean first passage time. Our approach helps identifying the origin of the potentials, which are commonly used in existing models for stress relaxation in star polymers. Moreover, it clearly displays the underlying approximations and allows easy generalization to the case of a tethered chain in a flow.

Introduction

Polymer melts and concentrated polymer solutions are quite well described by reptation theory.[1] It states that relaxation of long linear polymer chains happens through one-dimensional diffusive motion along the chain's backbone. This one-dimensional diffusion results from topological interactions with the surrounding molecules which prevents the molecule to move in lateral direction. Therefore, the molecule can be thought of as surrounded by a tube or cage consisting of entanglements with the surrounding molecules.

Recent microscopic descriptions of highly entangled polymer melts have revealed a nonmonotonic wall stress versus shear rate relation. These results indicated that a nonmonotonic wall shear stress as a function of shear rate may arise from an entanglement−disentanglement transition. This has been confirmed by modeling work on slip-stick boundary conditions.[2,3] Most models for stress relaxation in polymer melts concentrate on bulk chains. In order to find a model that describes stress relaxation for tethered chains, a clear understanding of constraint release in the tube model put forward by Doi and Edwards[1] is imperative. Star-shaped polymers in a melt relax in a way very similar to chains tethered to a wall. In this paper we concentrate on star-shaped polymers in a melt and have the intention to apply the gained insights to tethered molecules afterward.

Star-shaped and other branched molecules in polymer melts are subject to topological interactions with their surroundings but are deprived from reptation as a way to relax their stress. They have to resort to other ways for stress relaxation, namely, withdraw their arms from the tube. The problem of *stress relaxation* in star-shaped polymers in a *fixed network* was first addressed by Pearson and Helfand.[4] They predicted the correct exponential scaling of the relaxation time on the arm length, but the numerical factor in the exponent 15/8 proved to be way too large. This suggested that other relaxation mechanisms must also be present.

Ball and McLeish[7] and Milner and McLeish[9] realized that *constraint release* must be incorporated in order to obtain agreement with experimental results. They implemented this by applying the concept of a diluted tube, originally conceived by Marrucci.[13] It amounts to saying that the end part of the chain sees a diluted tube due to diffusion of the constraints. This idea proved to be successful in explaining the measurements of the relaxation modulus over 4 orders of magnitude.[9]

In this paper we present an *ab initio* derivation of stress relaxation for star-shaped molecules. The obtained results for the relaxation modulus $G(t)$, or rather $G^*(\omega)$, compare well with experimental findings. We also point out the relation between our approach and existing models in the literature. The present approach does not employ an "effective potential" description as is common in the literature, but instead starts from the Rouse equations for a chain restricted in a tube, whose diameter is varying due to constraint release. Constraint release gives rise to a widening of the tube. This effect depends on the position along the tube and is most prominent toward the end of the tube. To model tube dilution, we derive a stochastic differential equation for the movement of the end of the chain. This equation can easily be converted into a Fokker−Planck equation, which in its turn allows the calculation of the mean first passage time. This is a measure of how long it takes on average for the chain end to pass a given position along the tube. If we translate the results of our approach in terms of a potential description as is usual in the literature, we find that we obtain a softening of the widely used quadratic potential in quite a natural way. This softening is also used by Milner and Mcleish,[9] who introduced it on a more or less ad-hoc basis. The present approach elucidates the assumptions underlying the effective potential theories. It has the extra advantage that it can be easily generalized to long tethered chains in a melt.

This paper is organized as follows. In the model section we introduce the model for the simple case in which the chain is restricted to a tube of constant diameter. We demonstrate how to calculate the zero shear viscosity η_0 in this case, and we reproduce the results first obtained by Pearson and Helfand,[4] who followed a completely different approach. The next section where we discuss tube dilution is the core of the paper. There we introduce tube dilution as a time varying force on the chain end, and we derive and solve the equations for a time varying tube diameter.

*Corresponding author. E-mail: j.l.a.dubbeldam@tudelft.nl.

Finally, we discuss our results and propose possible avenues for a further comprehension of constraint release in the concluding section.

Model

Our description starts from a continuous Rouse chain, so a linearly elastic chain, moving in a tube. The motion of the chain in the tube is one-dimensional, and this allows us to represent the chain as a one-dimensional parametrized curve. The parameter x in this representation labels the chain elements along the polymer and runs over the interval $0 \leq x \leq L$, with L the equilibrium length of the chain. The position of chain element x in the tube at time t is indicated by $S(x,t)$, the arc length along the chain with respect to the tethered end point, i.e., the branch point in star polymers. See the sketch in Figure 1. In equilibrium we simply have that $S(x,t) = x$. The dynamics of the chain is governed by[1]

$$\zeta \frac{\partial s}{\partial t} = k \frac{\partial^2 s}{\partial x^2} + f(x,t) \qquad (1)$$

