End-evaporation dynamics revisited

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We present analytical results on the so-called end-evaporation kinetics in equilibrium polymeric systems following a temperature jump (T jump). A T jump prepares the system with a nonequilibrium length distribution, after which it relaxes back to its equilibrium state. Starting from a master equation, we develop a mean-field analytical theory based on a generating function approach, which allows explicit approximate expressions for the monomer and dimer concentrations to be derived in a discrete setting; the concentrations of the other chains as well as the average chain length were shown to be entirely expressible in terms of the monomer and dimer concentrations. We find that the calculated monomer and dimer concentrations as well as the average chain length are in good agreement with numerical simulation results and do not suffer from some of the defects of earlier continuum theories. Furthermore, the relaxation was shown to take place in three different stages. The first stage comprises the very fast relaxation of the monomers to almost their equilibrium concentration; the other polymer chains have hardly relaxed. During the second stage, which is highly nonlinear, a redistribution of material at practically constant monomer density takes place. Only in the final stage of the relaxation process the chain concentrations approach their true equilibrium values. In this stage there are only very small shifts in the concentrations of chains, which are governed by extremely slow “indirect” monomer-mediated processes.


I. INTRODUCTION

Equilibrium polymers belong to the class of supramolecular structures in which bifunctional molecular building blocks, referred to as monomers, can connect to each other and form quasi-one-dimensional polymerlike assemblies. The most common examples of equilibrium polymers are flexible wormlike surfactant micelles such as found in aqueous solutions of cetyltrimethylammoniumchloride (CTAC) or -bromide (CTAB) with added KBr or NaSal.

Another important example of equilibrium polymers is given by self-assembled stacks of discotic molecules,1,2 which have possible applications in plastic transistors and photovoltaics. A large number of studies on the equilibrium properties of equilibrium polymers have been published, both theoretical3-5 and experimental;5,6 for recent reviews on this subject see Refs. 5 and 7.

Investigations of the kinetics of equilibrium polymers were initiated by Cates et al. in the 1980s,8 see also Ref. 9. They proposed reversible-scission-and-recombination kinetics, presented in Fig. 1(a), in which a single chain can break at any point along the chain and visa versa: two chains can recombine to form a single linear chain. This process was later shown to agree with experimental stress relaxation measurements in wormlike micelles,10 which exhibit a single stress relaxation time for all but very short times. Moreover, it was found, using reversible-scission-and-recombination kinetics, that following a sudden temperature jump (T jump), the polymer length distribution relaxes on a time scale $t \sim (2k_1N_c)^{-1}$, where $k_1$ is the breaking rate of a single bond and $N_c$ denotes the average equilibrium chain length to which it relaxes after the jump. Later, three additional kinetic schemes were examined, two of which conserve the number of polymer chains: end-interchange and bond-interchange kinetics, which are depicted in Figs. 1(b) and 1(c), respectively. In bond interchange, two polymers collide temporarily forming a four-armed junction that subsequently decays such that effectively the two bonds at the junction are interchanged. In the end-interchange process one chain end collides with another chain at some random position along that chain, where a temporarily three-armed junction is formed.

FIG. 1. Four types of kinetics that could occur for equilibrium polymers. Reversible scission and recombination (a) applies to wormlike micelles. End interchange (b) and bond interchange (c) are less effective mechanisms to relax stress and conserve the mean chain length. End evaporation (d) is an extremely slow relaxation process which is expected to be pertinent to self-assembling discotic systems.

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This junction then decays almost immediately, so that effectively the chain ends are interchanged. As is clear from Figs. 1(b) and 1(c) the number of chains is conserved in these two types of kinetics. This makes their experimental verification by a $T$ jump experiment in which the relaxation of the mean chain length is monitored, such as in a radiation scattering setup, impossible. For a detailed discussion of different reaction kinetics, see Ref. 11.

A fourth possible reaction mechanism is the so-called end-evaporation kinetics, where a chain captures or loses one monomer at a time. This mechanism is presented in Fig. 1(d) which was investigated fairly extensively using a continuous approximation in Ref. 12 by Marques et al. and more recently, by numerical simulations, by Milchev et al. In this paper we revisit the problem of end-evaporation kinetics for three reasons:

(i) So far all theoretical investigations are limited to a mean-field description. Here, we present a derivation, starting from a master equation, of the equations underlying the kinetics that clarify the assumptions that are implicitly made in the mean-field approach of Refs. 8 and 11–13. Furthermore, the master equation allows us to generalize the equations and account, at least in principle, for the diffusion of the polymeric chains. This has recently been shown to be important, as some systems of equilibrium polymers in a melt are actually found to be diffusion controlled and not reaction controlled.

(ii) There are experimental systems in which end evaporation is the most likely governing reaction mechanism. A typical example is, for instance, given by supramolecular structures consisting of discotic molecules that self-assemble into rigid linear stacks (see Ref. 2 for a review) and that exhibit an extremely slow relaxation. Actually, the example of stacks of discotic molecules belongs to the more general class of rods that align in a magnetic field or in a nematic liquid-crystalline phase. In this case the dynamics is essentially one dimensional, as fluctuations in the other directions are strongly suppressed. Another example, which comes from biology, is the protein actin. This helical molecule is known to obey what is essentially an end-evaporation type of kinetics, albeit that an extra activation step is involved. In fact, that the end-evaporation mechanism should indeed be dominant for highly inflexible supramolecular structures can be rationalized as follows. Two rigid rods can only recombine to form a longer single rod if the difference in orientation angles between the rods is smaller than $\alpha = R/N_c$, where $R$ is the radius of the rod and $N_c$ is its equilibrium length. It is plausible that the reaction contribution to the relaxation process will be dominated by reactions between rods and monomers for sufficiently long rods. For reactions between rods become highly improbable for long rods, or equivalently, small $\alpha$. Note also that for breakage to occur at the ends, the energy loss due to breakage should be smaller at the ends than at other places along the chains. That this is indeed the case for stiff helical assemblies was shown, for example, in Ref. 18.

(iii) Almost all analytical theories use a continuous approximation, whereas real systems are subject to discrete dynamics because assemblies are consist of a discrete number of particles. Moreover, a continuous approximation has problems that are inherent to this method: The monomer concentration cannot directly be obtained and there are quantitative errors in the prediction of the other chain concentrations. For the discrete case only numerical studies have been performed concentrating on large $T$ jumps and very long times. From these studies it transpires that for times $k_1t \gg N_c^2$, with $k_1$ the breaking rate, the mean chain length $N(t)$ relaxes to its equilibrium value as $t^{-1}$ with $\tau \sim N_c^3$, a typical relaxation time.

In the present analytical work end-evaporation kinetics is studied for the case of parallel rods using a generating function approach that preserves the discrete character of the supramolecular structures. This powerful method allows us to obtain very good approximations for the concentration of the $n$-mers at all time scales. Our calculations show, in agreement with the findings of Refs. 12, 13, and 19, that the relaxation process can roughly be divided in three stages. During the first stage, which takes place for $t \leq 1/k_1N_c$, the monomers relax (exponentially) quite close to their equilibrium value. The other chains, however, relax so slowly that their concentrations hardly differ from their initial values during this short initial stage. In the second stage, for $1/N_c \lesssim k_1t \lesssim N_c^2$, the addition and shedding of monomers at nearly constant monomer density leads to a redistribution of mass among the chains. As soon as the concentration of $n$-mers approaches its equilibrium value, the system enters the third stage corresponding to $k_1t \approx N_c^2$ in which the system can be described as slightly perturbed from its equilibrium state. Since the final reshuffling of the mass over the chains is mediated via the monomers, the relaxation of the concentration of monomers and other chains then has approximately the same time dependence.

We have also analytically calculated the time evolution of the mean chain length $N(t)$, which is quite easily evaluated in terms of the generating function of the concentrations. Not surprisingly, we find that the average chain length $N(t)$ also shows a three-stage relaxation. In the first stage the monomers relax rapidly, and this leads to a fast initial relaxation of the chain length. The relaxation in stage two can, to a rather good approximation, be entirely expressed in terms of the time integral of the perturbation in the dimer concentration. For long times $k_1t \gg N_c^2$, it becomes important to take multiple reactions into account, which we ignore for simplicity. Therefore, in this regime deviations between the analytical and numerical results arise. Nevertheless, we find quite good agreement between numerical computations and our analytical calculations of the average chain length over a considerable time window.

