

Equilibrium and dynamical properties of semiflexible chain molecules with confined transverse fluctuations

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The partition function of a semiflexible chain molecule with harmonically confined transverse fluctuations is calculated. Equilibrium properties exhibit qualitative differences between the weak and the strong confinement behavior. The relaxation times of undulations perpendicular to the chain molecule contour are calculated on the basis of a Langevin equation approach. With increasing confinement a decrease of the relaxation times is found. As a consequence the mean square displacement of monomers and the dynamic structure factor are strongly influenced by the confinement. The comparison of the calculated mean square displacement with diffusing wave spectroscopy measurements of actin filaments exhibits good agreement. [S1063-651X(99)14810-4]

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I. INTRODUCTION

It has long been realized that the key physics determining the properties of long chain molecules in melts or in entangled solutions arises from the topological interaction between the molecules. The most popular theoretical framework in which topological interactions are taken into account is the tube model of de Gennes [1], and of Doi and Edwards [2]. The topological constraints by which the chain molecules may not cross each other are assumed to be equivalent for each molecule to a tube surrounding its own contour. Hence, motions perpendicular to the tube contour are confined while those along the contour are permitted. These motions have been visualized by video microscopy measurements of actin filaments [3] and of DNA in entangled solutions [4]. Thus, one has direct evidence that tubelike constraints exist in these systems.

Chain molecules trapped in a tube exhibit strikingly different features from those in a bulk. The chain molecules are deflected back and forth by the tube boundary. Depending on the tube radius, relaxation processes perpendicular to the tube axis are suppressed while the motion along the tube contour is the only unrestricted type of motion at times longer than an average monomer takes to diffuse across the tube radius. Consequently, equilibrium, as well as dynamical properties, are changed. Equilibrium properties of chain molecules confined within a tube, such as the free energy increase or the chain molecule conformation have been of intense interest [1,5–8]. Dynamical properties have been worked out for flexible linear chain molecules inside a tube [1,8–10]. Recently, there has been increasing interest in the dynamics of semiflexible chain molecules in confined environments [11–14].

The theoretical investigations on dynamical properties of confined chain molecules performed so far mainly concentrate on the curvilinear motion of the molecules along their contour. In this paper we focus on constraint fluctuations perpendicular to the molecules contour. These transverse fluctuations are of particular importance for rather stiff chain molecules, where internal longitudinal degrees of freedom

are suppressed due to the constraint of inextensibility. We determine the free energy of a semiflexible chain molecule in a harmonic confinement potential using the path integral for a general second-derivative Lagrangian. The relaxation times characterizing transverse undulations are calculated. Using these relaxation times we compute the mean square displacement of the monomers and the dynamic structure factor.

The paper is organized as follows. The chain model is introduced in Sec. I. The free energy of a polymer chain and equilibrium correlation functions are calculated in Sec. II. In Sec. III dynamical properties are discussed. Finally, Sec. IV summarizes our findings.

II. SEMIFLEXIBLE CHAIN MODEL

The semiflexible chain model is represented as a continuous, differentiable space curve $\mathbf{r}(s)$, where s indicates distances along the chain. The bending energy H_b of a chain molecule of contour length L is given by

$$\frac{H_b}{k_B T} = \frac{l_p}{2} \int_0^L ds \left(\frac{\partial^2 \mathbf{r}(s)}{\partial s^2} \right)^2, \quad (2.1)$$

where l_p is the persistence length [15]. Calculations of equilibrium properties of the semiflexible chain model are difficult due to the local inextensibility constraint $|\partial \mathbf{r}(s)/\partial s|^2 = 1$. A variety of approximations have been devised to approach this problem. The most successful approximation is to impose the global constraint

$$\left\langle \frac{1}{L} \int_0^L ds \left(\frac{\partial \mathbf{r}(s)}{\partial s} \right)^2 \right\rangle = 1 \quad (2.2)$$

rather than the local one [16–19]. The brackets designate an ensemble average. Thus, the term

$$\frac{H_m}{k_B T} = \frac{\mu}{l_p} \int_0^L ds \left(\frac{\partial \mathbf{r}(s)}{\partial s} \right)^2 \quad (2.3)$$

is added to the potential energy (2.1) and the dimensionless Lagrangian multiplier μ is determined by demanding the

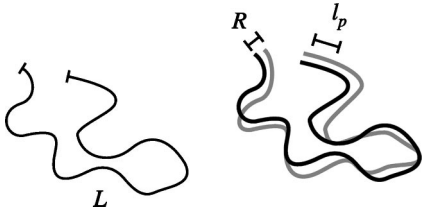


FIG. 1. Schematic presentation of a semiflexible chain molecule of contour length L and persistence length l_p . The thick black and gray lines represent possible configurations apart in time. The mean square displacement perpendicular to the chain contour (2.4) is given by R^2 .

constraint (2.2) to hold. This approximation is known to hold for the calculation of various equilibrium properties, such as the radius of gyration and the end-to-end distance [17,19].