Here, $k = 3k_B T/b^2$ represents the elastic stifness of the Rouse chain with b the Kuhn length, ζ the monomeric friction coefficient, and $f(x,t)$ the Brownian force. The Brownian force has average zero, so $\langle f(x,t) \rangle = 0$, and the correlation function given by $\langle f(x,t)\, f(x',t') \rangle = 2\zeta k_B T \delta(t - t')\delta(x - x')$. Equation 1 is supplemented with the boundary conditions $s(0,t) = 0$ and $(\partial s/\partial x)(L,t) = 1$. The first boundary condition implies that the chain is tethered, and the other one represents a pulling entropic force, which ensures that the chain has average length L. To make eq 1 dimensionless, we express time relative to $\tau = \zeta N_e L^2/3k_B T$, with N_e the number of monomers between two consecutive entanglements. Here, we use that $L = Nb/\sqrt{N_e}$.[1] We note that τ is actually the Rouse time up to a factor of π^2. The distances x and s are expressed relative to the equilibrium length L. This results in the dimensionless equation

$$\frac{\partial \bar{s}}{\partial \bar{t}} = \frac{\partial^2 \bar{s}}{\partial \bar{x}^2} + \bar{f}(\bar{x}, \bar{t}) \qquad (2)$$

with the definition $\bar{f} = fLN_e/k$. The function $\bar{f}$ has vanishing average, and its second moment is given by $\langle \bar{f}(\bar{x},\bar{t})\bar{f}(\bar{x}',\bar{t}') \rangle = (2N_e/3N)\delta(\bar{t} - \bar{t}')\delta(\bar{x} - \bar{x}')$. Since confusion is hardly possible, we shall not further use a special notation for the scaled variables. So, from now on the x-range is $0 \leq x \leq 1$ and the average length is set equal to 1. Equation 2 can appropriately be solved by introducing the difference $s(x,t) - x$, which satisfies not only eq 2 but also homogeneous boundary conditions.

Expanding this difference in Fourier modes that are consistent with the boundary conditions, we find that
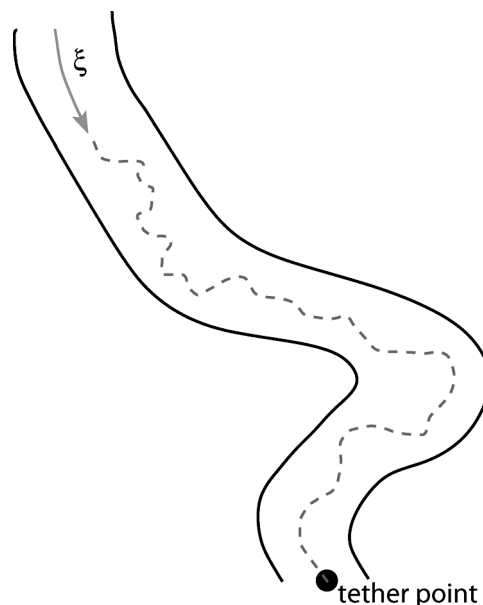
$$s(x,t) = x + \sum_{p=0}^{\infty} \phi_p(t) \sin\left(\left(p+\frac{1}{2}\right)\pi x\right) \qquad (3)$$

with $\phi_p(t)$ given by

$$\phi_p(t) = \phi_p(0)e^{-(p+1/2)^2\pi^2 t} + \int_0^t e^{-(p+1/2)^2\pi^2(t-t')} f_p(t')\, dt' \qquad (4)$$

Here, $f_p(t)$ is the Fourier sine transform of the Brownian force $f(x,t)$, i.e.

$$f_p(t) = 2\int_0^1 \sin\left(\left(p+\frac{1}{2}\right)\pi x\right) f(x,t)\, dx \qquad (5)$$

Figure 1. Sketch of one arm of star polymer molecule (dashed) in a melt that is tethered to its branch point and has retracted a distance ξ in the tube (solid). The tube is a consequence of the topological constraints due to the surrounding bulk polymer chains.

The prefactor stems from the normalization of the Fourier modes. The initial values $\phi_p(0)$ of the time-dependent expansion coefficients are determined from the initial chain configuration via the inverse Fourier transform:

$$\phi_p(0) = 2\int_0^1 (s(x,0) - x) \sin\left(\left(p+\frac{1}{2}\right)\pi x\right) dx \qquad (6)$$

Because of the presence of the stochastic Brownian force, $s(x,t)$ is a stochastic variable. We denote its probability density function by $P(s(x,t))$. This density function can be calculated from eq 3 with eq 4 by using its definition, which for arbitrary position S in the tube reads as

$$P(s(x,t) = S) = \langle \delta(S - s(x,t)) \rangle$$

$$= \langle \delta(S - x - \sum_{p=0}^{\infty} \phi_p(t) \sin((n+1/2)\pi x)) \rangle \qquad (7)$$

Here, the brackets denote ensemble averaging. The coefficients $\phi_p(t)$ are Gaussian as the $f_p(t)$ terms in eq 5 stem from white noise. As a result, $s(x,t)$ is also Gaussian distributed with an average given by the sum of the weighted averages of the $\phi_p(t)$ and with a variance that is equal to the weighted sum of all variances of the $\phi_p(t)$. This leads to

$$P(s(x,t)) = \frac{\exp\left[-\frac{(s(x,t) - x - A(x,t))^2}{2B(x,t)}\right]}{\sqrt{2\pi B(x,t)}} \qquad (8)$$

with the average $A(x,t)$ and the variance $B(x,t)$ given by

$$A(x,t) = \sum_{p=0}^{\infty} \sin\left[\left(p+\frac{1}{2}\right)\pi x\right]\phi_p(0)e^{-(p+1/2)^2\pi^2 t}$$

$$B(x,t) = \sum_{p=0}^{\infty} \sin^2\left[\left(p+\frac{1}{2}\right)\pi x\right]\frac{8N_e}{3N\pi^2}\left[\frac{1 - e^{-2(p+1/2)^2\pi^2 t}}{(2p+1)^2}\right] \qquad (9)$$

