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# Non-equilibrium relaxation law for entangled polymers

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**Abstract.** – We study the far-from-equilibrium relaxation of an initially stretched, entangled polymer by using an exactly solvable lattice gas model for reptation. Over a significant time range, including an initial universal power law regime, the predicted tube length relaxation is in very good agreement with experimental data for the relaxation of DNA. Experimental evidence and theoretical arguments suggest an observed systematic long-time deviation to be due to entanglement fluctuations. This view is confirmed by the analysis of an extension of the lattice gas model which appears to be a reliable foundation for further study of reptation dynamics.

In the framework of reptation theory [1] one imagines the large-scale motion of an entangled polymer as being confined to a tube which, loosely speaking, is the sequence of pores in the entanglement network occupied by the polymer chain. The motion of the polymer transverse to the tube direction is strongly suppressed due to the topological constraints imposed by the surrounding network. However, mass transport along the tube is possible by diffusion of stored length. 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 [2]. Traditionally, quantities such as the diffusion coefficient, the viscosity or the drift velocity in the presence of an electric field of entangled polymers have been measured as averages over ensembles of many polymers, by and large confirming the reptation picture. With recent technological advances the investigation of single polymer chains has become possible using flourescence microscopy [3, 4] and thus a direct experimental verification of some of the key assumptions of reptation theory could be achieved.

Nevertheless, there is still a number of rather perplexing open problems including the molecular weight dependence of the viscosity (where theoretical and experimental results are at variance), the influence of disorder, and dynamical properties of reptating polymer chains. In order to obtain a clear picture of the role of the many different factors determining the behaviour of entangled polymers it is tempting to try to address some of these questions by using simple model systems which capture the essential mechanisms of reptation and then to

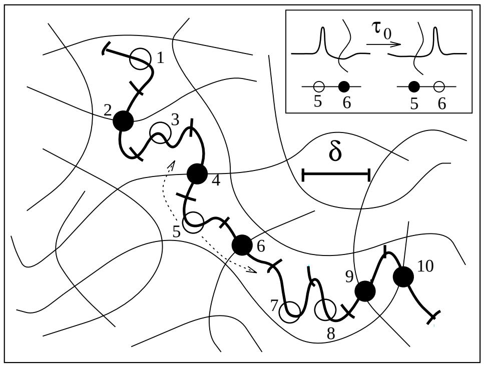

Fig. 1. – Reptation of an entangled polymer in the confining tube and mapping to the symmetric exclusion process. Polymer segments ("reptons") $1, \ldots, L = 10$ with a size of the mean entanglement distance $\delta$ move diffusively to neighboring pores. Segments connecting two consecutive "pores" of the surrounding network correspond to particles (full circles), segments fully contained in a pore correspond to vacancies (empty circles). Inset: Diffusion within the tube with rate $1/\tau_0$ to the right amounts to particle-hole exchange since repton 5 becomes a connecting segment (particle), while repton 6 becomes fully contained in the pore (vancancy). The motion of repton 1 to a neighboring pore would extend the tube and correspond to creation of a particle.

add to such models more refined details if experimental evidence necessitates improvement. The increasingly popular lattice gas approach to determine stationary properties of reptating polymers employs this strategy. Numerous interesting new predictions have been made in recent years using this method [5-10].

Not much is known about the quantitative reliability and accuracy of such models, which contribute to the uncertain status of some of the results obtained in this way in the past. However, numerical simulations [11] of the stationary properties of lattice gas models suggested by Rubinstein [12] and Duke [13] have shown to give excellent agreement [14] of the average drift velocity of polymers in an electric field with experimental data obtained from DNA gel electrophoresis [15]. In a similar spirit we introduce here an analytically tractable model for reptation and propose to extend the lattice gas treatment also to derive *time-dependent* properties of reptation rather than the traditional simulation of stationary and equilibrium quantities. This idea allows us to obtain the relaxation function of single stretched polymer chains under entanglement conditions. Together with predictions from standard reptation theory we are then in a position to make a first full quantitative analysis of the experimental data of Perkins *et al.* [4] for the relaxation of stretched DNA and at the same time to examine the merit of modelling time-dependent properties of entangled polymers by simple lattice gases.

In equilibrium an entangled polymer is not fully stretched but a certain amount of excess mass is stored inside the tube, hence giving rise to a fluctuating equilibrium tube length $\Lambda^*$ less than the actual polymer length $M$. Even though this tube is a rather theoretical construct, the implied tube diameter, *i.e.* the mean entanglement distance $\delta$, has been measured in neutron scattering experiments [16]. Indeed, the tube may be seen as a coarse-grained polymer contour and hence be identified with the experimentally observable visual contour of flourescence-marked polymer chains.

