About the lifetime of simple knots in stretched polymers

ANDREAS AREND[1], ROLAND RZEHAK[2] and WALTER ZIMMERMANN[1] (*)

[1] *Theoretische Physik, Universität des Saarlandes, D-66041 Saarbrücken, Germany*
[2] *Inst. für Festkörperforschung, Forschungszentrum Jülich, D-52425 Jülich, Germany*

PACS. 83.80.Rs – Polymer solutions.
PACS. 05.40.Jc – Brownian motion.
PACS. 02.10.Kn – Knot theory.

Abstract. – Knots on a flexible polymer, whose two ends are kept at a finite distance, are studied by means of Brownian dynamics simulation. Knots in open polymers represent long-lived metastable states and their average lifetime increases with the polymer length as well as with the magnitude of the forces applied to the polymer ends. Each knot migrates according to an identified whipping effect always to the nearest polymer end. This knot motion resembles a directed one–dimensional random walk in an inverted harmonic potential as described by a corresponding one–dimensional Fokker–Planck equation.

Introduction. – Knots occur in linear polymers, they are much appreciated in art and are important for many other circumstances, see *e.g.* Refs. [1, 2]. Knots in space curves may be characterized by their topology, but for polymers also the thermal motion is important, especially for the dynamical behavior of knots. Under conditions of thermal equilibrium, self–knotted conformations on linear and open polymers occur only with a low probability and hence do not play an important role for their physics except under poor solvent conditions, where the chain is collapsed into a rather dense globule [3]. For a DNA–strand stretched by a uniform flow, however, evidence for the existence of knotted conformations obtained from direct observation by fluorescence microscopy has been reported recently [4]. Furthermore, in elongational flow, a zoo of possible long–lived classes of polymer conformations has been described in Refs. [5–7] which may be interpreted as knots [8].

Tying a knot into a real DNA molecule has been proven possible in Refs. [9,10] by keeping their ends with attached latex spheres in the focus of two optical tweezers. Such a knotted conformation of a stretched linear and open polymer chain represents a long–lived metastable state and we investigate the dependence of its lifetime on various model parameters. To this end we perform Brownian dynamics simulations of a self–avoiding bead–spring chain whose two ends are kept at a finite distance. We predict that the knot on an open polymer with fixed ends always moves to the nearest polymer end by a so–called whipping effect. This symmetry breaking effect with respect to the diffusive knot motion decreases with increasing values of the pulling forces at the polymer ends while the lifetime of a knot increases.

(*) address of correspondence: wz@lusi.uni-sb.de

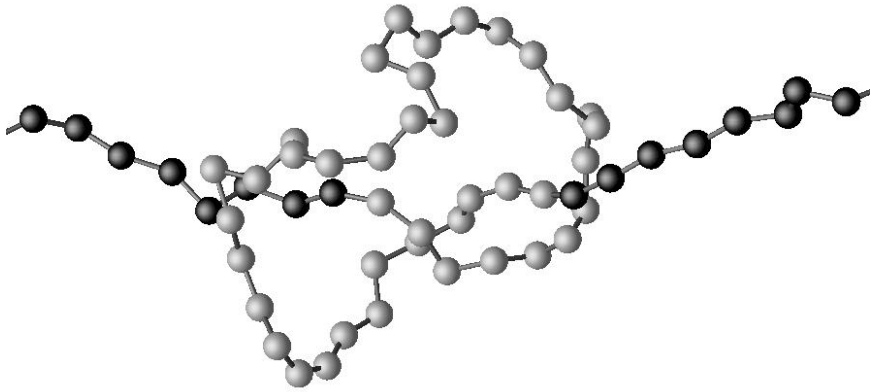

Fig. 1 – The "brezel"-knot used as initial conformation in our Brownian dynamics simulations. In a projection on the xy-plane, there are three crossings which according to the convention lead to a crossing number of $n = 3$. The bright beads belong to the localized knot while the dark beads are outside of it.