As is usual, N stands for the number of chain monomers. Note that $B(x,t)$ only depends on the length through N_e/N, the inverse of the total number of entanglements that constitute the tube, that the polymer is free to explore. In deriving eq 8, we did not correct for the fact that the beads cannot cross the wall. This will only lead to corrections of the proposed model when very large inward excursions are made. Since these are highly improbable, we neglect them. Equation 8 describes that the xth chain element makes small excursions with a typical variance $B(x,t)$ about its equilibrium position $s(x,t) = x$. The chain end with position $s(1,t)$ incessantly explores the tube it is confined to. If the chain end has retracted itself in the tube over a distance ξ (see Figure 1), say, then that part of the tube will immediately relax and thus no longer contribute to the stress in the chain. From eq 9 we see that for sufficiently long times only the slowest ($p = 0$) mode contributes to $B(x,t)$ and $A(x,t)$. However, this would definitely not lead to a correct expression for short times, as then all modes would contribute. For a review of the effect of higher order modes we refer to ref 11.

We resolve this issue as follows. First we set $x = 1$ in eq 8, as we are particularly interested in the behavior of the chain end. We notice that each modes satifies an Ornstein–Uhlenbeck process, but the behavior of the chain end that comes about due to all modes is much more complicated. In order to make contact with the work of Pearson and Helfand[4] as well as with that of Mcleish et al.[7,9] and to point out the approximations underlying their descriptions, we presume that we may approximate $A(1,t)$ and $B(1,t)$ by taking only the $p = 0$ term in eq 9, with an amplitude that is generated by all modes. Performing the summation $\sum_{p=0}^{\infty} 1/((2p+1)^2 = \pi^2/8$, we take care of preserving the variance of the distribution, so that in the long time limit the variance of the approximated probability distribution coincides with that of the original distribution (8).

Since only the fraction of the tube that is not visited by the chain end contributes to the stress, it is more natural to consider the deviation $\xi(t) = 1 - s(1,t)$ of the chain length from its equilibrium length. The probability density function of ξ is given by

$$P(\xi, t) = \frac{\exp\left[-\frac{(\xi - \xi_0 e^{-(\pi^2/4)t})^2}{(2N_e/3N)[1 - e^{-(\pi^2/2)t}]}\right]}{\sqrt{\frac{2\pi N_e}{3N}[1 - e^{-(\pi^2/2)t}]}} \qquad (10)$$

From this expression we recognize that ξ follows a standard Ornstein–Uhlenbeck process. The associated one-dimensional Fokker–Planck equation satisfied by $P(\xi,t)$ reads as[8,10]

$$\frac{\partial P}{\partial t} = \frac{\pi^2}{4}\frac{\partial(\xi P)}{\partial \xi} + \frac{\pi^2 Ne}{12N}\frac{\partial^2 P}{\partial \xi^2} \qquad (11)$$

The advantage of having this equation at our disposal is that the mean first passage time of the free chain end satisfies an equation (see eq 14) that directly follows from this one. The relevant experimental quantities are the zero-shear viscosity η_0 and the stress relaxation function $G(t)$. To derive expressions for them, we need to know the fraction of the original tube that survived until time t. To calculate the mean first passage time for vacating a portion q with $q > 0$ from the original tube, we require that the tube end does not vacate a fraction q of the original tube length in the time interval $[0,t]$, so the tube may stretch and shrink in this time interval, but the shrinkage is restricted to the interval $[-\infty,q)$. To represent this restriction, we solve eq 11 meanwhile requiring the boundary conditions $P(q,t) = 0$ and $\partial P(-\infty,t)/\partial \xi = 0$ to hold. As initial condition we simply take the chain to have its equilibrium length, so $P(\xi,0) = \delta(\xi)$.

There are a number of strategies to solve eq 11. Among them are the WKB approximation[4] and asymptotic expansions in terms of parabolic cylinder functions. Here, we choose to calculate the smallest positive eigenvalue. This smallest eigenvalue can be shown to be equal to the mean first passage time $\tau(q)$ of the chain moving a distance q into the tube.[8] This amounts to saying that the probability that a fraction $1 - q$ of the original tube survives at time t is given by $\exp(-t/\tau(q)) := F(q,t)$. If $F(q,t)$ is known, the relaxation modulus $G(t)$ can be obtained from the expression[9]

$$G(t) = 2G_0 \int_0^1 (1-q)F(q,t)\,\mathrm{d}q \qquad (12)$$

Then, the zero-shear viscosity η_0 follows from

$$\eta_0 = \int_0^\infty G(t)\,\mathrm{d}t = 2G_0\tau \int_0^1 (1-q)\tau(q)\,\mathrm{d}q \qquad (13)$$

with τ the Rouse time divided by π^2, as we defined before. The mean first passage time $\tau(q) = -\partial_t \int_0^q P(\xi,t)\,\mathrm{d}\xi$ can be shown[8,10] to satisfy the differential equation

$$-\frac{\pi^2 q}{4}\frac{\partial \tau}{\partial q} + \frac{\pi^2 N_e}{12N}\frac{\partial^2 \tau}{\partial q^2} = -1 \qquad (14)$$

with a reflecting boundary condition at minus infinity and an absorbing boundary condition at $q = 0$.

