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Conformational and Dynamical Properties of Semiflexible Polymers in the Presence of Active Noise

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Abstract. In the presence of active noise, flexible and semiflexible polymers exhibit drastically different conformational and dynamical features compared to the case of thermal (white) noise only. For a non-Markovian exponentially correlated temporal noise (colored noise), flexible polymers swell with increasing noise strength, whereas semiflexible polymers shrink first and, for larger noise strengths, swell similar to flexible polymers. Thereby, a suitable treatment of the finite polymer contour length is essential. The finite contour length implies a strong dependence of the polymer relaxation times on the noise strengths. We discuss the conformational and dynamical aspects in terms of an analytical model, adopting the continuous Gaussian semiflexible polymer description. Moreover, results of computer simulations are shown and compared with analytical results.

INTRODUCTION

Active matter systems, e.g., assemblies of active Brownian particles (ABPs) [1–10], exhibit a wide spectrum of fascinating phenomena, such as motility-induced phase separation or large-scale collective motion, emerging from the intrinsic nonequilibrium character of their constituents [3, 11–18]. The properties of connected active particles as in linear chains are particularly interesting, because of the intimate coupling of conformational properties and propulsion [19–39]. For a polymer, activity can be interpreted in two ways. On the one hand, our polymer can be considered as comprised of active monomers, e.g., active Brownian particles [21, 22, 35, 36, 38, 40]. On the other hand, the active force may originate from interactions with uncorrelated surrounding ABPs, hence, the polymer corresponds to a passive polymer dissolved in an active bath [30, 41, 42]. Examples for the latter can be found in biological system. Mixtures of active and passive components are a characteristics of eukaryotic cells with, e.g., the active cytoskeleton and an embedded large variety of passive colloidal and polymeric objects. Here, an influence of the active microtubule [43] or actin-filament [44] dynamics on the motion of chromosomal loci [45, 46] or that of chromatin has been detected [47].

In this article, we present results of the conformational and dynamical properties of flexible and semiflexible active Brownian polymers (ABPO). We adopt the Gaussian semiflexible polymer model [48, 49] composed of ABPs, which allows us to treat the problem analytically [36, 38]. Thereby, we account for the finite polymer extensibility and demonstrate that it strongly affects polymer relaxation behavior and dynamics. Specifically, activity induces a transition from semiflexible-polymer behavior, determined by bending elasticity, to the entropy-dominated behavior of flexible polymers with increasing activity. This severely affects the conformational properties. For a flexible polymer, activity leads to swelling over a wide range of activities. Interestingly, semiflexible polymers exhibit an activity-induced shrinkage. However, for large activities the polymer conformations are ultimately comparable with those of flexible polymers [36]. Moreover, we find a substantially enhanced diffusion of the active polymers, with three distinct regimes: a ballistic regime for short times, a Rouse-type polymer specific regime for intermediate times, and free diffusion for long times [38].
ACTIVE POLYMER: ANALYTICAL APPROACH

Equation of Motion

Within the Gaussian semiflexible polymer model, the polymer is considered as a continuous, differentiable space curve \( r(s, t) \), with the contour coordinate \( s \) along the linear chain of length \( L \) \((-L/2 < s < L/2)\) and the time \( t \) \([36, 38, 48, 50, 51]\). The equation of motion of \( r(s, t) \) is given by the Langevin equation \([36, 38, 52–56]\)

\[
\frac{\partial}{\partial t} r(s, t) = \mathbf{v}(s, t) + \frac{1}{\gamma} \Gamma(s, t) + \frac{k_B T}{\gamma} \left( 2 \lambda \frac{\partial^2}{\partial s^2} r(s, t) - \epsilon \frac{\partial^4}{\partial s^4} r(s, t) \right),
\]

with the boundary conditions

\[
\left[ 2 \lambda \frac{\partial}{\partial s} r(s, t) - \epsilon \frac{\partial^3}{\partial s^3} r(s, t) \right]_{s=\pm L/2} = 0,
\quad \left[ 2 \lambda_0 \frac{\partial}{\partial s} r(s, t) + \epsilon \frac{\partial^3}{\partial s^3} r(s, t) \right]_{s=\pm L/2} = 0.
\]