The remainder of this paper is organized as follows. First, in Sec. II, we present the model in terms of a meso-
copic master equation. From the master equation, it immediately follows that the commonly used kinetic equations are only exact if the correlations between the equal-point densities of different polymers vanish. Moreover, it gives a direct way to implement diffusive motion in our evolution equations, which we will analyze in a forthcoming work. In Sec. III, we study how the polymer concentration changes after a $T$ jump in Laplace space using the generating function formalism. In Sec. IV, we study the polymer concentrations and the average length distribution in the time domain and compare our results with numerical findings. Finally, we conclude in Sec. V with a summary and a discussion of our results.

II. THE MODEL

The system that we study consists of a collection of rigid rods, representing the polymers, with reactive end caps onto which monomers can adsorb or desorb. Initially, the rods are placed randomly on a quasi-one-dimensional double lattice with 2$M$ sites. For computational convenience and clarity, we have divided the even and even lattice positions into two lattices in Fig. 2. The upper lattice corresponds to the even and the lower lattice with the odd sites. The rods can move back and forth due to diffusion and shed or adsorb monomers without being hindered by the presence of the other polymers. This means that we do not invoke volume exclusion and envisage, in effect, a three-dimensional system in which the rods are perfectly aligned. A typical configuration is given in Fig. 2. An approximate experimental realization may be the end-evaporation kinetics in uniaxially aligned solutions of self-assembled discs such as in a nematic phase or in a high magnetic field.

The rods have two reactive ends, so a monomer can attach on either side of a chain or a chain can lose a monomer at either of its ends. We assume that the “off” or breakup rate (for a single chain end) is constant and given by $k_1$; the “on” or recombination rate (per chain end) of a chain of length $n$ with a monomer is denoted by $k_2$, which is also assumed to be constant. To eliminate finite-size effects, we impose periodic boundary conditions. The system is translationally invariant and therefore only the center-of-mass coordinates and the lengths of the chains need to be considered. As shown in Fig. 2, the monomers and all other chains of odd length are located on even lattice points (upper lattice), but dimers and, in fact, all chains of even length, have their center of mass positioned on odd lattice points (lower lattice). The length of a rod $n$ can only take on discrete values between 1 and $\infty$. A rod of length $n$ is said to be at position $i$, with $i=0,1,2,\ldots,2M-1$, if its center of mass is at $i$. The number of rods of length $n$ in a particular lattice point $i$ is denoted by $X^n_i$, which can take any integer value greater than or equal to zero. The size of a monomer and that of a lattice cell is set equal to unity, hence $X^n_i$ can also be considered as a number density.

We are interested in the probability $P\{X^n_i\},t$ that at time $t$ the system is in a particular configuration labeled by $X^n_i$. The probability $P\{X^n_i\},t$ satisfies the so-called master equation

$$\frac{\partial}{\partial t}P\{X^n_i\},t = k_1 R_{\text{off}} + k_2 R_{\text{on}} + R_{\text{diff}},$$

where $R_{\text{off}}$ and $R_{\text{on}}$ are the probabilities that the configuration $\{X^n_i\}$ is reached by some rod shedding or adsorbing a monomer, respectively. The $R_{\text{diff}}$ represents the probability to come to the state $\{X^n_i\}$ not via reactions but via the diffusive motion of chains.

Within end-evaporation kinetics, the expression for $R_{\text{off}}$ is given by

$$R_{\text{off}} = \sum_{i=0}^{2M-1} \sum_{n=1}^{2M-1} P(X^n_i, 1, X^n_{i+1} - 1, X^n_{i+1} - 1) + \sum_{i=0}^{2M-1} \sum_{n=3}^{2M-1} P(X^n_i, 1, X^n_{i-1} - 1, X^n_{i+1} - 1)$$

$$+ \sum_{i=0}^{2M-1} \sum_{n=2}^{2M-1} P(X^n_i, 1, X^n_{i-n} - 1, X^n_{i-n} - 1) + \sum_{i=0}^{2M-1} \sum_{n=2}^{2M-1} P(X^n_i, 1, X^n_{i+1} - 1, X^n_{i-n} - 1)$$

where the first two and the last term represent the process of losing a monomer at either chain ends. The third and fourth terms represent the shedding process for a dimer, which has to be treated separately as dimers have only a single bond that can break but can adsorb monomers at both chain ends.

The $R_{\text{on}}$ term is given explicitly by

$$R_{\text{on}} = \sum_{i=0}^{2M-1} P(X^n_i, 1, X^n_{i+1} + 1, X^n_{i+2} + 1) + \sum_{i=0}^{2M-1} P(X^n_i, 1, X^n_{i+1} + 1, X^n_{i+2} + 1)$$

$$+ \sum_{i=0}^{2M-1} P(X^n_i, 1, X^n_{i+1} + 1, X^n_{i+2} + 1) + \sum_{i=0}^{2M-1} P(X^n_i, 1, X^n_{i+1} + 1, X^n_{i+2} + 1)$$

$$- \sum_{i=0}^{2M-1} P(X^n_i, 1, X^n_{i+1} + 1, X^n_{i+2} + 1),$$

(3)
where the first and last terms represent reactions between monomers, and the four other terms are reactions between monomers and chains of length \( n > 1 \).

The diffusive part of the master equation \( R_{\text{diff}} \) reads

\[
R_{\text{diff}} = \sum_{j=0}^{2M-1} c_n(X_{i+2}^n + 1)P(X_t^n - 1)X_r^n + 1) - X_r^n P(\{X_r^n\}),
\]

where the first two terms represent the net hopping probability to the left, and the last two terms the net hopping probability to the right. Here, the \( c_r \) denote the diffusive hopping rates as a function of the rod length \( n \). We keep the diffusive contribution for the sake of completeness, although in our \( T \) jump calculations in Sec. III, we choose to ignore it. Hence, we presume in this work that diffusion is infinitely fast, so that the system will be homogeneous at all times and on all length scales. An analysis of the impact of a finite diffusivity on the on and off reactions is postponed to a future publication.

Integrating Eq. (1) over all possible values of \( X_t^n \) shows that the probability is indeed conserved, as it should. By multiplying Eq. (1) with \( X_t^n \) and summing over all possible values of \( n \) and \( i \), it is now straightforward to derive the evolution equations for the average occupation numbers of the cells denoted by \( \langle X_t^n \rangle \). This gives, e.g., for the average number of monomers at site \( i \),

\[
\dot{\langle X_i^1 \rangle} = k_1 \sum_{m=1}^{\infty} \langle X_{i+m}^m \rangle + k_2 \sum_{n=1}^{\infty} \langle X_{i+m+1}^m \rangle + \langle X_{i-1}^1 \rangle + c_i \langle X_{i-2}^1 \rangle - 2 \langle X_i^1 \rangle.
\]

For the dimers, the evolution equation reads

\[
\dot{\langle X_i^2 \rangle} = k_3 \langle X_{i-1}^3 \rangle + \langle X_{i+1}^3 \rangle - k_4 \langle X_{i-1}^1 \rangle + k_5 \langle X_{i+1}^1 \rangle + \langle X_{i-2}^2 \rangle - 2 \langle X_i^2 \rangle,
\]

and for all other \( n \)-mers with \( n > 2 \) we have

\[
\dot{\langle X_i^n \rangle} = k_1 \langle X_{i+n-1}^{n+1} \rangle + \langle X_{i+n}^{n+1} \rangle - 2 \langle X_i^n \rangle.
\]

The monomers and dimers have to be treated separately from the other chains, because monomers cannot disintegrate and dimers have only one bond that after breaking produces two monomers instead of just one.

From Eqs. (5)–(7), the evolution of the density of polymer chains can only be found provided that the pair correlations \( \langle X_t^n X_t^m \rangle \), which can be expressed in terms of three-point correlators and so on, are known. This produces a hierarchy of evolution equations that couple \( n \)-point correlation functions to \( (n+1) \)-point correlation functions. In order to solve this hierarchy, one needs to close this infinite set of equations. The simplest Ansatz is presuming that the pair correlations factorize. This mean-field approximation truncates the hierarchy at the pair-correlation level. The equations that arise in this case are indeed those of the earlier work of Refs. 8, 12, and 13 provided one sets \( R_{\text{diff}} = 0 \). We further note that at the level of a linearized theory, i.e., for small \( T \) jumps, the mean-field equations become exact. For larger \( T \) jumps, however, this is no longer the case.