Integrating twice, we obtain the expression

$$\tau(q) = \frac{12N}{\pi^2 N_e} \int_0^q e^{(3N/2N_e)y^2}\left[\int_{-\infty}^y e^{-(3N/2N_e)z^2}\,\mathrm{d}z\right]\mathrm{d}y \qquad (15)$$

This double-integral expression can in very good approximation be replaced by

$$\tau(q) = \frac{12N}{\pi^2 Ne} \int_0^q e^{(3N/2N_e)y^2}\,\mathrm{d}y \int_{-\infty}^\infty e^{-(3N/2N_e)z^2}\,\mathrm{d}z \qquad (16)$$

so we arrive at

$$\tau(q) = \frac{12}{\pi^2}\sqrt{\frac{2\pi N}{3N_e}} \int_0^q e^{(3N/2N_e)y^2}\,\mathrm{d}y \qquad (17)$$

We meet here with the errorfunction, which is readily approximated by

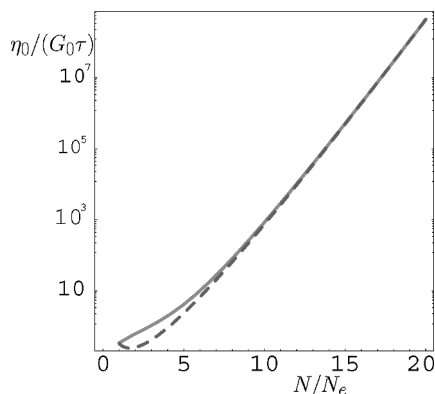$$\tau(q) = \frac{4}{\pi^2}\sqrt{\frac{2\pi N_e}{3N}}\left[\frac{e^{3Nq^2/2N_e}-1}{q}\right] \qquad (18)$$

The zero shear viscosity η_0 is now obtained from substituting this expression in eq 13

$$\eta_0 = \frac{8G_0\tau}{\pi^2}\sqrt{\frac{2\pi N_e}{3N}} \int_0^1 \frac{1-q}{q}\left[e^{3Nq^2/2N_e}-1\right]\mathrm{d}q \qquad (19)$$

Evaluation of the integral yields for $N_e/N \ll 1$

$$\eta_0 = \frac{G_0\tau}{\pi^2}\left(\frac{N_e}{N}\right)^2\sqrt{\frac{2\pi N_e}{3N}}\exp\left[\frac{3N}{2N_e}\right] \qquad (20)$$

In Figure 2, we plot the exact expression of $\eta_0/(G_0\tau)$ as defined by eq 13 and compare it with the approximate value given by eq 20.

Figure 2. Comparison of the exact solution of the zero shear viscosity η_0 given by eq 13, which is represented by the solid curve, with the approximate solution given by eq 20 and shown dashed. The two expressions lead to curves that practically coincide for $N/N_e \geq 5$, demonstrating the excellent quality of the approximations.

The curves are seen to collapse onto each other for $N/N_e \geq 5$, demonstrating that eq 20 is an excellent approximation to the exact value η_0. Moreover, the sharp increase of η_0 on N/N_e can easily be noticed from Figure 2. We conclude this section with three remarks. First, in eq 20 the viscosity grows exponentially with $3N/2N_e$. However, in refs 9 and 11 an alternative definition of N_e is employed which amounts to replacing N_e by $^4/_5 N_e$. With that definition, our result predicts exponential scaling with a factor of $15N/8N_e$, and this completely agrees with the exponent found by Pearson et al. and McLeish et al.[4,11] Second, our viscosity result slightly improves on the prefactor found in ref 4 by taking into account a correction factor proportional to $(N_e/N)^{5/2}$. However, the overall scaling which is dominated by the exponential agrees exactly with the result found in ref 4. Third, and most importantly, the numerical factor 15/8 (and also 3/2) in the exponent is way off the experimental value, which is about 0.6. It was first suggested by McLeish that this might be due to the finite lifetime of the entanglements. If entanglements disappear, the tube diameter will no longer stay constant in time but increase in time; the chain is admitted to explore more room, since it is less constrainted due to disappearing entanglements. In the next section we turn to the problem in which the tube diameter varies, the so-called "tube dilution problem", and show that with minor modifications the mathematical treatment pursued in this section can also be successfully applied in that case.