The influence of activity is captured by assigning the velocity \( \mathbf{v}(s, t) \) to the point \( r(s, t) \). Thereby, \( \mathbf{v} \) is a non-Markovian, but Gaussian stochastic process with zero mean and the correlation function \([15, 17, 35, 36, 42]\)

\[
\langle \mathbf{v}(s, t) \cdot \mathbf{v}(s', t') \rangle = \nu_0^2 e^{-\gamma_R |s-s'|} \delta(s-s').
\]

Here, \( \nu_0 \) is the propulsion velocity and \( \gamma_R = (d - 1)D_R \) the damping factor for the rotational motion of an ABP, with the rotational diffusion coefficient \( D_R \) of a passive particle and \( d \) the dimension (we will consider \( d = 3 \) only). More details on the derivation of Eq. (3) are presented in Ref. [36]. We introduce the length scale \( l \) in Eq. (3), which, in a touching-bead model of a discrete polymer, represents the bead diameter and bond length [36]. Hence, the ratio \( L/l \) can be interpreted as the number of uniformly distributed active sites along the polymer. In the following, if not indicated differently, we consider a polymer with \( L/l = 10^5 \).

The stochastic process \( \Gamma(s, t) \) for the translational motion of \( r(s, t) \) is assumed to be stationary, Markovian, and Gaussian with zero mean and the second moments

\[
\langle \Gamma_\alpha(s, t)\Gamma_\beta(s', t') \rangle = 2\gamma k_B T \delta_{\alpha\beta} \delta(s-s') \delta(t-t'),
\]

where \( T \) is the temperature, \( k_B \) the Boltzmann constant, \( \gamma \) the translational friction coefficient per length, which is related to the translational diffusion coefficient of an individual ABP via \( D_T = k_B T/\gamma l \), and \( \alpha, \beta \in \{x, y, z\} \).

The terms in the brackets of Eq. (1) represent the entropic degrees of freedom, with the stretching coefficient \( \lambda \), and restrictions by an intrinsic bending stiffness, with the bending coefficient \( \epsilon \). The coefficients \( \lambda_0 \) and \( \epsilon \) are determined via constraints for bond lengths and bending restrictions, respectively \([49, 57]\). Adopting the results for calculations of continuous semiflexible polymers exposed to external forces \([49]\), we set \( \epsilon = 3/4p \) and \( \lambda_0 = 3/4 \) for a polymer in three dimensions, where \( p = 1/2l_p \) and \( l_p \) is the persistence length. Within a mean-field approach for the bond constraints, we impose the global condition \([36]\)

\[
\int_{-L/2}^{L/2} \left( \left( \frac{\partial r(s, t)}{\partial s} \right)^2 \right) ds = L
\]

(5)

to capture the inextensibility of a polymer and to determine the stretching coefficient (Lagrangian multiplier) \( \lambda \).

Solution of Equation of Motion: Eigenfunction Expansion

The solution of the linear equation of motion (1) follows by an eigenfunction expansion \([36, 52, 58]\)

\[
r(s, t) = \sum_{n=0}^{\infty} \chi_n(t) \varphi_n(s),
\]

with the eigenfunctions \( \varphi_n(s) \) of the equation

\[
e k_B T \frac{d^2}{ds^2} \varphi_n(s) - 2\lambda k_B T \frac{d^4}{ds^4} \varphi_n(s) = \xi_n \varphi_n(s)
\]

(7)
and the mode amplitudes $\chi_n(t)$. Explicitly, the eigenfunctions read [52, 58]

\[
\varphi_0 = \sqrt{\frac{1}{L}},
\]

\[
\varphi_n(s) = \sqrt{\frac{c_n}{L}} \left( \zeta_n \frac{\sin \zeta_n s L}{\cosh \zeta_n L/2} + \xi_n \frac{\sin \xi_n s L}{\cos \xi_n L/2} \right), \quad n \text{ odd},
\]

\[
\varphi_n(s) = \sqrt{\frac{c_n}{L}} \left( \zeta_n \frac{\cosh \zeta_n s L}{\sinh \zeta_n L/2} - \xi_n \frac{\cos \xi_n s L}{\sin \xi_n L/2} \right), \quad n \text{ even},
\]

with

\[
\zeta_n^2 - \xi_n^2 = \frac{2\lambda}{\epsilon}, \quad \xi_0 = 0, \quad \xi_n = k_B T (\epsilon \zeta_n^4 + 2\lambda \zeta_n^2).
\]