The master equation method, which we follow here, has the advantage that it elucidates the assumptions underlying the mean-field equations. Moreover, if one performs a system-size expansion, as described, for example, in Ref. 21, one can even obtain a first-order noise correction to the mean-field equations. Here, we will not address this subject further, but focus instead on the mean-field equations and, in particular, examine the average length and the concentrations of the rods following a \( T \) jump.

Next, we introduce a position coordinate \( x = i/2 \), so that the rods of even length are at positions \( 1/2, 3/2, \ldots, M - 1/2 \), and those of even length at \( 0, 1, \ldots, M - 1 \). Moreover, for notational convenience we introduce the notation \( \psi(n, x, t) \) for the average density of rods at \( x \), i.e., \( \psi(n, x, t) \equiv \langle X_t^n \rangle \). The equations for the density \( \psi(n, x, t) \) obey

\[
\frac{\partial \psi(n, x, t)}{\partial t} = k_1 \left[ \psi(n+1, x+1/2, t) - (1 + \Theta(n-3)) \psi(n, x, t) + \psi(n+1, x-1/2, t) + k_5 \psi(n, x+1/2, t) \right] + k_2 \psi(n-1, x+1/2, t) \psi(1, x-(n-1)/2, t)

+ k_2 \psi(n-1, x-1/2, t) \psi(1, x-(n-1)/2, t) \Theta(n-3) - k_2 \psi(1, x-(n+1)/2, t) \psi(n, x, t)

- k_2 \psi(1, x+(n+1)/2, t) \psi(n, x, t) + c_i \left[ \psi(n, x-1, t) + \psi(n, x+1, t) - 2 \psi(n, x, t) \right],
\]

for \( n > 1 \). The Heaviside function \( \Theta \) takes care of the special case \( n = 2 \). For the monomers we have the equation

\[
\frac{\partial \psi(1, x, t)}{\partial t} = k_1 \sum_{n=2}^{\infty} \psi(n, x+(n-1)/2, t) + k_2 \sum_{n=2}^{\infty} \psi(n, x-(n-1)/2, t) - k_3 \psi(1, x-1/2, t) \psi(1, x-1/2, t)

- k_3 \psi(1, x+1/2, t) \psi(1, x+1/2, t) \Theta(n-3) - k_2 \psi(1, x-(n+1)/2, t) \psi(n, x, t)

- k_2 \psi(1, x+(n+1)/2, t) \psi(n, x, t) + c_i \left[ \psi(1, x-1, t) + \psi(1, x+1, t) - 2 \psi(1, x, t) \right].
\]
Equations (8) and (9) are, of course, not new. Apart from the presence of diffusive terms, the only difference with the rate equations from Refs. 8 and 13 is the way they were derived. The on and off rates appearing in Eqs. (8) and (9) are not independent but have to obey a detailed balance. For the homogeneous, stationary solution to Eqs. (8) and (9), we find

$$\psi_{eq}(n) = \langle X^n_{eq} \rangle = \frac{k_1}{k_2} \exp(\lambda_x n),$$

where $\lambda_x$ is the related to average chain length by

$$\lambda_x = \ln \left( 1 - \frac{1}{N_x} \right).$$

In fact $-\lambda_x$ is a chemical potential.$^7$ For $N_x \gg 1$, we have $\lambda_x \sim -1/N_x$. Due to mass conservation, $N_x$ is related to the total mass density $n = \sum_{n=1}^{\infty} n \psi_{eq}(n)$ via

$$N_x = \frac{1}{2} \ln \left( 1 + \sqrt{1 + 4\phi k_2^2/k_1} \right).$$

This reduces in the long chain limit $N_x \gg 1$ to the well-known square-root law

$$N_x = \sqrt{\frac{k_2 \phi}{k_1}}.$$ (13)

Presuming the system to be locally in thermal equilibrium, we can assume a detailed balance in which case the reaction rates $k_1$ and $k_2$ can be related to the bond or end-cap energy$^9$ $E$ according to $k_1/k_2 = e^{-E/k_BT}$. The end-cap energy represents the free-energy cost of breaking a chain into two. Typical values of $E$ are in the range of $(10–40)k_BT.$ This demonstrates that the reaction rates $k_1$ and $k_2$ vary with temperature $T$. Now that we have established the governing kinetic equations, we next turn to the question what happens when the system undergoes a sudden temperature change.

### III. T-JUMP CALCULATIONS

Starting from Eqs. (8) and (9), we perform a linear perturbation analysis. To that end we write

$$\psi(n,x,t) = \psi_{eq}(n) + \psi_n(x,t),$$

where the subscript $n$ in $\psi_n(x,t)$ indicates that we are dealing with a perturbation in the chain concentration rather than the actual concentration. For the perturbation expansion to be valid it is required that $|\psi_n(x,t)| \ll \psi_{eq}(n,x,t)$. However, as we shall see later, the perturbation expansion proves useful even for perturbations that cannot be considered small. If we substitute expression (14) for $\psi(n,x,t)$ in Eqs. (8) and (9), we obtain, after linearization, for the $n$-mers ($n \geq 2$)

$$\frac{\partial \psi_n(x,t)}{\partial t} = k_1 [\psi_{n+1}(x+1/2,t) - (1 + \Theta(n-3)) \psi_n(x,t) + \psi_{n+1}(x-1/2,t)] + k_1 e^{\lambda_x} [\psi_{n-1}(x+1/2,t) + \psi_{n-1}(x-1/2,t) \Theta(n-3)]$$

$$+ k_1 e^{\lambda_x} \psi_n(x-(n-1)/2,t) + \psi_{n-1}(x+(n-1)/2,t) \Theta(n-3)] - k_1 e^{\lambda_x} \psi_n(x-(n+1)/2,t) + \psi_{n+1}(x+(n+1)/2,t) - 2k_1 e^{\lambda_x} \psi_n(x,t) + c_n \psi_n(x-1,t) + \psi_n(x+1,t) - 2\psi_n(x,t),$$

and for the monomers

$$\frac{\partial \psi_1(x,t)}{\partial t} = k_1 \sum_{n=2}^{\infty} \psi_n(x+n-1/2,t) + k_1 \sum_{n=2}^{\infty} \psi_n(x-(n-1)/2,t) - k_1 e^{\lambda_x} [\psi_1(x+1,t) + \psi_1(x-1,t)] - 2k_1 e^{\lambda_x} \psi_1(x,t)$$

$$- k_1 e^{\lambda_x} \sum_{n=2}^{\infty} \psi_n(x+(n-1)/2,t) + \psi_n(x+(n+1)/2,t)] - 2k_1 e^{2\lambda_x} \psi_1(x,t)$$

$$+ c_1 [\psi_1(x-1,t) + \psi_1(x+1,t) - 2\psi_1(x,t)].$$

(16)

Because Eqs. (15) and (16) are nonlocal in space, we perform a spatial Fourier transformation. In the limit $c_n \to 0$, inhomogeneities relax instantaneously, hence we need only consider the limit of zero wave number. Of course, in this limit there are no longer any contributions from the diffusive terms to the relaxation processes. A more elaborate analysis for inhomogeneous systems with finite $c_n$, including the calculation of structure functions, will be presented in a separate paper.

For the case of zero wave number, one can actually solve the equation for the monomers in terms of the densities of the other chains with length $n > 1$. The solution reads

$$\psi_1(t) = e^{-h_{\text{fast}} t} \psi_1(0) + 2(1 - e^{\lambda_x}) \sum_{n=2}^{\infty} \psi_n(t) * e^{-h_{\text{fast}} t},$$

(17)

where the asterisk denotes a convolution and $\psi_1(0)$ is the surplus or deficit in the initial monomer concentration compared with the equilibrium monomer concentration at $t = \infty$. The fast relaxation rate $h_{\text{fast}}$ is given by
\[ h_{\text{fast}} = \left( 4e^{h_0} + \frac{2e^{h_0}}{1 - e^{h_0}} \right) k_1 = 2k_1N_\infty \left( 1 - \frac{1}{N_\infty^2} \right). \]  

This relaxation rate was calculated under the assumption that the perturbations \( \psi_n(t) \) are small. We note that for larger jumps, we still have initially an exponential decay of the perturbations in the monomer concentration, but with a modified relaxation rate \( h_{\text{fast}}' \). In particular, there is an asymmetry between a jump with \( N_0 < N_\infty \) and \( N_\infty < N_0 \), which has, in fact, also been reported by Milchev et al.\(^{13} \) For small jumps this asymmetry is not discernible as it is a higher order effect, and typically \( O(1/N_\infty^2) \), smaller than the leading terms.