Tube Dilution

As mentioned earlier, Marrucci[13] and Milner and McLeish[9,11] realized that some important relaxation mechanism must be missing since, according to experiment, the zero-shear viscosity η_0 scales as $\exp(0.6N/N_e)$, whereas in the theory of Pearson and Helfand,[4] rederived above in an alternative way, the prefactor is not 0.6 but 15/8. Therefore, a new ingredient was added to the theory: tube dilution. This simply means that, due to loss of constraints, the tube widens in course of the time. In ref 9 this effect was accounted for by taking N_e to be some decreasing function of time. We will now demonstrate that tube dilution is in a natural way incorporated in the present approach. We again start from the dimensionless Rouse equation (22). As for the boundary conditions we now take

$$s(0,t) = 0, \quad \frac{\partial s}{\partial x}(1,t) = F(t) \tag{21}$$

here to keep the approach general. The idea is that if this pulling force decreases in time, the equilibrium length of the chain will

gradually decrease. In this way we may represent the effect of tube widening. To obtain homogeneous boundary conditions, we apply the transformation $u(x,t) = s(x,t) - F(t)x$, which leads to the equation

$$\frac{\partial u}{\partial t} = \frac{\partial^2 u}{\partial x^2} - \frac{\partial F}{\partial t}x + f(x,t) \tag{22}$$

and boundary conditions $u(0,t) = 0$ and $(\partial u/\partial x)(1,t) = 0$. Its solution is again given by the expression in eq 3, but now with the coefficients $\phi_p(t)$ satisfying the differential equation

$$\dot{\phi}_p = -\left(p+\frac{1}{2}\right)^2 \pi^2 \phi_p - \dot{F}\frac{2(-1)^p}{\left(p+\frac{1}{2}\right)^2 \pi^2} + f_p(t) \tag{23}$$

with $f_p(t)$ as defined in eq 5. The time dependence of $F(t)$ leads to an adjustment of the probability density function $P(s(x,t))$. Let us focus now on the position of the end point, which follows from $U(t) = u(1,t)$. Its probability density function is given by

$$P(U,t) = \exp\left[-\left(U + 2\sum_{p=0}^{\infty}\int_0^t \frac{e^{-(p+1/2)^2\pi^2(t-t')}}{\left(p+\frac{1}{2}\right)^2 \pi^2}\dot{F}(t')\,dt'\right.\right.$$
$$\left.\left.- \sum_{p=0}^{\infty}(-1)^p e^{-(p+1/2)^2\pi^2 t}\right)^2 \middle/ 2B(t)\right] \middle/ \sqrt{2\pi B(t)} \tag{24}$$

with $B(t)$ equal to $B(1,t)$ as defined earlier in eq 9. Comparing eq 24 and eq 8, we conclude that tube dilution gives rise to an additional drift term in the probability distribution. For long times all terms with $p \neq 0$ become irrelevant, and we again meet with a standard Ornstein–Uhlenbeck process. The associated one-dimensional Langevin equation for U reads as

$$\dot{U} = -\frac{\pi^2}{4}U - \frac{8}{\pi^2}\dot{F}(t) + \Gamma(t) \tag{25}$$

where $\Gamma(t)$ denotes a Brownian process with the correct amplitude, that is due to all modes, as discussed in the previous section. Hence $\langle\Gamma(t)\rangle = 0$ and $\langle\Gamma(t)\Gamma(t')\rangle = (2N_e/3N)\delta(t - t')$. The distance over which the free end point of the chain retracts into the tube is given by $\xi(t) = 1 - s(1,t) = 1 - U(t) - F(t)$. It satisfies the equation

$$\dot{\xi} = \frac{\pi^2}{4}\xi + \frac{\pi^2}{4}(1-F) - \dot{F}\left(1 - \frac{8}{\pi^2}\right) + \Gamma(t) \tag{26}$$

To proceed, we have to specify $F(t)$. Since we follow an approach that is completely different from the literature on this point, it is illustrative to first compare with these other approaches. The usual description is to assume the chain to move in a potential, which in the first instance is taken to be quadratic in ξ. In ref 7, it was suggested to take N_e time dependent and more specifically to take this dependence as $N_e = N_e(\xi(t)) = N_e/(1 - \xi(t))$. This in fact amounts to softening the quadratic potential $^1/_8\xi^2$ to $^1/_8(\xi^2 - 2\xi^3/3)$, where we left out the factor π^2 as this can as well be absorbed by rescaling time. In ref 9 this potential was further modified leading to an even more "softened" potential, which was obtained by substituting $N_e \rightarrow N_e/(1 - \xi)^\alpha$, where α was argued to be 4/3. The value of α was retrieved using scaling arguments initially put forward by Colby and Rubinstein.[15] These scaling arguments were later questioned in ref 17. The

effective potential for general α is given by

$$V_{\text{eff}}(\xi, \alpha) = \left[\frac{1 - (1 - \xi)^{1+\alpha}(1 + (1+\alpha)\xi)}{4(1+\alpha)(2+\alpha)} \right] \quad (27)$$

where $\alpha = 1$ corresponds to the Ball–McLeish potential in ref 7 and $\alpha = 4/3$ to the Milner–McLeish potential in ref 9.