To describe reptation dynamics we consider the center of mass motion of $L = M/\delta$ individual polymer segments (reptons) of unit length $\delta$ (fig. 1). The continuous diffusive motion within the tube can be described by a random hopping of these segments between consecutive pores with an exponential waiting time distribution over a time unit $\tau_0$ which is the mean first passage time of the motion of one repton to a neighboring pore of the tube. We stress that in this description of the dynamics along the tube backbone a "hopping event" is defined as the first passage of a repton to its neighboring pore *along the tube*, independently of what happened between two consecutive hopping events. This eliminates the unphysical requirement that bulk polymer units may not (temporarily) move transverse to the tube direction by developing microscopic, transient hernias. To describe the interaction of the polymer with the network and with itself we impose the weaker 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.

By assigning 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 these dynamics become equivalent to the well-known one-dimensional symmetric exclusion process with open boundaries [18]. Each of the $L$ lattice sites can be occupied by at most one particle. The diffusion of stored length corresponds to particle-hole exchange with rate $1/\tau_0$, *i.e.* to particle hopping along the chain. In this mapping the tube length is given by $\Lambda = N\delta$, where $N$ is the total number of particles on the chain. The end-point dynamics of the tube correspond to injection and absorption of particles at the boundaries as if the particle system was connected to a reservoir of fixed density $\rho^* = \langle N \rangle^*/L = \Lambda^*/M$, where particles are injected with rate $\alpha = \rho^*/\tau_0$ and absorbed with rate $\gamma = (1-\rho^*)/\tau_0$. We note that for both ends free and the particular choice $\rho^* = 1/2$ the tube dynamics are then given by the Verdier-Stockmayer model restricted to one-dimensional polymer motion [19]. In the experimental set-up discussed below, one end of the chain is kept fixed in the network. This is described by one reflecting boundary with no particle exchange. An initially fully stretched polymer chain corresponds to an initially fully occupied lattice. The particle number $N(t)$ yields the tube length at time $t$.

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 [20], similar in spirit to the algebraic Bethe ansatz. We consider here the relaxation function

$$R(t) \equiv \frac{\Lambda(t) - \Lambda^*}{\Lambda_0 - \Lambda^*} = \frac{\langle N(t) \rangle - \langle N \rangle^*}{\langle N \rangle_0 - \langle N \rangle^*}\,, \tag{1}$$

which depends only on $L$ and $\tau_0$. The density dynamics are obtained from the solution of a lattice diffusion equation with one reflecting and one absorbing boundary. For a homogeneously stretched polymer of averaged initial tube length $\Lambda_0 = \langle N_0 \rangle \delta$ one obtains the exact expression

$$R(t) = \frac{1}{L(2L+1)} \sum_{n=0}^{L-1} \cot^2\left(\frac{p_n}{2}\right) e^{-\epsilon_n t/\tau_0} \tag{2}$$

with $p_n = \pi(2n+1)/(2L+1)$ and the inverse relaxation times $\epsilon_n = 2(1-\cos p_n)$.

It is interesting to compare this result with the corresponding quantity obtained from continuum reptation theory [17]. Within Rouse theory a polymer chain with bond length $b$ is assumed to consist of $M/b$ 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 focussing only on the contour length $\Lambda$ of the tube the reptation dynamics may be cast in a Langevin equation [17]

$$\zeta \frac{\partial}{\partial t} s(x,t) = \frac{3kT}{b^2} \frac{\partial^2}{\partial x^2} s(x,t) + f(x,t) \tag{3}$$

for the position $s(x,t)$ of the Rouse segments in the tube and $\Lambda(t) = s(M/b,t) - s(0,t)$. Here $\zeta$ is the friction constant of the Rouse segments and $T$ is the temperature. Randomness is accounted for by the Gaussian delta-correlated random force $f(x,t)$ with moments $\langle f(x,t) \rangle = 0$ and $\langle f(x,t)f(x',t') \rangle = 2\zeta kT\delta(x-x')\delta(t-t')$. The equilibrium tube length fixes $s'(x,t) = \Lambda^*$ at the boundaries $x = 0$ and $x = M/b$. In this approach the entanglement distance $\delta$ enters only indirectly in so far as $M \gg \delta \gg b$ is assumed.

