Nonequilibrium tube length fluctuations of entangled polymers

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Abstract

We investigate the nonequilibrium tube length fluctuations during the relaxation of an initially stretched, entangled polymer chain. The time-dependent variance $\sigma^2$ of the tube length follows in the early-time regime a simple universal power law $\sigma^2 = A\sqrt{t}$ originating in the diffusive motion of the polymer segments. The amplitude $A$ is calculated analytically both from standard reptation theory and from an exactly solvable lattice gas model for reptation and its dependence on the initial and equilibrium tube length respectively is discussed. The non-universality suggests the measurement of the fluctuations (e.g. using fluorescence microscopy) as a test for reptation models.

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The most successful framework for the theoretical understanding of systems of entangled polymers is the reptation theory developed by de Gennes, Edwards and Doi \[1,2\]. One imagines the large-scale motion of an entangled flexible polymer as being confined to a tube which, loosely speaking, is the sequence of pores occupied by the polymer chain within the entanglement “network”, made up by the surrounding polymer chains. The motion of the polymer transverse to the tube direction is strongly suppressed due to the topological constraints imposed by the surrounding polymers. However, mass transport along the tube is possible by diffusion of “defects”, i.e., folded polymer segments stored within the pores. The result of these dynamics is a snakelike random motion where polymer segments may retract into the existing tube at its ends (hence effectively shortening it) and subsequently diffuse into a new neighboring pore (hence stretching the tube and changing the tube contour at the end), while the bulk of the tube does not change its shape. Because of the defects the fluctuating equilibrium tube length $\Lambda^*$ is less than the actual polymer length $M$ of a fully stretched chain.

The basic notions of this picture have been verified experimentally, see \[3\] for the measurement of the entanglement distance $\delta$ implied in the tube concept, and \[4,5\] for the role of the surrounding chains as topological constraints. Also extensive molecular dynamics simulations confirm the reptation model \[3\]. The theoretical status of some dynamical consequences, however, remains rather unsatisfactory, a well-known example being the scaling behavior of the viscosity $\eta \propto M^\kappa$ for long flexible chains. Doi has suggested that the discrepancy between the empirical dependence $\kappa \approx 3.4$ and the reptation result $\kappa = 3.0$ be due to equilibrium tube length fluctuations \[4\], but this explanation has not remained unchallenged \[8,9\]. To this one may add that also the mass dependence of the effective exponent $\kappa$ obtained by Doi appears to be rather severe \[10\]. Since within the Doi picture such fluctuations alter also other observable quantities through a modification of relaxation times (in particular, the tube renewal time) we wish to address the question to which extent standard reptation theory with underlying Rouse dynamics for individual polymer segments provides a proper description of tube length fluctuations. Inspired by the fact that with present experimental techniques it is possible to observe and measure the nonequilibrium tube relaxation process for single entangled polymer chains \[5\], we go beyond the older equilibrium
analysis of Refs. [8,9] and calculate here the time-dependent variance of the tube length under far-from-equilibrium initial conditions mimicking those prepared experimentally.

The direct observation of the reptation dynamics was achieved in a series of remarkable experiments by Perkins et al. who have studied entanglement effects in a dense solution of long λ-phage DNA strands using fluorescence microscopy [5]. Attaching a polystyrene bead to one end of fluorescence-marked DNA molecule (entangled in a background of unmarked DNA) and pulling the bead with optical tweezers the DNA was brought into a nonequilibrium conformation with an elongated contour directly visible under a microscope. Since this contour describes the coarse-grained path of the polymer chain it may be identified with the tube. After stopping the bead the contour started to contract along its own path (i.e., the tube) as predicted by the reptation model. Since the bead was larger than the estimated entanglement distance it could not move and the contraction occurred only at the opposite free end of the DNA chain. Since the DNA chain used in the experiment was very long (about 160 times its Kuhn length) it may be regarded as sufficiently flexible to use reptation theory as an approximation to study its tube dynamics. In [11] we showed that within an universal initial time regime (but after a very short transient relaxation process) the measured tube length contraction is in agreement with the predictions from both standard reptation theory and an exactly solvable lattice gas model for reptation, related to the Verdier-Stockmeyer model [12] and the repton model of Rubinstein [13].