The constants $c_n$ are normalization coefficients, and the wave numbers $\zeta_n$ and $\xi_n$ are specified by the boundary conditions Eq. (2). $\varphi_0$ accounts for the polymer’s translational motion. The $\xi_n$ are the eigenvalues, which depend on the mode numbers and, in particular, the stretching coefficient $\lambda$, which itself is a function of activity [35, 36]. The stationary-state solution of the mode amplitudes is

\[
\chi_0(t) = \chi_0(0) + \int_0^t \left( v_0(t') + \frac{1}{\gamma} \Gamma_0(t') \right) dt', \quad \chi_n(t) = \int_{-\infty}^t e^{-(t-t')/\tau_n} \left( v_n(t') + \frac{1}{\gamma} \Gamma_n(t') \right) dt'.
\]

The $v_n(t)$ and $\Gamma_n(t)$ are the normal mode amplitudes of the velocity $v(s, t)$ and stochastic force $\Gamma(s, t)$, respectively, in terms of the eigenfunctions $\varphi_n(s)$, analogously to Eq. (6), and the $\tau_n$ are the relaxation times [36] ($n > 0$)

\[
\tau_n = \frac{\gamma}{\xi_n} = \frac{\gamma}{k_B T (\epsilon \zeta_n^4 + 2\lambda \zeta_n^2)}.
\]

**Results: Stretching Coefficient $\lambda$**

With the eigenfunction expansion (6), the equation of the bond-length constraint (5) becomes

\[
\sum_{n=1}^{\infty} \left( \frac{3k_B T}{\gamma} \tau_n + \frac{v_0^2 l}{1 + \gamma_R \tau_n} \right) \int_{-L/2}^{L/2} \left( \frac{d \varphi_n(s)}{ds} \right)^2 ds = L,
\]
and internal dynamics of an active polymer. Various activity-induced features reflected in the Lagrangian multiplier imply pronounced effects on the relaxation times, as displayed in Fig. 2 for various persistence lengths and Peclet numbers. In the limit of a flexible polymer, the relaxation times become fixed for $pL \approx 10^3$ and the Péclet numbers $Pe = 10^3, 3 \times 10^2, 10^2$, and $5 \times 10^2$ (bottom to top). The black squares (top) show the mode-number dependence of a flexible polymer with $pL = 10^3$. The solid lines indicate the relations for passive flexible ($\sim n^{-3}$) and semiflexible ($\sim (2n - 1)^{-4}$) polymers, respectively. The other parameters are the same as in Fig. 1. From Ref. [36].

where the relaxation times themselves depend on $\lambda$ in general. Figure 1 displays Lagrangian multipliers $\lambda = 3\mu\alpha/2$ as function of the Péclet number

$$Pe = \frac{v_0}{D_{\gamma}l},$$

for various bending stiffness values $pL = L/2\ell_p$. In the limit $Pe \to 0$, the multiplier assumes the value of a passive polymer $\mu = 1$. Activity leads to an increase of the multiplier $\mu$ with increasing $Pe$, where semiflexible polymers with $pL \lesssim 10$ exhibit a pronounced dependence on $Pe$ already for moderate Péclet numbers. Over the considered range of Péclet numbers, the curves exhibit the asymptotic dependence $\mu \sim Pe^{4/3}$ for large $Pe$, independent of the polymer stiffness. The increase of $\lambda$ with increasing $Pe$ reflects the tendency of the active force to stretch the polymer, which is compensated by an increase of the mean bond force in order to maintain the constant average contour length. The various activity-induced features reflected in the Lagrangian multiplier imply pronounced effects on the conformations and internal dynamics of an active polymer.

