

Non-Markovian models of the growth of a polymer chain

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ABSTRACT:

Using simple exactly solvable models, we show that event-dependent time delays may lead to significant non-Poisson effects in the statistics of polymer chain growth. The results are confirmed by stochastic simulation of various growth scenarios. Our interest in mathematical aspects of non-Markovian growth arises from recent successful application of delayed probability density functions in stochastic modelling of controlled radical polymerisation.

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I. INTRODUCTION

A substantial part of the polymer market is produced by free radical polymerisation (FRP). This is a chain-growth process that proceeds by addition of monomer units to a growing polymer chain. The addition of monomer units is called propagation. Chain growth may terminate by bimolecular termination (reaction of two growing chains) and by chain transfer of the radical to monomer and chain transfer agent. In the polymerisation of acrylic monomers transfer to polymer is frequent [1]. Intramolecular transfer, called backbiting, is the most common transfer to polymer process [2], where the radical is transferred to a monomer unit located two positions behind the unit where the radical was. It has been reported that the rate of backbiting may be affected by the presence of polar solvents [3]. The midchain radical formed by backbiting may a) react with a monomer, thus continuing the chain growth [2, 4], b) migrate along the chain [5], c) undergo beta-scission [6], and d) react with other species present in the medium, such as chain transfer agent [7], and solvents. The most likely event is propagation, Therefore, the chain does not stop growing, but simply it continues from a different monomer unit, and hence a branch is formed. In the last two decades, controlled radical polymerisation (CRP) has revolutionised free radical polymerisation allowing an unprecedented control of the polymer microstructure. In CRP of acrylic monomer an unexplained decrease of the branching level has been observed and has prompted a lively debate on the causes of such findings [8]-[11]. A recent publication [11] has shown that these and other kinetic anomalies can be explained by assuming a non-Markovian kinetics. With this in mind, we analyse below some simple exactly solvable non-Markovian delayed growth models.

The rest of the paper is organised as follows. In Sect. II we define the probabilities for different growth scenarios. In Sect. III we briefly review growth without a delay, leading to Markovian master equations for the probabilities of interest. In Sect. IV we consider linear growth with a fixed 'downtime' introduced after each attachment of a monomer. We show that such a delay leads to non-Poisson distribution of the polymer length, and a set of time delayed differential equations for the relevant probabilities. In Sect. V we study the short- and the long-time limits of the mean length of the grown polymer. In Sect. VI we consider

a branching process, whose delay is determined by the polymer's growth rate. In Sect, VII we confirm and extend our results by employing a numerical stochastic algorithm similar to the one pioneered by Gillespie [12]. Section VIII contains our conclusions.

II. LINEAR GROWTH

We start with the usual mathematical pre-requisit. Consider the growth of a linear polymer which proceeds by attaching monomers to, say, its right end at discreet times $t_j = jdt$.

We begin with a single monomer. At each t_j an extra monomer is added with the probability p_j , or else nothing happens with the probability $1 - p_j$. Thus, the probability to add a monomer after $J - 1$ unsuccessful attempts is $f(t_J) = p_J \prod_{j=1}^{J-1} (1 - p_j)$, while the probability for not adding a monomer up to and including t_J , is $g(t_J) = \prod_{j=1}^J (1 - p_j)$. In general, we may start the process at some t_i and let the probabilities depend on both t_j and t_i , $p = p_{j,i}$. In the continuum limit we should send $dt \rightarrow 0$ and introduce the growth rate $c(t_j, t_i)dt \equiv p_{j,i}$, assuming c to be a slowly varying function. The probability to add nothing for $t' \leq t'' \leq t$ is then given by

$$g(t, t') = \exp\left[-\int_{t'}^t c(t'', t')dt''\right], \quad (1)$$

while for the probability density function (PDF) to start at t' , and add the first monomer in the interval $[t, t + dt]$, we have

$$f(t, t') = c(t, t') \exp\left[-\int_{t'}^t c(t'', t')dt''\right] = -\partial_t g(t, t'). \quad (2)$$

By a given t , the monomer is either attached or not, so the two corresponding probabilities add to one,

$$\int_{t'}^t f(t'', t')dt'' + g(t, t') = 1. \quad (3)$$

With many monomers able to join the polymer chain between t' and t , we are looking for the probability $P(n, t, t')$ to have n new additions by the time t . This is just the probability for adding monomers at $t' \leq t_1 \leq t_2 \leq \dots \leq t_n \leq t$, multiplied by the probability that no

more monomers are added between t_n and t , and summed over all t_i , $i = 1, 2, \dots, n$,

$$P(n, t, t') = \int_{t'}^t dt_n \dots \int_{t'}^{t_2} dt_1 g(t, t_n) f(t_n, t_{n-1}) \dots f(t_1, t'), \quad n \geq 1 \quad (4)$$

$$P(0, t, t') = g(t, t').$$

One can check that Eq.(3) ensures the correct normalisation of the probabilities $P(n, t, t')$, $\sum_{n=0}^{\infty} P(n, t, t') = 1$.