In order to calculate fluctuations of the tube length from reptation theory we recall that within the underlying Rouse theory a polymer chain with bond length \( b \) is assumed to consist of \( N = M/b \) frictional units, called Rouse segments, which are connected by harmonic springs with mean square separation \( b^2 \). By not considering the actual position of the polymer in the network but focusing only on the contour length \( \Lambda \) of the tube the reptation dynamics may be cast in a Langevin equation [14]

\[
\zeta \frac{\partial}{\partial t} s(x, t) = \frac{3k_BT}{b^2} \frac{\partial^2}{\partial x^2} s(x, t) + f(x, t)
\]

for the position \( s(x, t) \) of the Rouse segments in the tube. Here \( \zeta \) is the friction constant of the Rouse segments and \( T \) is the temperature. Randomness is accounted for by a delta-correlated Gaussian random force \( f(x, t) \) with zero mean and \( \langle f(x, t)f(x', t') \rangle = 2\zeta kT \delta(x-x')\delta(t-t') \). By definition the mean tube length is given by \( \Lambda(t) = \langle s(N, t) - s(0, t) \rangle \). In the
experimental set-up considered above the position of one end is kept fixed. Hence we have
to solve (1) with boundary conditions \( s(0, t) = 0 \) and the entropic tensile force \( s'(x, t) = f_e \)
at \( x = N \) for all time \( t > 0 \). The entanglement distance \( \delta \) enters only indirectly in so far as
\( M \gg \delta \gg b \) is assumed. In the absence of noise (1) has the equilibrium solution \( s^*(x) = x f_e \). This yields the mean equilibrium tube length \( \Lambda^* = N f_e \).

In order to study the tube length dynamics it is convenient to consider \( \tilde{s}(x, t) = s(x, t) - s^*(x) \) and to introduce the inverse time scale \( w = 3k_B T/\zeta b^2 \). Solving first for
the homogeneous equation with \( f = 0 \) and then incorporating the special solution of the
inhomogeneous equation we obtain the full solution of the initial value problem

\[
\tilde{s}(x, t) = \sum_{n=-\infty}^{\infty} e^{-wp_n^2 t} \sin p_n x \times 
\left[ \tilde{u}_n(0) + \frac{1}{\zeta} \int_0^t d\tau \ g_n(\tau) e^{wp_n^2 \tau} \right]
\]

with the Rouse “momenta” \( p_n = \pi(2n + 1)/(2N) \), the sine transform \( \tilde{u}_n(0) = 1/N \int_0^N dy \sin (p_n y) \tilde{s}(y, 0) \) of the initial data and the sine transform \( g_n(\tau) \) of the noise
term \( f(x, \tau) \). For homogeneous initial stretching with initial tube length \( \Lambda_0 \) one has
\( \tilde{s}(y, 0) = (\Lambda_0 - \Lambda^*) y/N \) and obtains the mean non-equilibrium tube length

\[
\Lambda(t) = \Lambda^* + (\Lambda_0 - \Lambda^*) \frac{8}{\pi^2} \sum_{n=0}^{\infty} e^{-(2n+1)^2 t/(4\tau_R)} \frac{1}{(2n + 1)^2}.
\]

with the Rouse time \( \tau_R = N^2/(w\pi^2) \). At early times \( t \ll \tau_R \) one finds a universal power law behavior \( \Lambda(t) = \Lambda_0 - 2(\Lambda_0 - \Lambda^*)/\pi^{3/2} \sqrt{t/\tau_R} \) [11]. The origin of the scaling exponent 1/2 is the diffusive motion of the polymer segments. The reduced relaxation function \( \Delta_1(t) = (\Lambda_0 - \Lambda(t))/(\Lambda_0 - \Lambda^*) \) depends only on time.

The tube length fluctuations are determined by the noise term in (2). Specifically for
the variance \( \sigma^2(t) = \langle s^2(N, t) \rangle - \langle s(N, t) \rangle^2 \) one finds

\[
\sigma^2(t) = \frac{Nb^2}{3} \left( 1 - \frac{8}{\pi^2} \sum_{n=0}^{\infty} \frac{e^{-(2n+1)^2 t/(2\tau_R)}}{(2n + 1)^2} \right).
\]

In the prefactor one recognizes the well-known reptation result \( \sigma^2 = Nb^2/3 \) in equilibrium [2]. We point out that the amplitude depends neither on the initial stretching, i.e. on
\( \Lambda_0 \), nor on the equilibrium tube length \( \Lambda^* \). The term in the brackets yields the growth of fluctuations due to the randomness of the time evolution. At early times
\[ \sigma^2(t) = \sigma^* \frac{2\sqrt{2}}{\pi^{3/2}} \sqrt{\frac{t}{\tau_R}} \]  \hspace{1cm} (5)

which - not surprisingly - exhibits the same universal power law dependence as the tube length relaxation. Defining in analogy to the reduced relaxation function the quantity \( \Delta^2(t) = \sigma^2(t)/\sigma^*^2 \) we note the relation \( \Delta^2(t) = \Delta^1(2t) \) and, for early times, the simple relaxation ratio

\[ \frac{\Delta^2(t)}{\Delta^1(t)} = \sqrt{2} \]  \hspace{1cm} (6)

which does not contain any parameters of the Rouse-based reptation theory. This feature is characteristic for universal amplitude ratios not uncommon in scaling theory, but - as shown below - here it is an artefact of the reptation model.