**Results: Relaxation Times**

Activity affects the polymer wave numbers $\zeta_n$ and relaxation times $\tau_n$ via the stretching coefficient $\lambda$. Results for the Péclet-number and stiffness dependence of the wave numbers are presented in Ref. [38]. Polymer relaxation times (13) are displayed in Fig. 2 for various persistence lengths and Péclet numbers. In the limit of a flexible polymer, the relaxation times become

$$\tau_n = \frac{\tau_R}{\mu n^2}, \quad \tau_R = \frac{\gamma L^2}{3\pi^2 k_B T p},$$

where $\tau_R$ is the Rouse relaxation time [52, 59]. Since, $\mu$ is a monotonically increasing function of $Pe$, activity accelerates the relaxation process and the relaxation times become shorter. This is illustrated in Fig. 2(a) for the longest relaxation time $\tau_1$. For $pL \gg 1$, $\tau_1$ exhibits the predicted $1/\mu$ behavior, with $\tau_1 \sim Pe^{-4/3}$ for large $Pe$. At $Pe \lesssim 1$, the relaxation times of the stiffer polymers are determined by the bending modes, and $\tau_1$ approaches the persistence length and $Pe$ independent value $\tau_1 = \gamma L^3/36k_B T$ with decreasing $pL$. The increase of $\mu$ with increasing Péclet number causes a decrease of the relaxation time $\tau_1$, and in the limit $Pe \gg 1$, the relaxation times assume the asymptotic value of Eq. (16) independent of stiffness. Quantitatively, $\tau_1$ is given by Eq. (16) as soon as $\mu \gg (\pi/2pL)^2$ [36]. The latter is already satisfied for rather moderate Péclet numbers on the order of $Pe \sim 10^4 \sim 10^5$.

The mode-number dependence of the relaxation times $\tau_n$ of semiflexible polymers is illustrated in Fig. 2(b). At low $Pe$, we find the well-known dependence $\tau_n/\tau_1 \sim (2n - 1)^{-4}$ valid for passive semiflexible polymers [52, 56, 60]. With increasing $Pe$, the ratio $\tau_n/\tau_1$ shifts to larger values, and for $Pe \gtrsim 50$ the small-mode-number relaxation times
Results: Conformations

The conformational properties of the polymers can be characterized by their mean square end-to-end distance \(\langle r_e^2 \rangle = \langle (r(L/2) - r(-L/2))^2 \rangle\), which, in terms of the eigenfunction expansion, is given by

\[
\langle r_e^2 \rangle = 4 \sum_{n=1}^{\infty} \left( \frac{3k_B T}{\gamma} \frac{\tau_{2n-1}}{1 + \gamma \tau_{2n-1} \tau_{2n-1}} \right) \varphi_{2n-1}^2(L/2).
\] (17)

Results for active polymers are shown in Fig. 3 as a function of Péclet number for various persistence lengths. The dependence of the relaxation times on the activity determines the polymer conformations. If the relaxation times were independent of the active noise, the active-noise contribution to \(\langle r_e^2 \rangle\) would increase quadratically with \(v_0\), and hence, with the Péclet number. Here, we find the significantly slower increase of \(\langle r_e^2 \rangle \sim Pe^{2/3}\) with increasing \(Pe\).

There are several remarkable features of \(\langle r_e^2 \rangle\) for the various persistence lengths. For flexible polymers, \(\langle r_e^2 \rangle\) increases monotonically in a sublinear manner in the range \(1 \ll Pe < 10^3\) and approaches the asymptotic value \(L^2/2\) in the limit \(Pe \to \infty\) as a consequence of the finite contour length; interestingly, the polymers are not fully stretched in this limit. At large persistence lengths, \(\langle r_e^2 \rangle\) shows a nonmonotonic dependence on the Péclet number. Within a certain persistence-length-dependent range, a polymer shrinks with increasing \(Pe\). The shrinkage can be substantial for \(pL \approx 10\). Above a certain \(Pe\) value, the polymers swell again and approach the asymptotic dependence of a flexible polymer as a consequence of the dominating flexible modes in the relaxation times. It is important to note that the detailed quantitative activity-dependent behavior is a function of the number \(L/l\) of active sites along the polymer. Activity-induced swelling of flexible polymers and shrinkage of semiflexible polymers has been seen in various simulations [31, 41].