One can see from Eqs. (17) and (18) that on time scales of the order \( \ln(N_\infty)/N_\infty \) the second term in (17) can be neglected, and the monomer concentration relaxes essentially exponentially to the new equilibrium concentration. The relaxation rate \( h_{\text{fast}} \) is in this limit given by

\[ h_{\text{fast}} = 2k_1N_\infty. \]  

The initial relaxation time, given by \( h_{\text{fast}}^{-1} \), corresponds exactly to the breaking time in the reversible-scission-and-recombination scheme of Ref. 8. This can be easily understood as follows. If initially there is a surplus of monomers, the first step in the relaxation process consists of adsorption of monomers by the longer chains. For short times only direct processes will contribute in which case the reversible-scission-and-recombination and end-evaporation schemes lead to an equivalent relaxation rate. As there is symmetry for small \( T \) jumps, the same behavior will be found for the case in which there is a small deficit of monomers. However, as we will see later, only the monomers have such a small relaxation time for the initial stage of the relaxation process.

The relaxation of the \( n \)-mers with \( n > 1 \) is governed by

\[ \frac{\partial \hat{\psi}_n(t)}{\partial \tau} = 2k_1\hat{\psi}_{n+1}(t) - k_1(1 + \Theta(n - 3))\hat{\psi}_n(t) + k_1e^{h_0} \]

\[ \times \left[ 1 + \Theta(n - 3) \right] \hat{\psi}_{n-1}(t) + k_1e^{h_0-n}\hat{\psi}(t) \]

\[ \times \left[ 1 + \Theta(n - 3) \right] - 2k_1e^{h_0-n}\hat{\psi}_1(t) - 2k_1e^{h_0}\hat{\psi}_0(t). \]

Henceforth, we express time relative to the bond breaking time \( k_1^{-1} \) and introduce a dimensionless time \( \tau = k_1t \). In order to calculate the relaxation of the \( n \)-mers we introduce a generating function \( G(s, \tau) \) defined by

\[ G(s, \tau) = \sum_{n=1}^{\infty} \hat{\psi}_n(\tau)s^n = e^{-2(1+e^{h_0})s} \sum_{n=2}^{\infty} \hat{\psi}_n(\tau)s^n \]

\[ = e^{-2(1+e^{h_0})\tau}G(s, \tau), \]

where

\[ \hat{\psi}_n(\tau) = \psi_n(\tau)e^{2(1+e^{h_0})\tau - n\lambda_0/2} \quad \text{and} \quad s = se^{h_0/2} \]

are introduced in order to facilitate the calculations. The function \( G(s, \tau) \) satisfies a partial differential equation that can be derived by summing Eq. (20) over \( n \) after multiplying with \( s^n \). As is shown in Appendix A, this equation can be solved to produce the following expression:

\[ \hat{G}(s, \tau) = e^{-2(1+e^{h_0})\tau} \left( \sum_{n=2}^{\infty} \hat{\psi}_n(0)s^n \right) e^{2(1+e^{h_0})\tau - (s^2 - 2s e^{h_0/2})} \]

\[ \times \int_0^\tau e^{2(1+e^{h_0})\tau - (s^2 - 2s e^{h_0/2})} \hat{\psi}_1(t)dt' - 4 \sinh(\lambda_0/2) \]

\[ \times \sum_{n=2}^{\infty} s^n e^{\lambda_0 n/2} \int_0^\tau e^{2(1+e^{h_0})\tau - (s^2 - 2s e^{h_0/2})} \hat{\psi}_1(t)dt' \right). \]

(23)

If we next employ the fact that the generating function for the modified Bessel functions \( I_n(z) \) is given by

\[ \sum_{k=-\infty}^{\infty} e^{z e^{h_0/2}} I_n(z) = e^{z e^{h_0/2}}, \]

we can equate equal powers of \( s^2 \), which yields equations for \( \hat{\psi}_n(\tau) \) for \( n \geq 2 \); the other terms give identities that correspond with known rules for adding the Bessel functions \( I_n(z) \) and \( I_{n+1}(z) \). See, for example, Ref. 23.

By equating all terms of order \( s^2 \), we obtain the following integral equation for the perturbations in the dimer concentration \( \hat{\psi}_2(\tau) \) in terms of the perturbations in the monomer concentration \( \hat{\psi}_1(\tau) \):

\[ \hat{\psi}_2(\tau) = \sum_{n=2}^{\infty} \hat{\psi}_n(0) I_{n-2} [4e^{h_0/2}T] \]

\[ + \int_0^\tau I_0[4e^{h_0/2}(\tau - t')] \hat{\psi}_2(t')dt' - 2e^{h_0/2} \]

\[ \times \int_0^\tau I_0[4e^{h_0/2}(\tau - t')] \hat{\psi}_2(t')dt' \]

\[ - 4 \sinh(\lambda_0/2) \sum_{n=2}^{\infty} e^{\lambda_0 n/2} \]

\[ \times \int_0^\tau \hat{\psi}_1(t') I_{n-2} [4e^{h_0/2}(\tau - t')]dt', \]

(25)

with \( \hat{\psi}_0(0) \) representing the arbitrary but small initial perturbations in the concentration of rods of length \( n \). For concreteness, we now specify the \( \hat{\psi}_0(0) \) for a \( T \) jump. In this case, we have

\[ e^{h_0/2} \hat{\psi}_2(0) = \frac{\partial e^{h_0/2}}{N_0(N_0 - 1)} \frac{\partial e^{h_0/2}}{N_\infty(N_\infty - 1)}, \]

where \( N_0 \) and \( N_\infty \) are the initial and (final) average equilibrium lengths of the chain distribution, respectively, \( \lambda_0 = \ln(1 - 1/N_0) \), and \( \lambda_\infty \) is given in Eq. (11).

The integral equation (25) can be solved by performing a Laplace transform on \( \hat{\psi}_2(t) \), which we denote by \( \tilde{\psi}_2(s) \). As we have expression (23) for \( \hat{G}(s, \tau) \) in terms of the monomer and dimer concentrations, we need to determine (the perturbations of) the dimer concentration whose Laplace transformation \( \tilde{\psi}_2(s) \) we found to be given by
\[
\tilde{\psi}_2(s) = -\frac{4\phi}{N_0(N_\infty - 1)} \frac{e^{2\lambda_\infty}}{r(s) + 3s + 2(1 - e^{\lambda_\infty})} + \frac{4\phi}{N_0(N_0 - 1)}(2e^{\lambda_\infty - \lambda_0} - 1)r(s) + (1 + 2e^{\lambda_\infty - \lambda_0})s + 4e^{2\lambda_\infty - \lambda_0} - 6e^{\lambda_\infty} + 2
+ 8\tilde{\psi}_1(s)\frac{e^{\lambda_\infty}(1 - e^{\lambda_\infty})}{\sqrt{s^2 + 4(1 + e^{\lambda_\infty})s + 4(1 - e^{\lambda_\infty})^2} + 3s + 2(1 - e^{\lambda_\infty})},
\]

(27)

where we defined \( r(s) \) by

\[
r(s) = \sqrt{s^2 + 4(1 + e^{\lambda_\infty})s + 4(1 - e^{\lambda_\infty})^2}.
\]

Equation (27) is exact in the framework of linear perturbation theory. We remark that in the limit \( s \to 0 \), i.e., for long times,

\[
\tilde{\psi}_2 \rightarrow -\frac{\phi}{N_0(N_\infty - 1)} \frac{e^{2\lambda_\infty}}{1 - e^{\lambda_\infty}}
+ \frac{\phi}{N_0(N_0 - 1)} e^{2\lambda_0} + 2e^{\lambda_\infty} \tilde{\psi}_1(0).
\]

(29)

As we shall see, this expression turns out to be useful for calculating the time evolution of the length distribution of the polymers.