Here we consider a semiflexible chain molecule with harmonically confined transverse fluctuations

$$\left\langle \frac{1}{L} \int_0^L ds \mathbf{r}_\perp^2(s) \right\rangle = R^2, \quad (2.4)$$

where $\mathbf{r}_\perp(s)$ is the position vector perpendicular to the chain contour and R designates a tube radius. Due to this constraint the number of conformations allowed for the chain molecule is much smaller than in free space. The purpose of the constraint (2.4) is to restrict the transverse displacement considerably but not totally to an interval of width $2R$. Thus, the chain molecule is confined in a tube-like cage. Figure 1 shows a schematic presentation of the confined chain molecule. For the calculation of the allowed chain conformations we add the confinement potential

$$\frac{H_{con}}{k_B T} = \frac{\nu}{2l_p^3} \int_0^L ds \mathbf{r}_\perp^2(s) \quad (2.5)$$

to the potentials (2.2) and (2.3). The dimensionless Lagrangian multiplier is denoted as ν . The partition function of the semiflexible chain molecule, under the influence of the confinement potential, reads

$$Z = \int \exp \left[-\frac{l_p}{2} \int_0^L ds \left(\frac{\partial^2 \mathbf{r}(s)}{\partial s^2} \right)^2 - \frac{\mu}{l_p} \int_0^L ds \left(\frac{\partial \mathbf{r}(s)}{\partial s} \right)^2 - \frac{\nu}{2l_p^3} \int_0^L ds \mathbf{r}_\perp^2(s) \right] \mathcal{D}\mathbf{r}. \quad (2.6)$$

The position vector $\mathbf{r}(s)$ can be decomposed into its components $\mathbf{r}_\parallel(s)$ parallel to the chain molecule contour and $\mathbf{r}_\perp(s)$. Then the functional integral (2.6) is straightforward and corresponds to a path integral for a general second-derivative Lagrangian [20]. The Lagrangian multipliers μ and ν are obtained from demanding the expectation values [Eqs. (2.2) and (2.4)] to hold. Hence, the free energy $\mathcal{F} = -k_B T \ln Z$ is calculated and the functional

$$I = \frac{\mathcal{F}}{k_B T} - \frac{\mu L}{l_p} - \frac{\nu R^2 L}{2l_p^3} \quad (2.7)$$

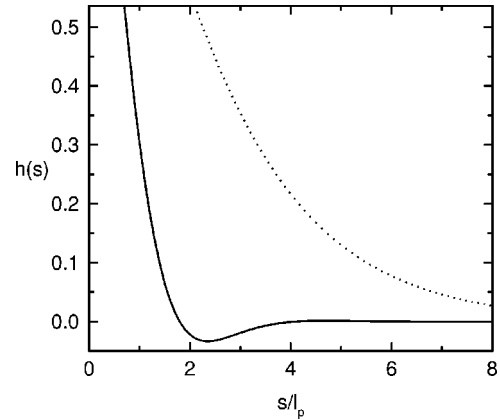


FIG. 2. Computed correlation function $h(s)$ for two R/l_p values according to Eq. (3.2): $R/l_p=0.3$, solid line; $R/l_p=1$, dotted line. The chain length was fixed to $L/l_p=25$.

is extremized with respect to μ and ν . Once the Lagrangian multipliers are computed for the system, various equilibrium and dynamical properties can be investigated.