The presence of a knot reduces the effective contour length of the polymer available for stretching by a flow causing a difference of the response compared to an unknotted polymer. This may also have various implications for the rheology of polymer solutions similar to topological constraints in polymer melts [11].

Bead Spring Polymer Model. – In our simulations we follow the Brownian dynamics of a bead spring model as described in more details in Refs. [12–14]. The equation of motion for the i-th bead ($i = 1, \ldots, N$) with position $\vec{R}_i$ is

$$\dot{\vec{R}}_i = \zeta^{-1} \left(\vec{F}_i^{ext} + \vec{F}_i^{int} \right) + \sqrt{2 k_B T \, \zeta^{-1}} \, \boldsymbol{\xi}_i \, . \tag{1}$$

Here, ζ is the friction coefficient of a single bead which may be linked to the bead radius a and the solvent viscosity η by Stokes'law $\zeta = 6\pi\eta a$; k_B is the Boltzmann constant and T the temperature. $\vec{F}_i^{ext} = f \, (\delta_{iN} - \delta_{i1}) \, \hat{\vec{x}}$ is the external force of magnitude f acting at each chain end to stretch the polymer along the x-direction. The internal forces $\vec{F}^{int}$ comprise a repulsive Lennard Jones force describing excluded volume interactions between the beads and next-neighbor bond forces for which we use the familiar FENE (**F**inite **E**xtensible **N**onlinear **E**lastic) force law. The latter provides a reasonable approximation of polymers with a fixed bond length b for forces $f \lesssim 50 k_B T / b$. The parameters appearing in the internal forces $\vec{F}^{int}$ are the same as in Ref. [15], where this choice was shown to prohibit bond crossings so that the bead spring chain becomes self-avoiding. Hydrodynamic interactions are not expected to play a prominent role for the phenomena considered in the present work and hence are neglected. The heat bath driving thermal motion of the polymer chain is modeled by the stochastic process $\vec{\xi}(t)$ which is an uncorrelated Gaussian white noise with zero mean and unit variance in order to satisfy the fluctuation dissipation theorem. Throughout this work a chain length of $N = 100$ is used. The values $\zeta = 1.0$, $k_B T = 1.0$ and $b = 0.961$ for the bond length fix the units

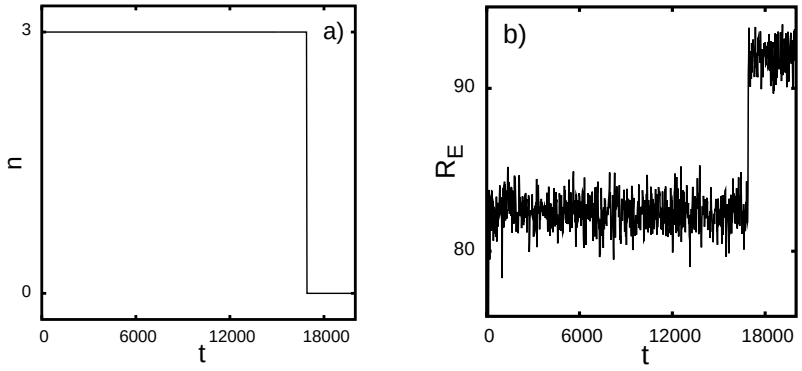

Fig. 2 – Part a) shows the time development of the crossing number n and b) the end-to-end distance R_E. Each picture is for the same realization of a polymer with $N = 100$ beads stretched by a force $f = 9.6\, k_{\mathrm{B}}T/b$ along the x–direction. The presence of the knot is characterized topologically by a value of $n = 3$ while for the unknotted chain by $n = 0$. Obviously, at time $t \approx 16900\zeta b^2/k_BT$ the knot slips off from the chain. This results in a significant increase in R_E since the contour length taken up by the knot becomes available to stretching.

of force, energy, length etc. Equation (1) is solved by means of a stochastic velocity-Verlet algorithm. During the implementation of methods to simulate strongly stretched polymers, it turns out that a Verlet neighbor–list is the most efficient method for the short-ranged excluded volume forces in this case.