In fact, we find that the dynamics of the entire length distribution and the densities of the polymers with length \( n > 2 \) are determined predominantly by the relaxation of the dimers. That this is true follows by equating the coefficients of \( \tilde{\psi}_n \) in the two expressions of the generating function \( \tilde{G}(\tilde{s}, t) \) analogously to the procedure applied to find the dimer concentration. We find

\[
\tilde{\psi}_n(\tilde{s}) = \sum_{k=2}^{\infty} \tilde{\psi}_n(0) I_n[-[4e^{\lambda_\infty/2}(\tilde{t})]}
+ \int_{0}^{\tilde{t}} I_n[-[4e^{\lambda_\infty/2}(\tilde{t} - t')]) \tilde{\psi}_n(t') dt'
- 2e^{\lambda_\infty/2}
\times \int_{0}^{\tilde{t}} I_n[-[4e^{\lambda_\infty/2}(\tilde{t} - t')]) \tilde{\psi}_2(t') dt'
- 4 \sinh(\lambda_\infty/2)
\times \sum_{k=2}^{\infty} e^{\lambda_\infty k^2} \int_{0}^{\tilde{t}} I_n[-[4e^{\lambda_\infty/2}(\tilde{t} - t')]) \tilde{\psi}_1(t') dt'.
\]

(30)

From Eq. (30) it is obvious that the dynamics of the \( T \) jump relaxation is known once the time evolution of the monomer and dimer concentrations are determined. This immediately implies that we need only to focus on the monomer and dimer concentrations, which is exactly what we do here. The equation for the monomers, in Laplace space, is obtained by substituting expression (23) for \( \tilde{G}(\tilde{s}, t) \) in Eq. (17) using Eq. (27) for the perturbations in the dimer concentration. We then find the following exact expression for the perturbations in the monomer concentration:

\[
\tilde{\psi}_1(s) = \left\{ \begin{array}{l}
\frac{2e^{2\lambda_0}}{N_0(N_0 - 1)} - \frac{2e^{2\lambda_\infty}}{N_\infty(N_\infty - 1)} + \frac{8e^{2\lambda_\infty}}{N_0(N_0 - 1)(r(s) + 3s + 2 - 2e^{\lambda_\infty})} \\
- \frac{8e^{\lambda_0 + \lambda_\infty}(1 - e^{\lambda_\infty})}{N_\infty N_0(N_0 - 1)(2e^{\lambda_\infty - \lambda_0} - 1)(r(s) + (1 + 2e^{\lambda_\infty - \lambda_0})s + 4e^{2\lambda_\infty - \lambda_0} - 6e^{\lambda_\infty} + 2)} + \frac{\psi_1(0)}{\phi} \\
\times \left[ s^2 + h_{\text{fast}} s - 4e^{\lambda_\infty}(1 - e^{\lambda_\infty}) + \frac{16e^{\lambda_\infty}(1 - e^{\lambda_\infty})^2}{r(s) + 3s + 2 - 2e^{\lambda_\infty}} \right]^{-1},
\end{array} \right.
\]

(31)

IV. COMPARISON OF NUMERICAL AND ANALYTICAL RESULTS IN THE TIME DOMAIN

In Appendix B we present the detailed calculations of the inverse Laplace transform of Eq. (31). We now briefly discuss the approximations that were involved in obtaining \( \tilde{\psi}_1(\tilde{t}) \). First, Eq. (31) is inverted by choosing a Bromwich contour.\(^{32}\) This gives \( \tilde{\psi}_1(\tilde{t}) \) in terms of integrals, which is still exact in the framework of perturbation theory. Next, these integrals are approximated. For the monomers we then obtain the extremely good approximation that is uniform in time and given by
\[
\psi_1(\bar{t}) = -\left( \frac{N_e - 1}{N_0^2} - \frac{N_0 - 1}{N_e^2} \right) \times \left( -\frac{2\bar{t}}{\pi N_e^2} e^{\bar{t}^2} + \text{erf}\left[ \frac{\sqrt{-s}}{N_0^2} \right] + \frac{\bar{t}}{N_0^2} \text{erf}\left[ \frac{\sqrt{-s}}{N_e^2} \right] \right) 
\times (1 - e^{-h_{\text{fast}}}) + \left( \frac{1}{N_0^2} - \frac{1}{N_e^2} \right) e^{-h_{\text{fast}}} + O\left( \frac{1}{N_e} \right),
\]
(32)

where \( \text{erf}(x) \) denotes the complementary error function.\(^{23}\) In this expression we introduced \( s_2 = -2(1 + e^{\lambda_3}) + 4 e^{2\lambda_3/2} \) that determines the slow relaxation time scale. For values of \( |\lambda_3| \ll 1 \) equivalent to the long chain limit \( N_e \gg 1 \), \( s_2 \approx -\lambda_3^2/2 \approx -1/2N_e^2 \). From Eq. (32) it transpires there are, in fact, three distinct time regimes for monomer relaxation, which can more precisely be captured in the following scheme:

\[
\psi_1(\bar{t}) = \begin{cases} 
\left( \frac{1}{N_0^2} - \frac{1}{N_e^2} \right) e^{-h_{\text{fast}}}, & \bar{t} < N_e^{-1} \\
\left( \frac{N_e - 1}{N_0^2} - \frac{N_0 - 1}{N_e^2} \right) \left( \frac{2\bar{t}}{\pi N_e^2} e^{\bar{t}^2} - \left( 1 + \frac{\bar{t}}{N_0^2} \right) \text{erf}\left[ \frac{\sqrt{-s_2}}{N_e^2} \right] \right), & N_e^{-1} \ll \bar{t} \ll N_e^2 \\
\left( \frac{N_e - 1}{N_0^2} - \frac{N_0 - 1}{N_e^2} \right) \left( \frac{2\bar{t}}{\pi N_e^2} e^{\bar{t}^2}, \bar{t} \gg N_e^2. \right. \end{cases}
\]
(33)

that is valid on a limited time interval, as is given in Eq. (C2) in Appendix C, or to a less accurate approximation that is uniformly valid in time. Indeed, we found that the following expression:

\[
\psi_2(\bar{t}) = -\frac{e^{\bar{t}^2}}{\sqrt{\pi \bar{t}} + 2} \left( \sqrt{2(N_e - 1)} - \sqrt{2(N_0 - 1)} \right),
\]
(34)

describes the perturbations in the dimer concentration fairly well for all times and small perturbations. In deriving Eq. (34) we estimate the integrals in Eq. (C2) by standard methodology,\(^{23}\) and impose the correct initial condition; for details, see Appendix C. In fact, Eq. (34) shows the same time dependence as found by Marques et al, in the continuous approximation and for long times. However, by taking the discrete character of the polymer chain length into account, we found the correct prefactors, which indeed are different from those of Ref. 12. We also succeeded in obtaining a good approximation for short times, which was not possible in the continuous theory.

To illustrate the quality of the approximate expressions (34) and (C2) we compare in Fig. 4 the exact dimer concentration, as given by Eq. (C1) with the two approximations for \( \psi_2(\bar{t}) \) discussed above, and the numerically computed dimer concentration. In Fig. 4(a) the numerically computed dimer concentration is shown (dots) together with the expression for \( \psi_2(2, \bar{t}) \) in integral form [Eq. (C1) in Appendix C] depicted by the solid curve. The agreement is again for all time scales nearly exact. In Fig. 4(b) the numerical results (dots) for \( \psi_2(2, \bar{t}) \) are compared with the uniform analytical expression Eq. (34) (solid curve) and the more complicated approximation for \( \psi_2(\bar{t}) \), given by Eq. (C2) in Appendix C, which is shown as dashed curve. It is clear that the uniform approximation describes the dimer relaxation process fairly well for all times, in particular, it is correct for \( \bar{t} = 0 \) and
\[ N(\bar{t}) = \frac{\sum_{n=1}^{\infty} n \psi(n,\bar{t})}{\sum_{n=1}^{\infty} \psi(n,\bar{t})}. \]  

(35)