Results: Diffusion

The mean square displacement (MSD) \(\langle \Delta r(s, t)^2 \rangle = \langle (r(s, t) - r(s, 0))^2 \rangle\) of a point \(r(s, t)\) along the polymer contour includes contributions from the polymer center-of-mass motion and displacements with respect to the center of mass.
Averaging over the polymer contour yields

\[
\langle (\Delta r(t))^2 \rangle = \langle (\Delta r_{cm}(t))^2 \rangle + \sum_{n=1}^{\infty} \frac{6k_BT \tau_n}{\gamma} \left( 1 - e^{-t/\tau_n} \right) + \frac{2\nu^2 t \tau_n^2}{1 + \gamma^2 \tau_n} \left( 1 - \frac{e^{-2\nu^2 t \tau_n^2} - \gamma \nu \tau_n e^{-t/\tau_n}}{1 - \gamma^2 \tau_n} \right). 
\]  

(18)

The center-of-mass contribution is similar to that of a single ABP [1, 15, 36, 38]. Figure 4 displays MSDs of flexible and semiflexible polymers. For passive polymers, we find the well-known Rouse dependence \( \sqrt{t} \) for flexible polymers [59] and the dependence \( t^{3/4} \) for semiflexible polymers [56, 61, 62] at \( t/\tau_1 \ll 1 \). In the presence of activity, the diffusivity is significantly enhanced, as already noted before [23, 41, 63]. We can identify three characteristic time regimes. At short times, an activity-specific ballistic regime appears, which is already well pronounced for \( Pe \approx 20 \).[23, 41, 63] For times \( \gamma \tau_R \approx 1 \), the MSD crosses over to a Rouse-type regime \( \sqrt{t} \) determined by the internal polymer dynamics. Finally, the center-of-mass motion dominates the MSD with a linear increase in time for \( t/\tau_1 \gg 1 \). It is worth emphasizing that this regime is dominated by activity rather than thermal noise, since \( \langle (\Delta r_{cm}(t))^2 \rangle \approx 2\nu^2 t t'/\gamma R L \). Thereby, the crossover time \( \gamma \tau_R \gg 1 \) from the ballistic to the Rouse-type regime shifts to smaller values with increasing Péclet number, as a consequence of the decreasing relaxation times \( \tau_n \) with increasing \( Pe \). Simultaneously, the polymer characteristic regime \( \sim \sqrt{t} \) becomes shorter and vanishes for large Péclet numbers. This shortening is a consequence of the finite extensibility of a polymer. There is a remarkable feature in the intermediate time regime \( 1 < \gamma \nu R \ll \gamma \nu \tau_1 \) for semiflexible polymers. Here, at sufficiently large Péclet numbers, the segmental MSD of semiflexible polymers exhibits the \( \sqrt{t} \)-dependence characteristic for flexible polymers [59]. This is a consequence of the crossover of the relaxation times from bending-mode dominated to Rouse-mode dominated with increasing activity. Such a change does not appear when the stretching coefficient of a passive polymer \( (\mu = 1) \) is used only. In this case, the \( t^{3/4} \) dependence persists for all \( Pe \) in the intermediate time regime.