Characterization of knotted conformations, end–to–end distance. – A knot is a three-dimensional space–curve and is most conveniently classified by looking at a plane projection, where the space–curve is crossing itself. The so–called crossing number n is defined as the least number of crossings that occur in any plane projection of the space–curve. For knots on closed curves, the crossing number is a topological invariant, *i.e.* it does not change when the knotted curve is deformed continuously and all knots are tabulated based on their crossing numbers. It must be mentioned that in a strict mathematical sense the notion of a knot refers to a closed curve [2] and hence applies to ring polymers [16,17] which cannot become untied. For the open knots considered here, invariance is no longer obeyed strictly, because the knot can slip off from the polymer changing the crossing number to zero.

In Fig. 2a) we plot the crossing number calculated from a simulation of the bead spring polymer starting from an initial conformation as shown in Fig. 1 for which the crossing number is $n = 3$. At first this value remains constant, except for occasional glitches due to the fact that the projection plane is kept fixed for simplicity. If such a glitch occurs, the result is checked several time steps later by repeating the calculation for n.

At $t \approx 16900\zeta b^2/k_BT$ the crossing number changes permanently to 0 indicating that the knot has slipped off from the polymer chain. This topological characterization of the knot is compared to the end–to–end distance in Fig. 2b). The latter first fluctuates around an average value of $R_{\mathrm{E}} \approx 83b$ and shows a remarkable increase again at $t \approx 16900\zeta b^2/k_BT$. This behavior is due to the fact that the knot takes up some fraction of the polymer contour length which is not available to stretch the chain. Once the knot slips off from the chain this length is set free and the chain can become stretched further. Thus, a sudden increase of the end–to–end distance provides an indicator from which the lifetime of the knot on the polymer chain can be inferred. The precise magnitude of this increase, of course, depends on the non–bonded interactions as well as on the strength of the stretching force and the type of the knot.

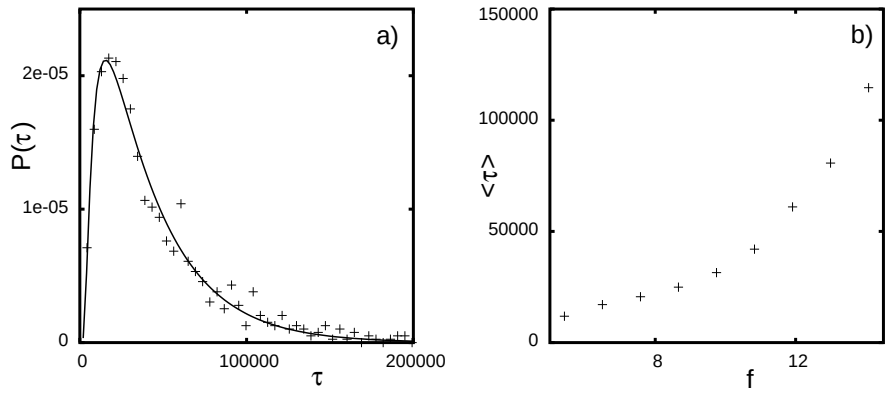

Fig. 3 – Part a) shows the distribution $P(\tau)$ of the lifetime of knots, τ, and part b) shows the mean value of the mean lifetime, $\langle\tau\rangle$, as function of the stretching force $\mathbf{f}$ applied to the polymer end. The data points are obtained from Brownian dynamics simulation of a bead–spring polymer chain with $N = 100$ beads stretched in part a) by a force $|\mathbf{f}| = 10k_{\mathrm{B}}T/b$ along the x–direction. The solid line in part a) is given by the formula in Eq. (4) for the parameters $k = 3.6 \times 10^{-5} k_B T/(\zeta b^2)$ and $D = 0.046 k_B T/\zeta$.