The dynamics of the average chain length is governed for short times by the monomers and for long times by the dimers, which follow from writing the average chain length in terms of the perturbations in the monomer and dimer concentrations. Since the total mass is conserved, the nominator in Eq. (35) is a constant and we only need to consider the denominator. If we write the chain concentration again as \( \psi(n,\bar{t})=\psi_{eq}(n)+\psi_{t}(\bar{t}) \) and perform the sum on the time-independent part and use Eq. (23), we obtain

\[ N(\bar{t}) = \frac{\phi}{\phi N_{0} + \psi_{1}(\bar{t}) - \psi_{1}(0) - \int_{0}^{\infty} \psi_{2}(t')dt' + 2e^{\lambda_{s}} \int_{0}^{\infty} \psi_{1}(t')dt'}. \]

(36)

Note that \( N(0)=N_{0} \) and that in the limit \( \bar{t} \to \infty \) we have \( N(\bar{t}) \to N_{eq} \), as it should, which is a consequence of Eq. (29). In fact, Eq. (29) suggests that a good approximation of the length can be obtained if in the time integral \( \int_{0}^{\infty} (2e^{\lambda_{s}} \psi_{1}(t') - \psi_{t}(t'))dt' \), only the \( \psi_{t} \)-independent parts, that is, the direct contributions, are taken into account. This guarantees that initially, the length has the correct value and that it relaxes to its correct equilibrium value \( N_{eq} \). In Appendix D an approximate expression for this integral is produced in terms of \( N_{0} \) and \( N_{eq} \). Since we have not taken any indirect processes into account, we do not expect this approximation of the integrals in the denominator, given by Eq. (D1) in Appendix D, to be very accurate for times \( \bar{t} \gg N_{eq}^{2} \).

In Fig. 5 we compare the numerical and analytical results of the average chain length for parameters \( N_{0}=54 \) and \( N_{eq}=50 \). The numerical result, represented by dots, is seen to correspond for almost all times quite well with the analytical expression depicted by the solid curve. However, the results are not as good as for the monomer and dimer concentrations, as indeed a small overshoot in the average length is
emerging for large $\overline{t}$. This demonstrates that the expression for the average length, as given by Eq. (35), can be used to compare, for example, the measured average length with the theoretical predictions for a rather large time window. However, care should be taken for too large times, since then “indirect reactions” come into play, which lead to modifications of Eq. (35). Although both the dimer concentration and the chain length were calculated taking only the “direct processes” into account, the dimer concentration agrees much better with our numerical results than the mean chain length. This is due to the accumulation of errors: There is only a small error in the predicted perturbations in the dimer concentration, but the chain length depends on the time integral of $\psi_2(t)$, which leads to the overshoot in the average chain length.

To also test the validity of expression (32) for large $T$ jumps, we calculated the monomer concentration for two such cases. In Figs. 6(a) and 6(b) we present the monomer concentrations in a linear and a log-linear plot, respectively, for a $T$ jump corresponding to a 50% length change from $N_0=15$ to $N_\infty=10$. Although the jump is considerable and can no longer be considered small, we still find good agreement between the numerical full nonlinear solution (dots), the analytical result Eq. (32) (solid curve), and the analytical expression without approximation of the integrals (B3) (dashed curve). From Figs. 6(a) and 6(b) it can be seen that initially the relaxation to equilibrium is slower than predicted by the calculation. This is due to the circumstance that all rods of length $n \geqslant 2$ relax only slowly to their equilibrium state. This means that the initial relaxation rate $h_{\text{fast}}$ should be replaced by an effective relaxation rate $h'_{\text{fast}}$, which takes this phenomenon into account. This can be done by substituting in Eq. (9) the initial rod concentrations $\psi(n,0)$ instead of their equilibrium values at $t=\infty$. This renders the following expression for the relaxation rate:

$$h'_{\text{fast}} = 2k_1N_\infty \left(\frac{(N_\infty-1)(N_0-1)}{N_0^2} - \frac{2}{N_\infty} + \frac{2}{N_\infty^2}\right),$$

(37)

which is smaller than $h_{\text{fast}}$ for the values of $N_0$ and $N_\infty$ chosen here. In Fig. 6(b) the solid curve, which has this renormalized relaxation rate $h'_{\text{fast}}$, is seen to be on top of the numerically obtained curve (dots) both for short and long times. Since the perturbative calculations for a jump in average length of 50% are still in such a good agreement with the full nonlinear numerical result, we have tested the validity of monomer concentration calculation for an even larger $T$ jump; we performed numerical simulations for an average length that was initially $N_0=2$ and in equilibrium $N_\infty=8$. In Fig. 7 we report our findings for this huge $T$ jump. The points refer to the numerical solution and are compared with the analytical solution Eq. (32) with relaxation rates given by $h_{\text{fast}}$ (dashed) and $h'_{\text{fast}}$ (solid). It can clearly be seen from Fig.
For a huge approximation Eq. (144912-11) End-evaporation dynamics revisited J. Chem. Phys. 123

7 that for $\bar{t}<0.1$, the analytical solution (dashed curve) with the relaxation rate given by $h_{\text{fast}}$ diverges from both the numerical solution and the analytical solution with the correct relaxation rate $h'_{\text{fast}}$. For times $\bar{t}>0.1$ agreement is good between both the dashed and solid curves and the points of the numerical result. The solid curve, which nearly coincides with the dots of the numerical solution, is clearly seen to decay exponentially with the correct relaxation rate given by Eq. (37). This once more illustrates that the monomers behave totally different from the other chains of length $n \equiv 2$.

For the dimers the comparison of theory with numerical calculations is presented in Figs. 8(a) and 8(b). Figure 8(a) corresponds to a jump in the average chain length from $N_0=15$ to $N_a=10$. We see again that the agreement between the dots, representing the numerical solution, and the analytical expression Eq. (C1), shown as a solid curve, is quite good. Even the cruder uniform approximation Eq. (34), represented by the dashed curve, works quite well in this case. For the huge jump from $N_0=2$ to $N_a=8$ results are shown in Fig. 8(b), where the dashed, solid, and dotted curves having the same meaning as in Fig. 8(a). From the dotted curve we see a new short-time relaxation process arising. This can be understood as the relaxation of the monomer concentration that indirectly affects the dimer concentration. Since we did not include this relaxation process in our analytical calculations, deviations are observed for short times ($\bar{t}<0.1$). Moreover, Fig. 8(b) illustrates that the uniform approximation is obviously not valid anymore for such a large $T$ jump on any time scale. But for times $\bar{t}>1$, when the monomer concentration is close to its equilibrium value, agreement between theory (solid curve) and numerical computation is again established. This is, of course, to be expected because then the monomers have almost relaxed and the small perturbation regime is entered again. We do not display any results on the average chain length for these large jumps, as these do not reveal any new features. For completeness we summarize our findings for the average chain length. On short time scales, there is again very good agreement between numerical results and theory. This was to be expected as the calculated monomer concentration follows the numerically obtained curve so well. For longer times quite a large overshoot arises due to discrepancies between the numerical and analytical dimer concentrations.

V. SUMMARY AND CONCLUSIONS

We have analytically studied the end-evaporation relaxation dynamics of a system of rigid rods in a quasi-one-dimensional setting. This kinetic mechanism, in which the association-dissociation processes involve single monomers only, is plausibly important in supramolecular structures of
chiral discotics, where the discotic polymers hierarchically self-assemble to form long one-dimensional columns.$^{2}$

We have derived a master equation for the reactions and diffusion of the rods on a lattice, focussing on the special case in which the system remains homogeneous, which corresponds to the reaction-limited scenario. This is equivalent to the mean-field description that is commonly used to study living polymers. By combining a perturbation analysis and a generating function method, approximate analytical expressions for the polymer concentrations are found for a $T$ jump experiment that agree remarkably well with results of numerical calculations. Even for the case of large $T$ jumps in which the average length changes by more than 50% and perturbation theory should break down, our method still gives results for long and short time scales that agree quite well, that is, within about 3% for the dimer concentration for the 50% jump in average length, with the numerical solution of the full nonlinear equations. The analytically calculated monomer density is in excellent agreement with the numerical results. This demonstrates the strength of the generating function method in obtaining the analytical approximations for living polymer systems.

Our calculations confirm the existence of three different relaxation regimes. On very short time scales we find that the monomers relax exponentially fast. After this initial relaxation stage which lasts about $(2kBN_0)^{-1}$ s, the second stage begins in which nonlinear effects play a role and there are some discrepancies between the solution of the nonlinear and the linearized equations. This second stage is therefore most difficult to describe. For longer times $\bar{t} \geq N_0^2$, the system enters the third stage of its relaxation process and is close to its equilibrium distribution. During this stage the perturbation theory expressions are nearly identical to the full nonlinear solution.