The result (3) for the tube length relaxation has been recovered within a lattice gas approach in which the reptation dynamics are described by the center of mass motion of \( L = M/\delta \) individual polymer segments (reptons) of unit length \( \delta \) which we take as the experimentally accessible mean entanglement distance in the melt or dense solution [11].

The continuous diffusive motion within the tube is modelled by a random hopping of these segments between consecutive pores with an exponential waiting time distribution with mean \( \tau_0 \). This elementary time scale is the mean first passage time of the motion of one repton to a neighboring pore of the tube. To describe the interaction of the polymer with the network and with itself we impose the constraint that the consecutively labeled reptons may not pass each other within the tube. End reptons may move freely to new pores but are of course not allowed to detach from the polymer.

We assign the label ‘particle’ to a repton that connects two neighboring pores and the label ‘hole’ to a repton that is fully contained in a pore, i.e., to a “defect” in the language of de Gennes (Fig. 1). The diffusion of the defects then corresponds to particle-hole exchange with rate \( 1/(2\tau_0) \), i.e. to particle hopping along the chain with hard-core on-site repulsion. The end-point dynamics of the tube correspond to injection and absorption of particles at the boundaries. These dynamics are equivalent to the well-known one-dimensional symmetric exclusion process with open boundaries [15]. In contrast to Verdier/Stockmeyer [12] and Rubinstein resp. [13] we treat one boundary of the particle system (representing the free end of the polymer chain) as connected to a reservoir of fixed density \( \rho^* = \Lambda^*/M \) from which
particles are injected with rate \( \alpha = \rho^*/(2\tau_0) \) and absorbed with rate \( \gamma = (1 - \rho^*)/(2\tau_0) \). The fixed end is described by a reflecting boundary with no particle exchange. We stress that the treatment of noise in this approach is rather different from the assumptions inherent in the Langevin description \([1]\). In particular, because of particle interactions in the lattice gas the noise depends on the local hole ("defect") density and hence implicitly on \( \rho^* \) which determines the equilibrium particle density.

In this mapping the mean tube length is given by \( \Lambda = \delta \langle N \rangle \) where \( N = \sum_k n_k \) is the total number of particles on the lattice and \( n_k = 0, 1 \) is the particle number on site \( k \). Correspondingly, \( \sigma^2 = \delta^2(\langle N^2 \rangle - \langle N \rangle^2) \) where averages are taken over many realizations of the stochastic dynamics, starting from some given nonequilibrium initial distribution of tube lengths. An initially fully stretched polymer chain corresponds to an initially fully occupied lattice. The Markov generator of this stochastic lattice gas is known as the quantum Hamiltonian of the spin-1/2 ferromagnetic Heisenberg chain with boundary field. This is an integrable model which can be fully solved by a dynamical matrix product ansatz \([16]\), similar in spirit to the algebraic Bethe ansatz. The defect diffusion as described by the exclusion process is the classical analog of the quantum spin waves in the Heisenberg ferromagnet and one obtains expressions for expectation values \( \langle n_{k_1}(t) \ldots n_{k_r}(t) \rangle \) in terms of sums over Bethe wave functions \([17]\). Since we are interested in the early time regime \( t \ll \tau_R \) during which the bulk conformation remains unchanged we may treat both boundaries separately. The tethered end of the chain (caught up in the entanglement) does not contribute to the dynamics and the particle number fluctuations induced by the free end can be calculated by taking the thermodynamic limit \( L \to \infty \). The Bethe sums then turn into integrals over pseudomomenta (the analogues of the Rouse modes).

The calculation of the local density \( \rho_k(t) = \langle n_k(t) \rangle \) and hence of \( \Lambda(t) \) reduces to the solution of a relatively simple random walk problem \([11]\) and one finds \( \rho_k(t) = 1 - (1 - \rho^*) [1 - \sum_{m=1}^{2k} \exp(-t/\tau_0) I_{k-m}(t/\tau_0)] \). Here \( I_k(x) \) are the modified Bessel functions. By identifying \( w = 1/(2\tau_0) \) one recovers the Rouse result \([3]\) in the regime \( \tau_0 \ll t \ll \tau_R \).