Knot motion, lifetime. – Besides the rather obvious reduction of the end–to–end distance by a knot, a very natural question to ask for is how long a knotted state persists, *i.e.* what is the time a knot needs to reach one end of the open polymer. For the diffusive motion of a knot along a stretched polymer chain, its lifetime τ will be expected to be a random variable. In our simulations the lifetime distribution of single knots per chain, $\mathcal{P}(\tau)$, is obtained by accumulating a histogram of values obtained from simulation of an ensemble of ~ 1000 realizations of the knot motion starting with an initial position of the knot in the middle of a stretched polymer chain. A typical result is shown in Fig. 3a). If a knot is off the middle of the polymer chain it performs a directed one–dimensional random motion to the nearest polymer end. This symmetry breaking effect is explained below.

A model of such a one–dimensional diffusive knot motion is the Fokker-Planck equation

$$\partial_t \mathcal{P} = -\partial_l (A(l)\mathcal{P}) + \partial_{ll} (B(l)\mathcal{P}) \tag{2}$$

for the transition probability $\mathcal{P}(l, t|l', t')$ that the knot is at position l at time t while it was at position l' at time t'. A solution of Eq. (2) with suitable initial conditions can be used to infer the distribution of the lifetime of knots. Specifically, if we set the knot initially in the middle of the chain, then $L/2$ is the distance it has to move along the polymer before it slips off of either end and one has $\mathcal{P}(\tau) \propto 2\mathcal{P}(L/2, \tau|0, 0)$. The imposed initial condition is $\mathcal{P}(l, t|l', t') = \delta(l - l')$ at $t = t' = 0$.

For the simplest case of free diffusion, where $A(l) = 0$ and $B(l) = D$, the solution of the Fokker-Planck equation is known analytically [18] and one finds for the distribution of the knot lifetime τ

$$\mathcal{P}(\tau) \propto \frac{1}{2\sqrt{\pi D \tau}} \exp\left(-\frac{L^2}{4D\tau}\right) = \frac{1}{2\sqrt{\pi D \tau}} + \mathcal{O}(\tau^{-3/2}) \,. \tag{3}$$

The asymptotic behavior for large values of τ clearly rules out this simple model.

The next simplest case is a model for the so-called inverted parabolic potential with $A(l) = \frac{1}{2}kl$ and $B(l) = D$. Again, the solution of the Fokker-Planck equation is known analytically [18]

and the distribution of the lifetime τ is given by

$$\mathcal{P}(\tau) \propto \sqrt{\frac{k}{2\pi D(1-\exp(-2k\tau))}} \exp\left(-\frac{kL^2\exp(-2k\tau)}{2D(1-\exp(-2k\tau))}\right) \exp(-k\tau)\ . \qquad (4)$$

As shown by the solid line in Fig. 3a), this model is in accord with the simulation results, whereby the two model parameters $k = 3.6 \times 10^{-5}\ k_BT/(\zeta b^2)$ and $D = 0.046\ k_BT/\zeta$ have been obtained by fitting the simulation data generated for the end force $|\mathbf{f}| = 10.4 k_{\mathrm{B}}T/b$. The value of L has been determined in the following way and independent of the fit: The beads defining the polymer model can be numbered consecutively. Consider a single crossing in a plane projection, where two parts of the space–curve are crossing themselves. Since each part of the space–curve is defined by two successive beads, one crossing point may be defined by four beads. The "brezel"-knot in Fig. 1 has three crossings, *i.e.* one has the crossing number $n = 3$ and there are twelve beads involved in the three crossings. It can be said that the knot consists of the part of the chain between lowest and highest bead index that is involved in the crossings. In some manner this locates the knot on the polymer. Subtracting its length from the contour length of the polymer gives twice the length the knot has to move before it reaches one of the chain ends. An average value of $L = 88b$ is obtained for our model. Due to conformational fluctuations there are usually more than three crossings among which the "right" ones are singled out by assuming that their positions change only little during one time step of the simulation.