We also examined the evolution of the average chain length following a $T$ jump and found that its prediction is less accurate than that of the monomer and dimer concentrations. This is due to the approximations we made in calculating the mean length $N(\bar{t})$. Indirect processes, involving reactions with more than one monomer, were left out in order to make calculations more tractable. However, although this assumption leads only to small errors in the dimer concentration, its effect on the chain length is more significant. In fact, it leads to an erroneous nonmonotonicity of $N(\bar{t})$ for $\bar{t} \gg N_0^2$, which is in the regime where indirect reactions start to become significant. During the first and second stages of the relaxation process there is a good agreement with the numerical calculations. The fact that we did not take into account indirect processes also explains why we did not recover the scaling of Ref. 13. Scaling was found in the very long time limit, when indirect processes become relevant.

To conclude, an important issue that needs to be discussed in the future is, of course, the effect of diffusion on the reaction scenario discussed in this paper. Since, as we have shown, the formalism presented here carries over to this more general case including diffusion, future work on this could further exploit the generating function method presented here.

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**APPENDIX A: DERIVATION OF THE GENERATING FUNCTION $G$**

To obtain the generating function $G$, we multiply Eq. (20) by $s^n$ and sum from $n=2$ to $n=\infty$. This leads to

$$\frac{\partial G}{\partial \bar{t}} - 2e^{\lambda_\omega/2}\left(1 + \frac{1}{s} + \frac{1}{\bar{s}}\right)G + 2G(1 + e^{\lambda_\omega})$$

$$= -2\psi_1(\bar{t})\left(1 - e^{-\lambda_\omega}\right)\sum_{n=2}^{\infty}\bar{s}_n\lambda_\omega^n/2$$

$$+ (e^{-\lambda_\omega}s^2 - 2\bar{s}_n e^{-\lambda_\omega})\psi_2(\bar{t}),$$

(A1)

where we used the definition $\bar{s} = e^{\lambda_\omega/2}s$. By integrating Eq. (A1) over $\bar{t}$, we find expression (23). If we now separate in expression (23) all terms to equal order in powers of $s$, we find the time evolution of the concentration of all chains of length $n \geq 2$,

$$\hat{\psi}_n(\bar{t}) = \sum_{k=2}^{\infty} \hat{\psi}_0(0)I_{n-2}[4e^{\lambda_\omega/2}(\bar{t})]$$

$$+ \int_0^\infty I_{n-2}[4e^{\lambda_\omega/2}(\bar{t} - t')]\hat{\psi}_2(t')dt' - 2e^{\lambda_\omega/2}$$

$$\times \int_0^\infty I_{n-2}[4e^{\lambda_\omega/2}(\bar{t} - t')]\hat{\psi}_2(t')dt' - 4 \sinh(\lambda_\omega/2)$$

$$\times \sum_{k=2}^{\infty} e^{\lambda_\omega k/2} \int_0^\infty I_{n-2}[4e^{\lambda_\omega/2}(\bar{t} - t')]\hat{\psi}_1(t')dt'.$$

(A2)

**FIG. 9.** (Color online) Representation of the Bromwich contour that was chosen to invert the Laplace-transformed monomer concentration. The only contributions arise from the pole in $s = -H_{\text{fast}}$ and the branch cut between $s_1$ and $s_2$. The pole in $s = 0$ is removable.
Here, we introduced the quantity $\hat{\psi}_s(t)$ that is related to $\psi_s(t)$ according to $\hat{\psi}_s(t) = e^{2(1+\lambda_s)t}\psi_s(t)e^{-\lambda_s t/2}$.

**APPENDIX B: MONOMER CONCENTRATION**

An expression for the time-dependent monomer concentration can be found by inverting the Laplace-transformed monomer concentration in Eq. (31). We first note that the numerator $D(s)$, which is given by the term

$$D(s) = s^2 + h_{\text{fast}} - 4(1 - e^{\lambda_s})e^{\lambda_s} + \frac{16e^{\lambda_s}(1 - e^{\lambda_s})^2}{r(s) + 3s + 2(1 - e^{\lambda_s})},$$

(B1)

has only two poles: one in $s = 0$ and one in $s = -h_{\text{fast}}(1 + O(1/N_s^2))$. One can easily show that the pole in $s = 0$ is removable, so we are left with the single pole in $s = -h_{\text{fast}}$. In order to find the inverse Laplace transform of Eq. (17), we integrate along the Bromwich contour depicted in Fig. 9. We choose the branch cut running from $s_1$ to $s_2$ as shown in the figure, where

$$s_1 = -2(1 + e^{\lambda_s}) - 4e^{\lambda_s/2} = -8,$$

$$s_2 = -2(1 + e^{\lambda_s}) + 4e^{\lambda_s/2} = -\frac{4}{2},$$

(B2)

where the approximate equalities hold in the long chain limit $\lambda_s \rightarrow 0$. The only contributions to the integral come from the pole in $s = -h_{\text{fast}}$ and the branch cut.

By taking together the first and the fourth terms on the right-hand side of Eq. (17), we can do the integrations and we find that in excellent approximation with increasing accuracy as $\lambda_s$ goes to zero,

$$\psi_s(t) = \int_{s_1}^{s_2} e^{st}w(s)ds$$

with $w(s) = \sqrt{s-s_1}\sqrt{s-s_2}$. The different terms can be identified as follows. The first three terms on the right-hand side stem from all chains ($n \geq 2$) that have a nonequilibrium length and that shed or absorb monomers. The fourth term on the right-hand side is the effect of the monomer concentration being out of equilibrium. The fifth term guarantees that at time $t=0$ there will only be contributions from the monomers, so this term cancels the first three terms at $t=0$. Finally, the last term in Eq. (B3) represents the long-time relaxation of the monomers involving indirect processes. Since this term is of order $\lambda_s^2$ smaller than the other contributions, we will neglect this last term.

This expression having three different poles in $s = -h_{\text{fast}}, s = 0$, and $s = 1$ already suggests that there are three different time regimes. If we next neglect the last term in Eq. (B3), we find the following approximate expression for the monomer concentration:

$$\psi_s(t) \approx -\sqrt{8(N_s-1)} N_s^3 h_s \left( e^{(s_2+1)^2} \text{erfc}\left[\sqrt{t}\right] - \text{erfc}\left[\sqrt{s_2}\right] - e^{s_2^2} \sqrt{\frac{t}{\pi}} - \frac{1 - 2s_2}{2\sqrt{s_2}} \text{erfc}\left[\sqrt{s_2}\right] \right) + \left( \frac{N_0 - 1}{N_s^2} \right) e^{-h_{\text{fast}} t},$$

(B4)

where we set $s_1 = -8$. In the limit of large $t$, so that the $\text{erfc}\left[\sqrt{t}\right] \sqrt{t}$ term can be expanded, Eq. (B4) reduces to

$$\psi_s(t) \approx -\left( \frac{N_0 - 1}{N_s^2} \right) + \frac{N_0 - 1}{N_s^2 N_s^2} \left( - \sqrt{\frac{2t}{\pi N_s^2}} e^{s_2^2} \text{erfc}\left[\sqrt{s_2}\right] + \frac{\sqrt{t}}{N_s^2} \text{erfc}\left[\sqrt{s_2}\right] \right) \left( 1 - e^{-h_{\text{fast}} t} \right) + \left( \frac{1}{N_0} - \frac{1}{N_s^2} \right) e^{-h_{\text{fast}} t} + O\left( \frac{1}{N_s^2} \right).$$

(B5)