The calculation of the variance requires the knowledge of the two-point correlation function \( C_{k,l}(t) = \langle n_k(t)n_l(t) \rangle - \langle n_k(t) \rangle \langle n_l(t) \rangle \) from which one obtains \( \sigma^2 = \delta^2[\sum_k \rho_k(t)(1 - \rho_k(t)) + 2 \sum_k \sum_{l>k} C_{k,l}(t)] \). Computing the correlation function from the Bethe wave function...
yields after some manipulations the exact expression

\[ C_{k,l}(t) = F_{k+l-1,k-l}(t/\tau_0) + F_{k+l,k-1+l}(t/\tau_0) - F_{k-l-1,k+l}(t/\tau_0) - F_{k-l,k+l+1}(t/\tau_0) \]  

(7)

with

\[ F_{m,n}(x) = -\frac{4(1 - \rho^*)^2}{\pi} \int_0^{\pi/2} d\theta \cos \theta \int_0^x dv e^{2v\cos^2 \theta} \times \]

\[ e^{-2x} I_m(2(x - v) \cos \theta) \cos [v \sin (2\theta) + n\theta]. \]  

(8)

Taking the Laplace transform of this expression, summing over the lattice indices and expressing the result in terms of elliptic integrals finally yields the asymptotic law \((\tau_0 \ll t \ll \tau_R)\)

\[ \sigma^2(t) = \sigma^*^2 g(\rho^*) \frac{2\sqrt{\pi t}}{\tau_0^{3/2}} \]  

(9)

with the equilibrium variance \(\sigma^*^2 = \delta^2 L\rho^*(1 - \rho^*)\) of the lattice gas model and \(g(\rho^*) = 1 + (1 - \rho^*)(3 - 2\sqrt{2})/\rho^*\). The details of the rather lengthy calculation will be presented elsewhere \[18\]. From (9) we recover the expected scaling exponent of the growth of fluctuations in time. However, considering a different initial conformation \[18\] reveals that unlike in the standard reptation approach the amplitude depends not only on equilibrium quantities, but also on the initial tube length. Furthermore, the relaxation ratio of the fully stretched chain

\[ \Delta_2(t)/\Delta_1(t) = g(\rho^*) \]  

(10)

turns out to be a non-universal function depending on the equilibrium defect density \(1 - \rho^* = 1 - \Lambda^*/M\) (Fig. 2).

Our main results are the establishment of the universality of the tube length relaxation exponent, the proof of nonuniversality of the relaxation ratio \(g\), and the unexpected lack of dependence on initial conditions of the amplitude of the variance \(\sigma^2(t)\) in standard reptation theory. While the lattice gas is a phenomenological model as is standard reptation theory, it is somewhat more microscopic in nature. Unlike the bead-spring model underlying \[1\] it incorporates the impossibility of stretching the polymer chain and therefore lacks the physically problematic parameter \(b\). Hence we believe the master equation describing the
lattice gas dynamics to be more trustworthy than its coarse-grained Langevin counterpart. This view is confirmed by the amplitude of the tube length fluctuations which vanish in the lattice gas description for vanishing equilibrium defect density $1 - \rho^*$ as they must for a chain without defects (whose motion at the boundaries is responsible for the tube length fluctuations). In standard reptation theory the amplitude turns out to be unrelated to the defect density which points to a conceptual flaw in the treatment of the fluctuations. We conclude that the earlier notion that a significant modification of the equilibrium fluctuation theory is required extends to non-equilibrium dynamics, in particular, to the treatment of noise. Our lattice gas approach suggests that one should incorporate the entropic tensile force in the noise amplitude (via multiplicative noise) in order to capture the effect of chain connectivity.

We remark that the experimental data of Ref. [5] are not suitable for a quantitative comparison with our results. On a qualitative level, however, they lend support to the small magnitude of the theoretical expression (8). In similar experiments specifically designed for the purpose of measuring tube length fluctuations, the model dependence of this quantity may serve as a test for the reliability of reptation models.

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Figure captions:

Fig. 1: Reptation dynamics in terms of the symmetric exclusion process. The polymer conformation in the tube (of diameter $d \approx \delta$) is divided into twelve segments of length $\delta$ occupying six pores corresponding to the particle configuration $A0A00A4000A0$ (from left to right).

Fig. 2: Exact relaxation ratio $g(\rho^*)$ calculated from the symmetric exclusion process. The constant at $g = \sqrt{2}$ is the standard reptation result.
Fig. 1
Fig. 2