**ACTIVE POLYMER: COMPUTER SIMULATION**

For the simulation, we consider a discrete polymer of touching beads, each being an ABP. The equation of motion of bead \( i (i = 1, \ldots, N) \) is given by

\[
m \ddot{r}_i + \gamma \dot{r}_i(t) = \dot{\gamma} \nu \dot{e}_i(t) + F_i + \hat{\Gamma}_i(t).
\]

(19)

Here, \( \gamma = \nu l \) is the friction coefficient of a bead, \( F_i \) the forces on a bead, and \( \hat{\Gamma}_i \) an stationary, Markovian, and Gaussian process analogous to Eq. (4). The forces follow from the considered potentials

\[
U_i(R_i) = \frac{k_b}{2} (|R_i| - l)^2, \quad U_{ij}(R_i, R_{i+1}) = \frac{k_b}{2} (R_{i+1} - R_i)^2
\]

(20)
for bonds \( (U_i) \) and bending restrictions \( (U_b) \), where \( \mathbf{R}_i = r_{i+1} - r_i \) is the bond vector [64, 65]. In addition, excluded volume interactions are captured by a truncated and shifted Lennard-Jones potential [64, 66]. The orientation \( \mathbf{e}_i(t) \) (unit vector) of an APB monomer changes in a diffusive manner according to
\[
\dot{\mathbf{e}}_i(t) = \hat{\eta}_i(t) \times \mathbf{e}_i(t).
\]  
Here, \( \hat{\eta}_i(t) \) is a Gaussian and Markovian stochastic process with zero mean and the second moments
\[
\langle \hat{\eta}_i(t) \cdot \hat{\eta}_j(t') \rangle = 2(d - 1)D_R \delta_{ij} \delta(t - t').
\]
Equation (19) is integrated by a Verlet-type algorithm [67], whereas for Eq. (21) an Euler-type scheme is applied (cf. appendix of Ref. [8]).

Results for polymers with \( N = 50 \) monomers, i.e., \( L = 49l \), are presented in Fig. 5. We set \( \gamma = 10 \sqrt{k_B T m / l} \) and use an integration time step of \( 10^{-3} \sqrt{m l^2 / k_B T} \). Persistence lengths and, hence, \( pL \) values for the considered bending stiffness parameters \( \kappa_b k_B T / l^2 = 0, 1, 10, \) and 100 follow by a fit of the mean square end-to-end distance
\[
\langle r_e^2 \rangle = \frac{L}{p} - \frac{1}{2p^2} \left( 1 - e^{-2pL} \right)
\]
of a passive semiflexible polymer to the numerically obtained mean square end-to-end distances, which yields \( pL = 49, 18, 1.75, \) and 0.25, respectively.

The numerically obtained results (Fig. 5(a)) are in close agreement with the theoretical prediction discussed in the previous sections. The mean-field theoretical approach somewhat overestimates the deformation and the discrete polymers assume a somewhat smaller value than \( L^2 / 2 \) in the limit \( \text{Pe} \to \infty \). Despite that, the simulations predict a monotonic swelling of the flexible polymers, a shrinkage of the semiflexible polymers followed by a swelling similar to that of a flexible polymer for large Péclet numbers. Excluded-volume effects are naturally only visible in the coiled state of a polymer and disappear with increasing swelling of the polymer, either by increasing of stiffness \( (pL \to 0) \) or increasing Péclet number \( (\text{Pe} \to \infty) \). Consequently, we see an excluded-volume induced swelling for \( pL = 49 \) and 18 at \( \text{Pe} \approx 10 \) only, as illustrated in Fig. 5(b). Interestingly, the flexible polymer with excluded-volume interactions seems to monotonically swell with increasing \( \text{Pe} \) and that for \( pL = 18 \) shows a relative shrinkage comparable to that without such interactions. The monotonic swelling of the flexible polymer is in contrast to similar simulations of active polymers in two dimensions [40]. The latter simulations yield a significant polymer shrinkage for \( \text{Pe} \gtrsim 1 \). As discussed in Ref. [40], the initial shrinkage can be attributed to caging by neighboring monomers. Such an effect is much less relevant for polymers on tree dimension, which explains our monotonic swelling.
Conclusions

The results for linear polymers illustrated the emergent novel features of bound particles exposed to active noise (colored noise). As mentioned in the introduction, polymers and semiflexible filaments are an integral part of biology cells and, moreover, are omnipresent in technical applications. Surprisingly, the implications of active noise on the polymer properties have received little attention so far. We expect that incorporation of activity will shed new light on the properties of active polymer materials and will provide novel insight into mixtures of active and passive components.

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