III. EQUILIBRIUM PROPERTIES

The determination of the Lagrangian multipliers leads to nonlinear equations which are solved numerically. But some characteristic features can be obtained from analytical approximations. An evaluation of the partition function (2.6) exhibits that the functional I reads approximately

$$\frac{Il_p}{L} = \sqrt{\frac{\mu}{2}} + (\mu + \sqrt{\mu^2 - \nu})^{1/2} + (\mu - \sqrt{\mu^2 - \nu})^{1/2} - \mu - \frac{\nu}{2} \left(\frac{R}{l_p} \right)^2. \quad (3.1)$$

As a result, the Lagrangian multipliers do not depend on the contour length. In the limit of weak confinement $R/l_p \gg 1$, the Lagrangian multipliers are given by $\mu=9/8$ and $\nu=4(l_p/R)^4/9$ whereas, for strong confinement $R/l_p \ll 1$, we find $\mu=1/8$ and $\nu=(l_p/R)^{8/3}/2^{2/3}$. From the numerical calculations it follows that there is a transition point $R/l_p \approx 0.9$ with $\mu^2 = \nu$. To study the effect of this transition on equilibrium properties, we determine the correlation function

$$h(s) = \frac{\langle \vec{r}_\perp(s) \cdot \vec{r}_\perp(0) \rangle}{\langle \vec{r}_\perp(0) \cdot \vec{r}_\perp(0) \rangle}. \quad (3.2)$$

In Fig. 2 we present this correlation function for two different R/l_p values. From the figure it is apparent that $h(s)$ exhibits a qualitatively different behavior below and above the transition point. While it decays purely exponentially above the transition point, there are additional oscillatory modulations below the transition point. In this limit the correlation function is approximately given by

$$h(s) = \sqrt{2} \exp \left[-\left(\frac{1}{4l_p R^2} \right)^{1/3} s \right] \sin \left[\left(\frac{1}{4l_p R^2} \right)^{1/3} s + \frac{\pi}{4} \right]. \quad (3.3)$$

The period of the oscillations in the small R/l_p regime is the Odijk deflection length $\lambda = (4l_p R^2)^{1/3}$ [7], at which a chain molecule is deflected by the tube boundary in order to conform to the constraints (2.4). The observed transition is due to competing effects in a one-dimensional system with local interactions and is similar to the one recently found by Liverpool *et al.* for their double-stranded semiflexible chain model [18].

In the small R/l_p regime the confinement free energy $\Delta\mathcal{F}$, defined by the increase in the free energy of a chain molecule enclosed within a tube with respect to the one in the bulk, scales like

$$\frac{\Delta\mathcal{F}}{k_B T} \sim \frac{L}{\lambda}. \quad (3.4)$$

This expression corresponds to the one derived by Helfrich and Harbich for confined membrane surfaces [21].

IV. DYNAMICAL PROPERTIES

In the following we investigate the dynamics of fluctuations perpendicular to the chain molecule contour. The energy functional in the exponent of Eq. (2.6) gives the restoring force to a fluctuation. Neglecting the inertia force as compared to the friction force, the Langevin equation for the motions perpendicular to the chain molecule contour is given by

$$\begin{aligned} \gamma \frac{\partial}{\partial t} \mathbf{r}_\perp(s, t) - \frac{2\mu}{l_p} k_B T \frac{\partial^2}{\partial s^2} \mathbf{r}_\perp(s, t) + l_p k_B T \frac{\partial^4}{\partial s^4} \mathbf{r}_\perp(s, t) \\ + \frac{\nu}{l_p^3} k_B T \mathbf{r}_\perp(s, t) = \mathbf{f}_\perp(s, t), \end{aligned} \quad (4.1)$$

where γ is the friction constant per unit length of the chain molecule and $\mathbf{f}_\perp(s, t)$ is a white noise stochastic force. The frictional force results from irreversible short time viscous processes. The second and third terms in Eq. (4.1) describe intramolecular forces, while the fourth term represents the confinement force. An s -dependent friction coefficient may be used to take the hydrodynamic interaction in a dilute solution into account [22]. The expansion of the position vector

$$\mathbf{r}_\perp(s, t) = \sum_{n=1}^{\infty} \boldsymbol{\chi}_n(t) \psi_n(s), \quad (4.2)$$

in terms of the eigensolutions

$$\psi_n(s) = \sqrt{\frac{2}{L}} \cos\left[\frac{n\pi}{L}s\right] \quad (4.3)$$

of the corresponding eigenvalue equation

$$\begin{aligned} \frac{\gamma}{\tau_n} \psi_n(s) = \frac{2\mu}{l_p} k_B T \frac{\partial^2}{\partial s^2} \psi_n(s) \\ - l_p k_B T \frac{\partial^4}{\partial s^4} \psi_n(s) - \frac{\nu}{l_p^3} k_B T \psi_n(s), \end{aligned} \quad (4.4)$$