**APPENDIX C: DIMER CONCENTRATION**

The time evolution of the dimer concentration follows similarly to that of the monomer concentration. By performing a contour integration along the contour depicted in Fig. 10, we obtain
\[
\frac{\psi_2(\bar{t})}{\phi} \approx -\frac{(N_{\infty} - 1) e^{2\bar{t}}}{2\pi N_{\infty}^3} \left[ e^{\gamma^2 \sqrt{\bar{y}} \sqrt{\bar{s}_2 - \bar{s}_1 - y}} \int_{\bar{s}_2 - \bar{s}_1 - y}^{\bar{t}_2 - \bar{s}_1} e^{-\gamma^2 \sqrt{\bar{y}} \sqrt{\bar{s}_2 - \bar{s}_1 - y} dy} \right] \\
+ \frac{(N_0 - 1)(2 e^{\lambda_0 - \lambda_0} - 1)}{2\pi N_0^3} \left[ e^{\lambda_0 \gamma^2 \sqrt{\bar{s}_2 - \bar{s}_1 - y}} \int_0^{\bar{t}_2 - \bar{s}_1} e^{\lambda_0 \gamma^2 \sqrt{\bar{y}} \sqrt{\bar{s}_2 - \bar{s}_1 - y} dy} \right] \\
+ \frac{2(N_0 - 1)^2 e^{2\lambda_0 \gamma^2 \sqrt{\bar{s}_2 - \bar{s}_1 - y}}}{N_0^2 N_{\infty}^2 \pi} \int_0^{\bar{t}_2 - \bar{s}_1} e^{\gamma^2 \sqrt{\bar{y}} \sqrt{\bar{s}_2 - \bar{s}_1 - y} dy} \left( \frac{(N_0 - 1) e^{2\lambda_0 \gamma^2 \sqrt{\bar{s}_2 - \bar{s}_1 - y}}}{N_0^2 \pi} \right) \int_0^{\bar{t}_2 - \bar{s}_1} e^{\lambda_0 \gamma^2 \sqrt{\bar{y}} \sqrt{\bar{s}_2 - \bar{s}_1 - y} dy}.
\]

(C1)

In deriving Eq. (C1) we neglected the process responsible for the fast relaxation of the dimers, as this is of order $\lambda_0^2$ smaller than the largest term, for all but very long times. One should further notice that the last two terms in (C1) represent the contribution to the dimers that arises from monomer reactions. In calculating the integrals of the last two terms of Eq. (C1), we set $\lambda_0 = 0$ in order to make the calculation more tractable. In principle, one can write down an exact expression for $\psi_2(\bar{t})$, which is not needed, however, to find quite good agreement with numerical simulations.

An approximation to these integrals which is valid up to order $\lambda_0^2$ can be found by extending the integration domain from 8 to $\infty$ and setting $8 - y$ equal to its value in $y = 0$ for it gives the dominant contribution for large $\bar{t}$. The approximation we obtain for large $\bar{t}$ is given by

\[
\frac{\psi_2(\bar{t})}{\phi} = -\frac{\sqrt{2}(N_{\infty} - 1)}{N_{\infty}^3(2 e^{\lambda_0} - 1)} \left[ e^{(2 e^{\lambda_0} - 1) \gamma^2} \text{erfc}\left( \sqrt{(2 e^{\lambda_0} - 1 - s_2) \bar{t}} \right) \sqrt{2 e^{\lambda_0} - 1 - s_2 - \sqrt{s_2}} \text{erfc}\left( \sqrt{s_2} \right) \right] \\
+ \frac{\sqrt{2}(N_0 - 1)(2 e^{\lambda_0 - \lambda_0} - 1)}{N_0^3(2 e^{\lambda_0} - 1 + 2(1 - e^{\lambda_0 - \lambda_0})/N_0)} \left[ e^{(2 e^{\lambda_0} - 1) \gamma^2} \text{erfc}\left( \sqrt{(2 e^{\lambda_0} - 1 - s_2) \bar{t}} \right) \sqrt{2 e^{\lambda_0} - 1 - s_2 - \sqrt{s_2}} \text{erfc}\left( \sqrt{s_2} \right) \right].
\]

(C2)

where $q_0 = -2(1 - e^{\lambda_0})(1 - e^{\lambda_0 - \lambda_0})$. For short times we have to resort to a different strategy, as the approximation that $\sqrt{y - s_1} \approx \sqrt{-s_1}$ then no longer holds as the dominant contribution no longer comes from $y = 0$. In this case we can simply perform a Taylor expansion of $e^{-\gamma^2 \sqrt{y}}$ and subsequently perform the integrals. This calculation will, however, not be reproduced here. Instead we demonstrate that it is possible to obtain a uniform approximation in $\bar{t}$ by starting from Eq. (C2) and using the asymptotic expansion of the complementary error function $\text{erfc}$. Moreover, if we force the solution to satisfy the initial conditions, we find an approximate expression for $\psi_2(\bar{t})$ that is uniformly valid within about 3% (for jumps in the average length of 50%) for all times (and improving for $\lambda_0 \to \lambda_{\infty}$). The resulting, much more tractable expression is given by

\[
\frac{\psi_2(\bar{t})}{\phi} = -\frac{e^{2\lambda_0 \gamma^2 \sqrt{\bar{s}_2 - \bar{s}_1 - s_2}}}{\sqrt{\pi t + 2}} \left( \frac{\sqrt{2}(N_{\infty} - 1)}{N_{\infty}^3} - \frac{\sqrt{2}(N_0 - 1)}{N_0^3} \right).
\]

This expression is not valid for $N_0 = 2$. However, a similar expression for the dimer concentration can also be derived for this case. We will not reproduce this calculation.

**APPENDIX D: AVERAGE CHAIN LENGTH EVOLUTION**

To obtain the average chain length as a function of time, we need to perform the integral of $\psi_2(\bar{t}) e^{\lambda_0 \gamma^2 \sqrt{\bar{s}_2 - \bar{s}_1 - s_2}}$ over $\bar{s}_2$ keeping only the $\psi(\bar{t})$-independent terms. If we first integrate Eq. (C2) over $\bar{t}$ keeping only the first two terms and then perform the integration over $s$, the resulting expression reads

---

**FIG. 10.** Sketch of the contour that was chosen to calculate the dimer concentration. The pole in $s = -h_{fast}$ is not considered as it hardly contributes to the dimer concentration.
\[
\int_0^t \frac{\psi_2(t') - 2e^{\lambda_v} \psi_1(t')}{\phi} dt' = \left( N_v - 1 \right) \frac{\sqrt{s_2 - s_1}}{N_v^2 (2e^{\lambda_v} - 1)} \left[ - \frac{1}{2} \sqrt{\frac{t}{\pi}} e^{s_2 t} + \frac{1 - 2st}{4 \sqrt{s_2}} \text{erfc} \left( \sqrt{s_2 t} \right) \right] + \frac{\sqrt{s_2} \text{erfc} \left( \sqrt{s_2 t} \right)}{2 (2e^{\lambda_v} - 1)} \]
\[
\left( N_0 - 1 \right) (2e^{\lambda_v - \lambda_0} - 1) \frac{\sqrt{s_2 - s_1}}{2N_0 (2e^{\lambda_v} - 1)} \left[ - \frac{\sqrt{q_0 - s_2 \text{erf} \left( \sqrt{(q_0 - s_2)t} \right)}}{2e^{\lambda_v} - 1 - q_0} \right] + \sqrt{s_2} \text{erfc} \left( \sqrt{s_2 t} \right)
\]
\[
- \left( N_v - 1 \right) \frac{\left( 2e^{\lambda_v} - 1 - 2s_2 \right) (s_2 - s_1) - 2s_2 (2e^{\lambda_v} - 1 - s_2)}{2 \sqrt{s_1 s_2} (2e^{\lambda_v} - 1)^2}
\]
\[
- \frac{q_0 \sqrt{2e^{\lambda_v} - 1 - s_1 \sqrt{2e^{\lambda_v} - 1 - s_1} - (2e^{\lambda_v} - 1) \sqrt{q_0 - s_2 \sqrt{q_0 - s_1}}}}{(2e^{\lambda_v} - 1) q_0 (2e^{\lambda_v} - 1 - s_1)}
\]
\[
+ (N_0 - 1) (2e^{\lambda_v - \lambda_0} - 1) \frac{\sqrt{s_1 s_2}}{(2e^{\lambda_v} - 1) q_0},
\]
\]

(D1)

with \( q_0 = -2(1 - e^{\lambda_0})(1 - e^{\lambda_v - \lambda_0}) \). Equation (D1) is not valid for \( N_0 = 2 \), since this implies \( q_0 = 2e^{\lambda_v} - 1 \), but for this case a similar expression can be derived. On inspection of Eq. (D1) one sees immediately that the correct value 0 at \( t = 0 \) is reproduced in the highest order of \( N_v \). For \( t \to \infty \) we find that the exact value of Eq. (29) is reproduced, so that the average length \( N(t) \) attains the correct value for both short and long times.