Generally, a coarse-grained Langevin description obscures the precise nature of the interactions —in the present case between polymer segments and with the network— and there is no *a priori* reason to expect identical results to those obtained from the somewhat more microscopic lattice gas approach. Yet, solving (3) with the appropriate boundary conditions yields the $\delta \to 0$ limit (with $M = L\delta$ fixed) of (2), where $\tau_0/\delta^2 = \zeta/(3kT)$ is related to the friction constant $\zeta$ of the Rouse segments. In the $\epsilon_n$ one recognizes the lattice analogues of the Rouse modes. We arrive at the conclusion that the symmetric exclusion process represents an exactly solvable lattice gas model for reptation.

From the correspondence to the Verdier-Stockmayer model this agreement is not unexpected, but given the rather different salient features of the two approaches it is quite remarkable and encouraging as it indicates a certain robustness of predictions of reptation theory with respect to the precise realization of the process. For early times in the range $\tau_0 \ll t \ll t^*$ with the crossover time $t^*$ defined by $R(t^*) = 1/2$, we obtain from (2) the universal relaxation law

$$R(t) = 1 - \frac{4}{\pi^{3/2}}\sqrt{\frac{t}{\tau}}\,, \tag{4}$$

where the Rouse relaxation time $\tau = 4M^2\tau_0/(\pi^2\delta^2)$ is the only fitting parameter.

The relaxation of an initially stretched entangled DNA has been measured by the observation of the visual length of a single flourescence-marked DNA strand moving in a dense, monodisperse solution of shorter, unmarked DNA [4]. The DNA was prepared in a stretched initial conformation by attaching a polystyrene bead to one end and pulling it with optical tweezers through the solution which provides the entanglement network. After some time the bead is stopped and the relaxation of the attached DNA is recorded with a video camera. Before comparing the theoretical predictions (2), (4) to the data presented in fig. 4 of ref. [4], the experimental conditions must be examined. i) As pointed out by Perkins *et al.*, the DNA test chains are much longer than Kuhn length (0.12 micron) and hence the polymer may be regarded as flexible. ii) From the density of the solution (12 DNA molecules per $\mu$m$^3$) we can estimate the entanglement distance $\delta$ to be roughlyly 0.5 micron. iii) According to Perkins *et al.*, the perturbation of the network by the bead (which has a diameter of 1 $\mu$m) relaxes to equilibrium after a time $t_0$ of less than one second. Until that time the DNA relaxes essentially freely and hence comparison with predictions from reptation theory become meaningful only for times larger than $t_0$. iv) After long times (of the order of 10 seconds) a bulk deformation of the polymer contour is clearly seen. Since the entanglement by the background DNA strands in the solution does not form a rigid network with fixed crosslinks but a fluctuating and reptating structure by itself, constraint release of the surrounding network appears to be a likely cause for this deformation. As a result, the experimentally observable equilibrium length $\tilde{\Lambda}^*$ is not identical to the hypothetical tube length $\Lambda^*$ that would result from a rigid network. Network fluctuations are captured neither in the continuum approach nor in the lattice gas model as described above, but require additional input, see below.

These difficulties have little effect on the determination of the crossover time $t^* \approx 2.2$ s which limits the range of validity of the power law regime (4). On a double logarithmic plot of the experimental data for $1-R(t)$ *vs.* $t$ one observes a marked deviation from linear behaviour for the measurements taken at less than 0.5 s. This is consistent with the observation that only after a time of somewhat less than a second reptation sets in. Hence in what follows we shall take $t_0 = 0.5$ s as initial time and the corresponding measured length $\Lambda_0 \approx 12$ $\mu$m as

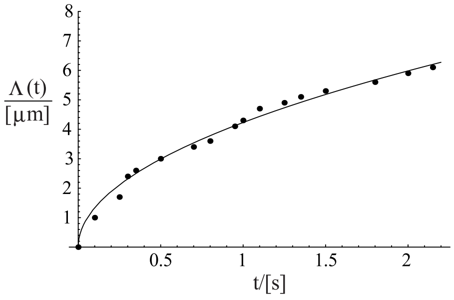

Fig. 2

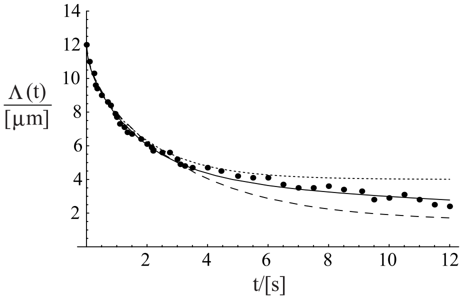

Fig. 3

Fig. 2. – Relaxation of the visual length of an initially stretched DNA. The full curve shows the power law increase of $\Delta(t) = \Lambda_0 - \Lambda(t)$ as a function of time as predicted from eq. (4). The dots are experimental data taken from fig. 4 of ref. [4] in the range $t_0 = 0.6$ s $\leq t \leq 2.8$ s. The time is measured relative to $t_0$ where reptation sets in.