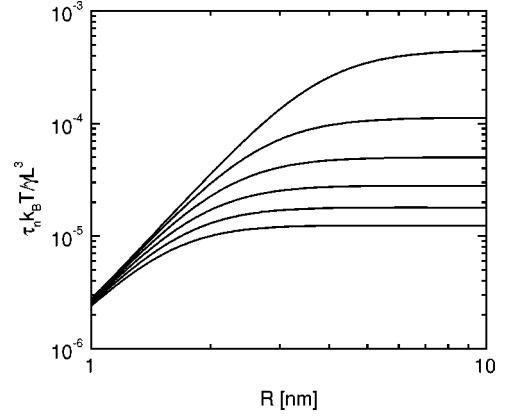


FIG. 3. First six relaxation times for a confined chain molecule of length $L=100$ nm and of persistence length $l_p=1$ nm as function of the tube radius R . Mode number n increases from top to bottom.

yields an equation for amplitude $\boldsymbol{\chi}_n(t)$ and from there for the time correlation function $\langle \boldsymbol{\chi}_n(t) \cdot \boldsymbol{\chi}_n(0) \rangle$:

$$\frac{\partial}{\partial t} \langle \boldsymbol{\chi}_n(t) \cdot \boldsymbol{\chi}_n(0) \rangle = -\frac{1}{\tau_n} \langle \boldsymbol{\chi}_n(t) \cdot \boldsymbol{\chi}_n(0) \rangle. \quad (4.5)$$

The solution of this differential equation is given by

$$\langle \boldsymbol{\chi}_n(t) \cdot \boldsymbol{\chi}_n(0) \rangle = \frac{2k_B T}{\gamma} \tau_n \exp\left[-\frac{t}{\tau_n}\right], \quad (4.6)$$

where τ_n are the relaxation times of the normal mode analysis and read

$$\frac{\gamma}{\tau_n k_B T} = \frac{2\mu}{l_p} \left(\frac{n\pi}{L}\right)^2 + l_p \left(\frac{n\pi}{L}\right)^4 + \frac{\nu}{l_p^3}. \quad (4.7)$$

The first six relaxation times are plotted in Fig. 3 as a function of the tube radius R . In the calculations the contour length $L=100$ nm and the persistence length $l_p=1$ nm were fixed. With decreasing tube radius we find a decrease of the relaxation times. At a short time scale a chain molecule undergoes local wriggling motions within the tube. These motions are described by undulations with large mode numbers n . Therefore, relaxation times with large mode numbers are less influenced by the constraints than those with small mode numbers. In particular, bending modes $\tau_n \sim L^4/n^4$ become dominant for short times [23].

The relaxation times presented in Fig. 3 should not be confused with the much longer relaxation times characterizing the curvilinear reptational motion. Reptation theories for entangled polymers assume that temporary topological constraints formed by surrounding polymers force the polymers to move anisotropically through the melt by favoring motion along their own contours [1,2]. For reptating chain molecules the relaxation times describing the curvilinear motion are enhanced relative to the relaxation times of unentangled chain molecules. This increase has been confirmed by computer simulations [24] and is an essential ingredient in theories of long-time dynamics in polymer melts (see, for example, [25–27]).

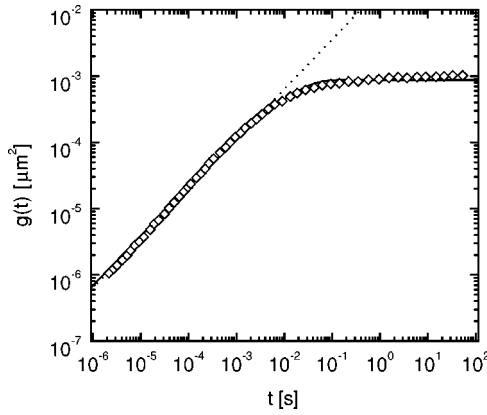


FIG. 4. Computed mean square displacements $g(t)$ (solid line) together with experimental data (open diamonds) of actin filament networks [28]. The dotted line displays the power law $g(t) \sim t^{3/4}$.