The drift term in the model described by Eq. (2) breaks the translational symmetry along the polymer chain, meaning that there is a systematic motion of the knot towards the nearer chain end. The following mechanism is suggested as an explanation: The parts of the polymer chain to either side perform thermal fluctuations. The longer part is composed of N_1 segments and the shorter one by $N_2 < N_1$ segments, whereby the fluctuation amplitudes of each part of the polymer scale as $f_{p1} \propto \sqrt{N_1}$ and $f_{p2} \propto \sqrt{N_2}$ [19], respectively. Each part shakes the knot to the other chain end and according to the different amplitudes, to the end of the shorter part. This whipping effect is crucial and it causes a net motion of the knot towards the nearer chain end. For rather long chains and knot positions in the range close to the center, the ratio between fluctuation amplitudes of the parts to each side of the knot is $\sqrt{N_1/N_2} \approx 1$. Accordingly, in this regime the symmetry breaking effect is expected to be small, as for instance in a recent experiment about knot diffusion close to the center of a DNA molecule whose ends are also fixed by forces [10].

Parameters as functions of the stretching force f. – The parameter k and the diffusion constant D in Eq. (4), of course, depend on the strength of the force f which stretches the polymer. Repeating the simulations and the fitting procedure as described in the previous section, the parameters k and D are determined as a function of the force f as shown in Fig. 4 and in a range of f, where the directed knot diffusion can be easily detected. In this f-range R_E varies $66b \lesssim R_E \lesssim 83b$ with increasing values of f while D as well as k are decreasing nearly linear.

The contour length taken up by the knot and therefore the value of L turned out to depend only weakly on the stretching force f in the observed range. Hence, the value $L = 88b$ has been used for all fits in Fig. 4. In the range $f > 12.5 k_BT/b$ and beyond that as shown in Fig. 4, the pulling force dominates the thermal forces and the parameters D and k become rather small. So for large values of f the knot becomes eventually immobile. Our data indicate the possibility that this might occur for a finite stretching force, but a definitive conclusion on this point cannot be drawn at present. This behavior is in accord with the whipping effect

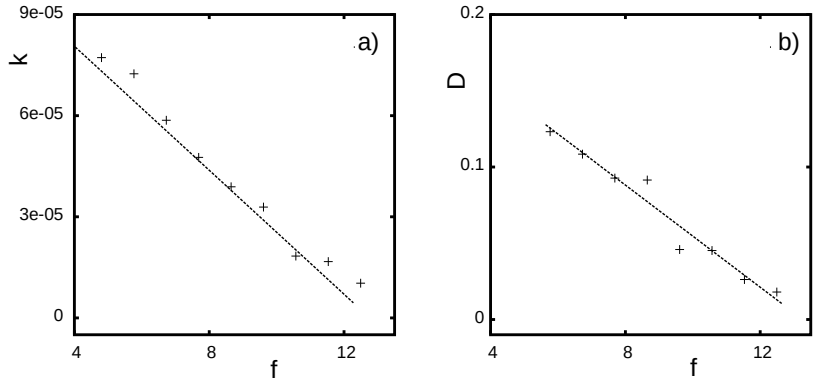

Fig. 4 – In part a) the model parameter k and in part b) the diffusion constant D is shown as functions of the stretching force f and as obtained by fitting simulation results with the formula in Eq. (4). For a large stretching force f the knot becomes less mobile.

suggested in the previous section being the cause for the observed drift: for a larger stretching force, the fluctuations of the two parts of chain decrease and thus remove the cause of the drift.

In the range below that as shown in Fig. 4 the thermal motion becomes more and more vigorous and knot diffusion increases, for instance at $f \sim 4.8 k_B T/b$ already by a factor of about four, *i.e.* $D \sim 0.5$. This also explains why knotted polymer conformations are not important for chains in equilibrium. For a medium stretched chain, in contrast, the knot is tighter and its diffusive motion becomes less important than the systematic drift.