To clarify the difference between the effective potential approach of McLeish et al. and our force method, and at the same time motivate our choice of the function $F(\xi)$ appearing in eq 26, we note the following. When one considers the end of a polymer chain moving in an effective potential as given in eq 27 in conjunction with a stochastic force, it implies that the equation of motion for the chain end coordinate ξ is given by

$$\dot{\xi} = -\pi^2 \frac{\partial V_{\text{eff}}(\xi)}{\partial \xi} + \Gamma(t) \quad (28)$$

with $\Gamma(t)$ as defined below eq 25 and the factor π^2 originating from our choice of the unit of time equal to the Rouse time divided by π^2. For the case $\alpha = 1$, considered in ref 7, this amounts to the following equation of motion:

$$\dot{\xi} = -\frac{\pi^2 \xi}{4} + \frac{\pi^2 \xi^2}{4} + \Gamma(t) \quad (29)$$

We will next use these findings to motivate our choice for F. We remark that the idea of softening of the potential can easily be interpreted in terms of the force F. It boils down to taking F depending on ξ. A justification of any particular choice of $F(\xi)$ is hard to give on theoretical grounds. The situation is comparable to the status of the softened potential V_{eff}. To derive this potential from first principles, the work in refs 5 and 6 which deals with fixed entanglement networks, should be extended to include constraint release. Derivation of $F(\xi)$ constitutes a similar task. This is outside the scope of this paper and subject of further research. We therefore take a phenomenological approach which was also employed in the papers of Mcleish et al. It boils down to assuming a dependence of F on ξ, which is consistent with eq 29. It is not hard see that choosing $F(\xi) = 1 - \xi^2$ leads to the following evolution equation of motion for ξ

$$\dot{\xi} \left[1 - 2\xi \left(1 - \frac{8}{\pi^2} \right) \right] = -\frac{\pi^2 \xi}{4} + \frac{\pi^2 \xi^2}{4} + \Gamma(t) \quad (30)$$

The term between brackets on the left-hand side stems from the term with the time derivative $\dot{F}$ in eq 26. If one would ignore the $\dot{F}$ term, and hence put the term in brackets equal to 1, one obtains exact agreement with eq 29, the result of ref 7. This strongly suggests that the present description in terms of an effective tube diameter retains more details of the dynamics. In fact, we shall later see that the term in brackets leads to a natural further softening of the cubic potential $V_{\text{eff}}(\xi)$ with $\alpha = 1$. Including the extra term between brackets on the left-hand side of eq 30 leads to small differences in calculations of, e.g., the loss and storage modulus, which are experimentally well-accessible, compared to the findings in refs 7 and 9.

To interpret the choice $F(\xi) = 1 - \xi^2$, we should keep in mind the picture in Figure 3. When the chain end has retracted over a maximal distance ξ, the tube has a part of length ξ and a remaining part of length $1 - \xi$. The first tube part has diameter $a_1(t)$; the second is still narrow and has diameter a_0. If we assume that the force F equals the entropic pulling force for a chain with a tube diameter given by the average of $a_1(t)$ and a_0, that is, of
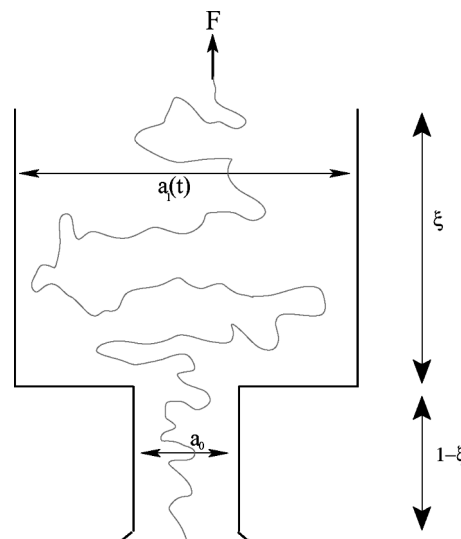
Figure 3. Tube diameter varies as a function of time. However, only the upper part of the tube has a wider diameter $a_1(t)$; the lower part still has a diameter equal to the equilibrium value a_0.

diameter $a_1(t)\xi + a_0(1 - \xi)$, we find that its size obeys

$$F(t) = \frac{a_0}{a_0(1 - \xi(t)) + a_1 \xi(t)} = [1 - \xi(t) + h(t)\xi(t)^{-1}] \quad (31)$$

where $h(t) = a_1(t)/a_0$. As we know that h should be equal to 1 when $\xi = 0$, and increases for increasing ξ, we may take the following form for $h(\xi)$

$$h(\xi) = 1 + \xi + \xi^3 + \xi^5 + \ldots = 1 + \frac{\xi}{1 - \xi^2} \quad (32)$$

The time-dependent term in this expression is odd in ξ, as one would expect from the symmetry of the fluctuations. Substitution in eq 31 yields $F(\xi) = 1 - \xi^2$.

We remark that the present approach provides an opportunity to study different kinds of tube behavior. Fitting the data to a specific functional dependence of F on ξ could provide information about the dynamics of the tube. Of course, as experimental data on varying tube widths along arms of star polymers are not available, testing against experiments is not yet possible. To see in which way predictions by effective potential models differ from the model we propose, we calculate the relaxation modulus $G(t)$ and its Fourier transform $G^*(\omega)$, which is given by

$$G^*(\omega) = 2G_0 \int_0^1 (1 - q) \frac{-i\omega\tau(q)}{1 - i\omega\tau(q)} \, dq \quad (33)$$

Once the characteristic relaxation time, i.e., the mean first passage time $\tau(q)$, is known, the relaxation moduli can be calculated. We therefore turn to the calculation of $\tau(q)$, invoking similar techniques as in section 2.