The dynamics of chain molecules is often characterized by its mean square displacements. Here we investigate the transverse mean square displacement $g(t)$. Using the transformation (4.2) and the correlation function (4.6), this quantity is given by

$$g(t) = \frac{1}{L} \int_0^L ds \langle (\mathbf{r}_\perp(s,t) - \mathbf{r}_\perp(s,0))^2 \rangle = \frac{4k_B T}{\gamma L} \sum_{n=1}^{\infty} \tau_n \left(1 - \exp\left[-\frac{t}{\tau_n}\right] \right). \quad (4.8)$$

In Fig. 4 we present $g(t)$ (solid line) together with experimental data of actin filament networks [28]. In the calculations the persistence length, the tube radius, and the contour length were fixed to $l_p = 12 \mu\text{m}$, $R = 16 \text{ nm}$, and $L = 40 \mu\text{m}$. From the figure it follows that, at short times, $g(t)$ does not increase linearly in time but instead increases sub-diffusively with a power law $g(t) \sim t^{3/4}$. This power law is a direct consequence of the bending relaxation times $\tau_n \sim 1/n^4$ [23] and is well known for actin filaments and microtubules [29–31]. Furthermore, there is a crossover to a plateau at longer times where the mean square displacement is only very weakly time dependent. The plateau value $g(t) = 4R^2$ provides a direct measure of the confinement. On the time scale of the plateau, the normal modes are already equilibrated. Small deviations between our model calculations and the experimental data are most likely due to superimposed diffusion of the spherical probes inside the actin network [28].

The calculation of $g(t)$ for flexible chain molecules ($l_p = 0.5 \text{ nm}$) exhibits a power law $g(t) \sim t^{1/2}$ for short times and a long-time plateau. These results are in agreement with Monte Carlo simulations of flexible chains confined into straight tubes [10].

In general, the calculation of dynamical properties, such as dynamic structure factors and viscoelastic moduli requires the knowledge of the time evolution of the position vector $\mathbf{r}(s,t)$. Because we are mainly interested in transverse fluctuations, we study only time and length scales dominated by transverse motions. In dynamic scattering experiments the incoherent dynamic structure factor

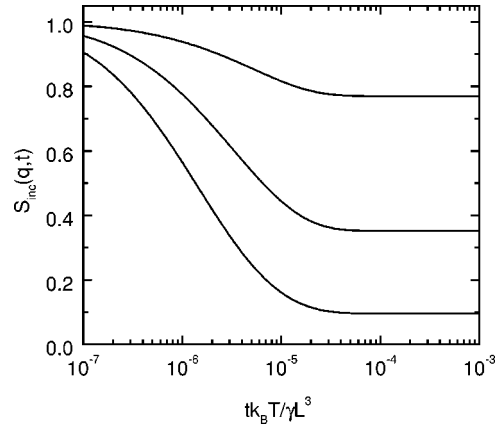


FIG. 5. Incoherent dynamic structure factor for different scattering vectors: $q = 0.5, 1, \text{ and } 1.5 \text{ nm}^{-1}$. The scattering vector increases from top to bottom. The contour length and the persistence length are given by $L = 100 \text{ nm}$ and $l_p = 1 \text{ nm}$, respectively. The tube radius is fixed to $R = 1.5 \text{ nm}$.

$$S_{inc}(\mathbf{q}, t) = \frac{1}{L} \int_0^L ds \langle \exp[-i\mathbf{q} \cdot (\mathbf{r}(s,t) - \mathbf{r}(s,0))] \rangle \quad (4.9)$$

is studied as a function of time and scattering vector \mathbf{q} . Large scattering vectors used in neutron scattering experiments do not probe long-time curvilinear motions. In this scattering vector regime the incoherent dynamic structure factor is dominated by the constraint motions of the chain molecules. Since the distribution of $(\mathbf{r}_\perp(s,t) - \mathbf{r}_\perp(s,0))$ is Gaussian for our chain model, the calculation of the ensemble average yields

$$S_{inc}(\mathbf{q}, t) = \frac{1}{L} \int_0^L ds \exp\left(-\frac{q^2}{4} \langle (\mathbf{r}_\perp(s,t) - \mathbf{r}_\perp(s,0))^2 \rangle\right), \quad (4.10)$$