Conclusions. – For the simple model problem of a polymer stretched by pulling on its ends, we have demonstrated that a knotted conformation represents a long-lived state. The lifetime of such a state has been determined from simulations and a simple Fokker-Planck model has been presented which reproduces the simulation results. Our most important finding was that a symmetry breaking occurs leading to a systematic motion of the knot towards the nearer chain end. A whipping effect has been suggested to explain this directed motion. The model problem we have chosen is similar to a recent experiment [10]. However, in this case the polymer was rather long and the diffusive knot was mainly detected close to the center of the polymer, where the whipping effect is expected to be rather weak and without hitting the end. In our simulations of a model polymer we have also found a rather plausible dependence of the diffusion constant on the pulling force, whereas it was rather independent of the pulling force f in Ref. [10]. One reason might be, that the polymer was already in a rather stretched state in Ref. [10], where the diffusion constant becomes also rather independent of f in our simulations. The semi–flexibility of the DNA molecule may also come into play in the range of a strong pulling regime and may modify the f-dependence. The effects of semi–flexibility on the knot motion are investigated elsewhere.

Since the somewhat more complex case of extensional flow has attracted a great deal of attention recently [5–8], one may also use our findings to discuss this case as well. Since in extensional flow a stretching force applies at each bead, all these forces sum up in the middle of the polymer causing a strong stretching there. Based on a direct application of our results we thus expect a very long lifetime of knots, which are initially close to the middle of the polymer contour. However, the possibility of other mechanisms driving a systematic motion of the knot must be considered in addition to the whipping effect described here. Specifically,

a gradient of tension along the polymer chain might also cause a systematic knot motion by pulling it tighter on one end and leaving it looser on the other. The relative magnitude of this gradient–effect may be estimated by $\tilde{k} \propto \Delta f \propto f/R_E$. Since R_E increases with f this is smaller than the magnitude of the drift caused by the whipping effect which is $k \propto f$. Hence we conclude that to a first order approximation the lifetime of knots on polymers stretched in an extensional flow should be similar to the problem discussed here when the force acting in the center of the chain is substituted for f.

* * *

REFERENCES

[1] P.-G. d. Gennes, *Scaling Concepts in Polymer Physics* (Cornell University Press, Ithaca NY, 1981).
[2] C. L. Adams, *The Knot Book* (Freeman, New York, 1994).
[3] F. Brochard and P. G. deGennes, Macromolecules **10**, 1157 (1977).
[4] T. T. Perkins, S. R. Quake, D. E. Smith, and S. Chu, Science **264**, 822 (1994).
[5] D. E. Smith and S. Chu, Science **281**, 1335 (1998).
[6] T. T. Perkins, D. E. Smith, and S. Chu, Science **276**, 2016 (1997).
[7] T. T. Perkins, D. E. Smith, and S. Chu, in *Flexible Chain Dynamics*, edited by H. Kausch and T. Nguyen (Springer, Heidelberg, 1997).
[8] P.-G. d. Gennes, Science **276**, 1999 (1997).
[9] Y. Arai *et al.*, Nature **399**, 446 (1999).
[10] X. R. Bao, H. J. Lee, and S. R. Quake, Phys. Rev. Lett. **91**, 265506 (2003).
[11] K. Iwata and S. F. Edwards, J. Chem. Phys. **90**, 4567 (1989).
[12] R. Rzehak, A. Arend, D. Kienle and W. Zimmermann, in *Numerical Solutions of Polymer and Cell Dynamics* (Birkhäuser, Basel, 2003).
[13] R. Rzehak, Eur. Phys. J. E **11**, 335 (2003).
[14] R. Rzehak, W. Kromen, T. Kawakatsu, and W. Zimmermann, Euro. Phys. J. **E 2**, 3 (2000).
[15] G. S. Grest and K. Kremer, Phys. Rev. A **33**, 3628 (1986).
[16] Y.-J. Sheng, P.-Y. Lai, and H.-K. Tsao, Phys. Rev. E **58**, R1222 (1998).
[17] S. R. Quake, Phys. Rev. Lett. **73**, 3317 (1994).
[18] H. Risken, *The Fokker–Planck Equation* (Springer, Heidelberg, 1989).
[19] M. Doi and S. F. Edwards, *The Theory of Polymer Dynamics* (Clarendon Press, Oxford, 1986).
[20] S. R. Quake, H. Babcock, and S. Chu, Nature **388**, 151 (1997).