Another useful quantity is the probability density $W(n, t, t')$ for n monomers to be attached in the interval $[t', t]$, with the last of them added in $[t, t + dt]$,

$$W(n, t, t') = \int_{t'}^t dt_{n-1} \dots \int_{t'}^{t_2} dt_1 f(t, t_{n-1}) \dots f(t_1, t'), \quad n \geq 1, \quad (5)$$

in terms of which $P(n, t, t')$ is expressed as

$$P(n, t, t') = \int_{t'}^t dt'' g(t, t'') W(n, t'', t'), \quad n \geq 1. \quad (6)$$

The quantities $W(n, t, t')$ have the advantage that they satisfy the simple evolution equations,

$$\partial_t W(n, t, t') = f(t, t) W(n-1, t, t') + \int_{t'}^t dt'' \partial_t f(t, t'') W(n-1, t'', t'). \quad (7)$$

Their use will be described below.

At least three cases need to be distinguished.

A. The growth rate depends only on the current time, and not on the previous history of the chain,

$$c(t, t') = c(t), \quad f(t, t') = c(t) \exp\left[-\int_{t'}^t c(t'') dt''\right]. \quad (8)$$

For example, an increase in the temperature may make the attachment of monomers more probable at later times. This is the *Markovian* case we will briefly review in the next Section.

B. The growth rate depends only on the chain's past, and is not manipulated externally.

$$c(t, t') = c(t-t'), \quad f(t, t') = f(t-t') = c(t-t') \exp\left[-\int_0^{t-t'} c(t'') dt''\right]. \quad (9)$$

Here one may think that after each time a monomer is added, some additional time is needed before the next monomer can be attached [11]. This the *non-Markovian* case is the main subject of this paper.

C. Finally, the growth rate, which depends on the polymer's history in the sense outlined above, may also be manipulated externally. In this case c is a function of both t and t' , and the process is also non-Markovian.

III. MARKOVIAN GROWTH

Consider the case when there is an unlimited supply of monomers to be added to the chain, and the probability to add one at a given time is modified externally, e.g., by varying the temperature at which the process takes place. The growth begins at some t' , and we are interested in the length of a polymer at a time t . The probability for adding a monomer in $[t, t + dt]$ is $c(t)dt$, and the function g and the PDF f in Eqs. (1) and (2) are of the form

$$g(t, t') = \exp\left[-\int_{t'}^t c(t'')dt''\right], \quad (10)$$

$$f(t, t') = c(t) \exp\left[-\int_{t'}^t c(t'')dt''\right].$$

Inserting (10) into Eq.(4), and recalling that $\int_{t'}^t dt_n \dots \int_{t'}^{t_2} dt_1 c(t_n) \dots c(t_1) = [\int_{t'}^t c(t'')dt'']^n/n!$, we recover a Poisson distribution [13] (the subscript M stand for 'Markovian'),

$$P_M(n, t, t') = \frac{I(t)^n}{n!} \exp(-I(t)), \quad n \geq 1 \quad (11)$$

$$P_M(0, t, t') = \exp(-I(t)),$$

where

$$I(t) = \int_{t'}^t c(t'')dt''. \quad (12)$$

From Eqs. (11)-(12) it follows that the mean length of the chain,

$$\langle n(t) \rangle = \bar{c}(t, t')(t - t'), \quad (13)$$

where $\bar{c}(t, t') = (t - t')^{-1} \int_{t'}^t c(t'')dt''$ is the average of the growth rate c over the growth period. If the external conditions remain unchanged, $c(t) = \text{const}$, the growth is linear with time, $\langle n(t) \rangle = c(t - t')$. In the special case (10), differentiating Eq.(6) [or, directly, Eq.(11)] yields a closed master equation for the probabilities $P_M(n, t, t')$

$$\partial_t P_M(n, t, t') = c(t)[P_M(n - 1, t, t') - P_M(n, t, t')], \quad n \geq 1, \quad (14)$$

$$\partial_t P_M(0, t, t') = -c(t)P_M(0, t, t'),$$

to be solved with the initial condition

$$P(n, t', t') = \delta_{n0}, \quad (15)$$

where δ_{nm} is the Kronecker delta. Equations (14) are obviously Markovian, as the rate at which a $P_M(n, t, t')$ changes depends only on the current state of the system, $\{P(n, t, t')\}$, $n = 0, 1, 2, \dots$