To evaluate eq 30, it is useful to introduce a new variable η defined by

$$\eta(\xi) = \int_0^\xi \left[1 - 2\xi' \left(1 - \frac{8}{\pi^2} \right) \right] d\xi' = \xi - \beta\xi^2 \quad (34)$$

Here, $\beta \equiv 1 - 8/\pi^2 \simeq 0.2$. Inverting eq 34, we obtain. Combining eqs 34 and 30, we find that η satisfies the equation

$$\dot{\eta} = -\frac{\pi^2}{4} \xi(\eta) + \frac{\pi^2 \xi^2}{4} + \Gamma(t) \quad (35)$$
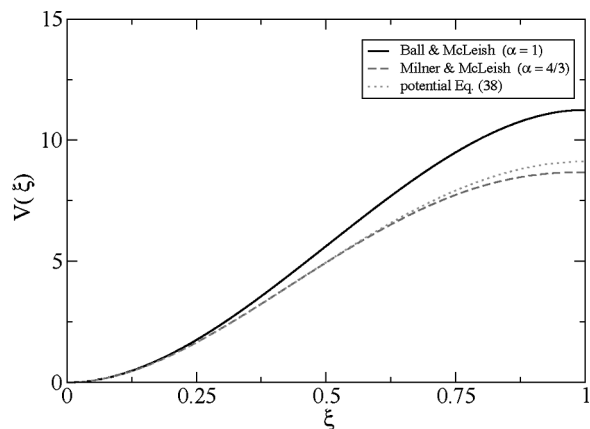
Figure 4. Mean potentials compared. The solid (black) curve corresponds to the Ball−Mcleish model, which corresponds to potential (27) with $\alpha = 1$. The dashed (red) curve corresponds to the Milner−McLeish model, corresponding to $\alpha = 4/3$. The potential given by eq 38 is the one proposed in this work.

Substituting eq 31, we can rewrite this as

$$\dot{\eta} = -\frac{1}{8\beta}\left[1 - \frac{1}{\beta}\right] + \frac{1}{8\beta}\left(1 - \frac{1}{\beta}\right)\sqrt{1 - 4\beta\eta} - \frac{\eta}{4\beta} + \Gamma(t) \quad (36)$$

According to the general theory in refs 8 and 10, this equation is associated with the following Fokker−Planck equation for the probability density function $P(\eta, t)$:

$$\frac{\partial P}{\partial t} = \pi^2 \frac{\partial}{\partial \eta}(V'(\eta)P) + \frac{\pi^2 N_e}{12N}\frac{\partial^2 P}{\partial \eta^2} \quad (37)$$

where $V'(\eta)$ is the derivative of the potential

$$V(\eta) = \frac{\eta^2}{8\beta} + \frac{1}{8\beta}\left[1 - \frac{1}{\beta}\right]\eta + \frac{1}{48\beta^2}\left(1 - \frac{1}{\beta}\right)[1 - 4\beta\eta]^{3/2}$$
$$- \frac{1}{48\beta^2}\left(1 - \frac{1}{\beta}\right) \quad (38)$$

The corresponding mean first passage time can be expressed in terms of an integral containing this potential:

$$\tau(q) = \frac{12N}{\pi^2 N_e}\int_0^{q - \beta q^2}\exp\left[\frac{12N}{N_e}V(y)\right]\int_{-\infty}^{y}\exp\left[-\frac{12N}{N_e}V(z)\right]\,dz\,dy \quad (39)$$

Note that the upper integration limit in eq 39 is shifted due to the coordinate transformation from ξ to η. We evaluate this expression numerically, and after that we may use the result to calculate the real and imaginary part of $G^*(\omega)$, the so-called storage and loss modulus, respectively. E.g., the loss modulus is given by the expression

$$G''(\omega) = 2G_0\omega\int_0^1\frac{(1 - q)\tau(q)\,dq}{1 + \omega^2\tau^2(q)} \quad (40)$$

In Figure 4 we present the potentials that correspond to the different models. We find that our model leads to a potential that is in between the Ball−McLeish and Milner−McLeish result, so it predicts a softening of the cubic potential, but slightly less than that obtained by setting the exponent $\alpha = 4/3$ in eq 27. The difference in the potentials is, of course, also reflected in the $\tau(q)$
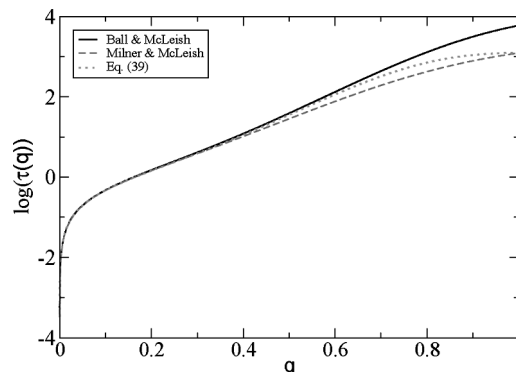

Figure 5. Mean first passage time for the three different models. The solid (black) curve corresponds to the Ball−McLeish model and the dashed (red) curve is the Milner−McLeish result, whereas our result is the dotted (blue) curve.

curves that are depicted in Figure 5. The same coding is used in all figures, so the solid (black) curve is the $\alpha = 1$ theory, which in our approach is retrieved when putting the term multiplying ξ in eq 26 equal to one; the $\alpha = 4/3$ result is represented by the (red) dashed curve, and the (blue) dotted curve corresponds to our numerical calculation of the integral in eq 39. Our result coincides with the solid curve for small q, but for q close to one it approaches the $\alpha = 4/3$ curve. This suggests that our approach leads to a natural interpolation between the solutions obtained in refs 7 and 9.