Fig. 3. – Experimental relaxation data $\Lambda(t)$ as a function of time taken from fig. 4 of ref. [4] in the range 0.6 s $\leq t \leq$ 12 s (dots) and theoretical predictions from the lattice gas model. The pure reptation prediction (3) with hypothetical tube length $\Lambda^* = 4$ $\mu$m (dotted curve) and $\Lambda^* = 1.5$ $\mu$m (dashed curve) respectively show a systematic deviation at long times. The full curve shows the prediction from (3) with the effective time-dependent quantity $\Lambda^*_{\text{eff}}$.

initial tube length for reptation. Figure 2 shows good agreement between the predicted initial power law behaviour of the relaxation function (4) and the experimental data of Perkins *et al.* The only adjustable parameter is the combination $(\Lambda_0 - \Lambda^*)/\sqrt{\tau} \approx 5.9(1)$ $\mu\text{m}/\sqrt{\text{s}}$.

Now we turn to a discussion of the intermediate and long-time regime which requires an investigation of the role of $L$. The estimated experimental entanglement distance implies $L > 20$ for the DNA test chain. A more precise determination is not necessary as in this regime the explicit $L$-dependence of (2) written in terms of the Rouse relaxation time $\tau$ is very weak. On the scale of fig. 3 below curves for $L = 60$ and those shown for $L = 20$ would not be distinguishable and both lie well within the experimental fluctuations. The full range of data points is shown in fig. 3, together with the theoretical prediction (2) of the lattice gas model for two values of the additional fitting parameter $\Lambda^*$. One finds very good agreement beyond $t^*$, however, after a time of $4 \ldots 6$ s a systematic deviation appears.

Network fluctuations leading to constraint release and a possible creation of new topological constraints can be accounted for in the lattice gas approach by allowing for local particle annihilation and creation processes. Such processes which lead to an exponential relaxation of the local particle density [21] mimic the disappearence and emergence of pores by the reptation of the surrounding network. This process takes place on the long time scale of the tube renewal time of the network strands. Therefore, we may use an adiabatic approximation which leads to an exponential relaxation of the effective asymptotic tube length $\Lambda^*_{\text{eff}} = \tilde{\Lambda}^* + (\Lambda^* - \tilde{\Lambda}^*)e^{-t/\tilde{\tau}}$ from its hypothetical value $\Lambda^*$ to the experimental value $\tilde{\Lambda}^* \approx 1.5$ $\mu$m. As hypothetical equilibrium length we regard the actual tube length of 4.5 $\mu$m at $t = 5$ s when the deviation sets in. Analysis of the Laplace transform of the experimental data gives a peak at 14 s [4] which we identify with $\tilde{\tau}$. With the resulting expression for $\Lambda^*_{\text{eff}}$ the effective relaxation function $R_{\text{eff}}(t)$ gives a markedly improved fit of the experimental data compared to the pure reptation result (fig. 3).

There are three distinct conclusions to be drawn from our dynamical lattice gas approach. 1) We obtain a relaxation law for the tube length relaxation of a homogeneously stretched entangled polymer which includes an initial universal power law regime. 2) This power law behaviour has been confirmed by comparison with experiment. More specifically, it appears that the robustness of the reptation mechanism allows for a understanding of the experimentally observed relaxation process beyond what one might have hoped for. An extended variant of the model captures the effect of network fluctuations and allows for a quantitative understanding of the experimental data beyond the universal regime. Concerning the problem of the dependence of the viscosity of a polymer chain on its molecular weight this good agreement lends support to a lattice gas result [12] which agrees with a long-standing [22], but not undisputed [23, 24] claim that the discrepancy between predictions from reptation theory and experimental data is due to finite-size effects. 3) Finally, with a view on the feasibility of modelling complex polymer dynamics by relatively simple, easy-to-simulate lattice gas systems our results suggest that not only the stationary average properties of many polymers may be described, but also time-dependent properties of single chains are predicted to very good accuracy. The basic features of the experimentally observed reptation dynamics can be captured with an exactly solvable lattice gas model which we believe may serve as a suitable starting point for readdressing some of the open issues of reptation theory and —by incorporating further interactions— for exploring new consequences of polymer dynamics under entanglement conditions.

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