where

$$\langle (\mathbf{r}_\perp(s,t) - \mathbf{r}_\perp(s,0))^2 \rangle = \frac{4k_B T}{\gamma} \sum_{n=1}^{\infty} \tau_n \psi_n^2(s) \left(1 - \exp\left[-\frac{t}{\tau_n}\right] \right), \quad (4.11)$$

using Eqs. (4.2) and (4.6). The result (4.10) applies to a purely transverse scattering geometry with $\mathbf{q} \cdot (\mathbf{r}_\parallel(s,t) - \mathbf{r}_\parallel(s,0)) = 0$. This is what one expects for networks, where the longitudinal degree of freedom is suppressed and thus cannot contribute to incoherent scattering. In a polymer melt, however, the evolution of longitudinal motions is coupled to transverse undulations and causes a reptational motion at long times. The incoherent scattering properties of a reptating chain molecule were already described qualitatively by de Gennes [32].

Figure 5 represents $S_{inc}(\mathbf{q}, t)$ for various scattering vectors. In the calculations, the contour length and the persistence length were fixed to $L = 100 \text{ nm}$ and $l_p = 1 \text{ nm}$, respectively. The lateral confinement of the chain molecules is characterized by the tube radius $R = 1.5 \text{ nm}$. From the figure it is apparent that the incoherent dynamic structure factor exhibits a plateau indicating the tube constraints. This plateau becomes more pronounced with decreasing scattering

vector. At small scattering vectors the dynamics on larger length scales are probed. Thus, by studying the incoherent dynamic structure factor at different scattering vectors, the tube radius can be extracted.

Using the transformation (4.2) and the correlation function (4.6), the coherent dynamic structure for a purely transverse scattering geometry

$$S(\mathbf{q}, t) = \frac{1}{L^2} \int_0^L ds \int_0^L ds' \langle \exp[-i\mathbf{q} \cdot (\mathbf{r}_\perp(s, t) - \mathbf{r}_\perp(s', 0))] \rangle \quad (4.12)$$

can be calculated. $S(\mathbf{q}, t)$ exhibits a rapid relaxation for short times, which changes into a plateau for longer times. We have already discussed the initial decay of the coherent dynamic structure factor and found a strong dependence of this quantity on molecular stiffness [33]. The major result of the present calculations is the plateau similar to that found for the incoherent dynamic structure factor. A time-independent plateau of the coherent dynamic structure is well known from the theory of the dynamics of polymer melts (see, for example, [34–36]). But the underlying physical mechanisms are different. In the local reptation model of de Gennes [34] the time-independent plateau arises from internal dilatations and contractions of a flexible chain molecule inside a fixed tube. Des Cloizeaux formulated a rubberlike model with fixed entanglement points [36]. Two branches of a flexible polymer chain, which are separated by a fixed entanglement point, are considered as independent from each other. Coherent scattering from two branches is therefore assumed to be time independent [36]. But the plateau of the coherent dynamic structure factor observed in our calculations arises from restricted transverse fluctuations. These transverse fluctuations are of particular importance for semiflexible chain molecules because internal longitudinal fluctuations are suppressed by the constraint of inextensibility.

V. SUMMARY

We have studied equilibrium and dynamical properties of semiflexible chain molecules in a harmonic confinement potential using an analytical approach. The chain molecules are confined in tubelike cages. The partition function of the chain molecules can be calculated exactly. Equilibrium properties exhibit qualitative differences between the weak and the strong confinement behavior. For strong confinement there are additional oscillatory modulations of the position vector correlation function. The period of the spatially damped oscillations is found to be the deflection length first introduced by Odijk [7].

The dynamics of the transverse fluctuations is discussed by means of a Langevin equation which is solved in terms of a normal mode analysis. The confinement force acts to suppress normal modes with amplitudes larger than the tube radius. Our calculations of the mean square displacement of the monomers and the incoherent dynamic structure factor exhibit a time-independent plateau. This plateau indicates the reduced transverse mobility due to the constraints. Generally, we found a crossover from single chain to constraint dominated behavior with increasing time. A comparison of the theoretical calculations with measurements of the mean square displacement of actin filament networks shows good agreement.

The studies presented in the current article indicate that the semiflexible chain model in a harmonic confinement potential captures essential features of chain molecules in confined environments. In further studies it should be interesting to include more complicated confinement potentials. This can be achieved by using a variant of the Feynman-type variational principle [37] for the partition function of the effective Gaussian chain model presented in this paper.

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