In Figure 6 we present the numerically obtained results for the loss (left) and storage (right) moduli G' and G'', respectively. For small $\omega\tau$ we find that all three models yield the same slope for $G''(\omega)$; however, the dashed curve is slightly shifted to the right compared to the dotted curve. The fact that the $\alpha = 4/3$ curve had to be shifted over a distance 0.3 in a log−log plot of $G''(\omega)$ versus $\omega\tau$ in order to find correspondence with the experimental data of ref 14 was already noticed in ref 9 but remained so far unexplained. As the blue dotted curve, corresponding to our explicit tube dilution picture, is shifted over precisely this distance, this suggests that this effect may indeed have a physical cause and is related to the term multiplying ξ in eq 30. We further note that for higher frequencies the loss modulus rapidly drops for all three models. This is because the model loses its validity for very short times. This is clearly recognized in our derivation, as for short times we should have taken all modes in account. In ref 9 the high-frequency regime was treated as a simple Rouse motion of the chain, and an interpolating expression for the mean first passage time was constructed. Here, we will not consider the high frequencies, as we could adopt a procedure similar to the one followed in ref 9 to obtain agreement with experimental results also in this frequency regime. Since the mean first passage time would then be the same for all models, this would not lead to different results for the three models compared here. The storage modulus depicted in Figure 6 displays much less interesting behavior. All three curves look rather similar.

Discussion

We have investigated stress relaxation in star polymers and developed a model with varying tube diameter. The proposed model gives an analytic expression for the mean first passage time of the chain retracting over a certain fraction of the tube length. The mathematical derivation clearly reveals the assumptions underlying this theory. This is in contrast to models earlier published in the literature, which were formulated in terms of potentials. The loss and storage moduli were calculated and compared with the results of the existing models. We find that our model offers a natural explanation for the softening of the potential as introduced by Ball and McLeish. Our model also
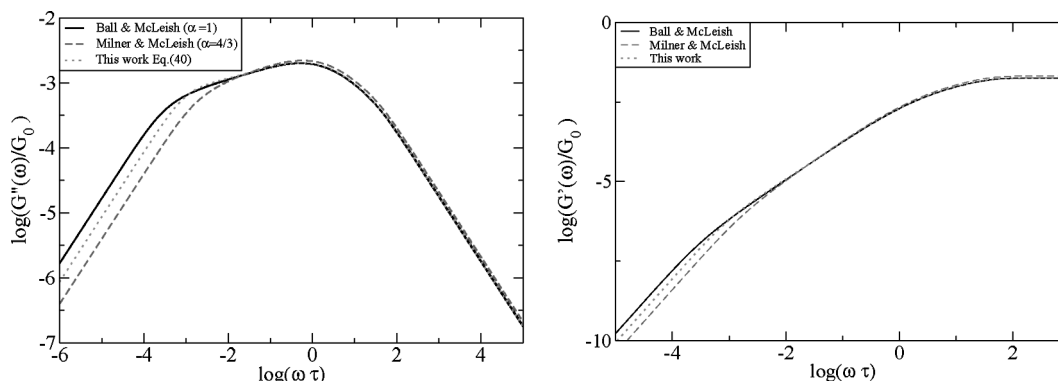
Figure 6. Mean loss (left) and storage (right) moduli $G''(\omega)$ and $G'(\omega)$ calculated by the present model (blue dots). For comparison, also results for the model by Ball−McLeish ((black) solid lines) and Milner−McLeish ((red) dashed curves) are given. In all cases the value $N/N_e = 17$ is used, in correspondence with the value of refs 7 and 9.

provides a natural explanation for the shift with a factor 0.3 that was necessary in the work of Milner and McLeish to get agreement with the experimental data.

The most important consequence of the work presented here is that we have demonstrated that a better mathematical justification of the theory of relaxation of star polymers, as has been earlier developed, is possible. Our work gives insight into the approximations made and a direct interpretation in terms of tube that has a varying diameter. In our work we relied on phenomenology and consistencies with earlier works to derive the form of the function F. For chains in a tube with constraint release no derivations or numerical simulations exist that allow one to determine the retraction potential. This open question is still subject of further research. Possibly generalizations of the model proposed by Khalliulin and Schieber could offer a way out.

We further like to stress that the model we propose here can be easily generalized to the theory to tethered chains. The dynamics of tethered chains resembles that of star polymers but differs from it in an important respect: the environment. Star-shaped molecules in solution are generally surrounded by other star-shaped molecules that *cannot use reptation* as a relaxation mechanism. This in contrast to tethered polymers, which are mostly surrounded by bulk molecules that *can reptate*. Another difference is that chains tethered to a wall are in general shorter than the polymer chains in the bulk, whereas in monodisperse star-shaped molecules in a melt all arms are considered to have the same length. These differences notwithstanding, the two species of polymers—stars and tethered chains—have much in common as far as their relaxation mechanism is concerned, since in both

species constraint release plays an important role to relax polymer stress. Therefore, application of the present theory to tethered chains will be the topic of future investigations.

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