IV. NON-MARKOVIAN GROWTH WITH DELAYS

Suppose next that, as in the previous Section, there is an unlimited supply of monomers, and the external conditions remain unchanged. But each added monomer, except the first, now needs a time τ to properly settle into the chain structure, only after which the chain is ready to attach again, with the same constant growth rate c . The process is now explicitly non-Markovian: to check whether a monomer can be added, one needs to know the history of the chain. Accordingly, the probability $c(t)$ depends not on the time elapsed since t' , but on the time elapsed since the last monomer was added. In Eq.(4) we, therefore have $c(t, t') = c(t - t')$. Explicitly, we obtain (*NM* stands for 'Non-Markovian')

$$c(t - t') = \begin{cases} 0, & 0 \leq t - t' < \tau \\ c, & t - t' \geq \tau \end{cases} \quad (16)$$

and

$$g_{NM}(t, t') = g_{NM}(t - t') = \begin{cases} 1, & 0 \leq t - t' < \tau \\ \exp[-c(t - t' - \tau)], & t - t' \geq \tau. \end{cases} \quad (17)$$

From (2) we also have

$$f_{NM}(t, t') = f_{NM}(t - t') = c\theta(t - t' - \tau) \exp[-c(t - t' - \tau)], \quad (18)$$

where $\theta(z) = 1$ for $z \geq 0$ and 0 otherwise. The physical background of Eqs.(16)-(18) is as follows: In classical kinetics, the pseudo-first order processes are considered purely stochastic, i.e., described by an exponential probability distribution function. However, this is intuitively difficult to justify because the probability density that a reaction occurs at $t=0$ should be 0, since instantaneous reactions do not occur. This concept has been used to analyse the competitive processes occurring in CRP and to explain the reduction of branching in CRP of acrylic monomers [17]. Equation (17) can be considered a simplification of the linear-exponential equation used in reference [17]. This simplification allows us to obtain solutions analytically.

It is easy to see that the model described by Eqs.(16)-(18) has a simple exact solution. Indeed, returning to Eq.(5) and putting $t' = 0$, we note that the probability $W(n, t, t' = 0) \equiv W(n, t)$ is the same as for growth with a constant c , but for a shorter time. The effective time of growth, t_{eff} , is, therefore, the elapsed time t minus the total time the growth was

shut down due to adding $n - 1$ monomers, i.e., $t_{eff} = t - (n - 1)\tau$. Should $(n - 1)\tau$ exceed t , the process is not possible, and the corresponding probability is zero. From (5) and (18) we easily find

$$W_{NM}(n, t|\tau) = c \frac{[I_n(t, \tau)]^{n-1}}{(n-1)!} \exp[-I_n(t, \tau)], \quad n \geq 1, \quad (n-1)\tau < t, \quad (19)$$

$$I_n(t, \tau) = c[t - (n-1)\tau].$$

The physical probabilities $P(n, t, t' = 0) \equiv P(n, t)$ are no longer given by a Poisson distribution, but can be obtained as quadratures using Eqs.(6), (17) and (19)

$$P_{NM}(n, t|\tau) = \int_0^{t-\tau} \exp[-c(t-t'-\tau)] W_{NM}(n, t'|\tau) dt' + \int_{t-\tau}^t W_{NM}(n, t'|\tau) dt', \quad n \geq 1, \quad (20)$$

$$P_{NM}(0, t|\tau) = \exp(-ct).$$

It is instructive to look at the evolution equations (EE) satisfied by the probabilities. There are no simple EE, similar to Eqs.(14), for the P_{NM} 's in Eqs.(20). There are, however, EE (7) which, since $\partial_t f(t) = c\delta(t-\tau) - cf(t)$, read

$$\partial_t W_{NM}(n, t|\tau) = c[W_{NM}(n-1, t-\tau|\tau) - W_{NM}(n, t|\tau)], \quad n \geq 2, \quad 0 < (n-1)\tau < t.$$

$$W_{NM}(1, t) = c \exp(-ct). \quad (21)$$

Unlike Eqs.(14) in the Markovian case, Eqs.(21) depend on the state of the system in the past through $W_{NM}(n-1, t-\tau|\tau)$. Since for any suitable function $F(t)$, $F(t-\tau) = \exp(-\tau\partial_t)F(t) = \sum_{n=0}^{\infty} (-1)^n \frac{\tau^n}{n!} \partial_t^n F(t)$, Eqs.(21) are, effectively, of infinite order in the time derivative ∂_t , and their properties may differ significantly from those of (14), as will be illustrated in the next Section.

V. MEAN CHAIN LENGTH FOR A DELAYED GROWTH

One quantity of practical interest is the mean length of the chain grown in the presence of a delay,

$$\langle n(t, \tau) \rangle_{NM} = \sum_{n=1}^{\infty} n P_{NM}(n, t|\tau), \quad (22)$$

shown in Fig.1 for various values of the parameters $c\tau$. Figure 2 shows the standard deviation of the length for $c\tau = 10$. As $c\tau \rightarrow 0$ we recover the Poisson distribution (11), and for

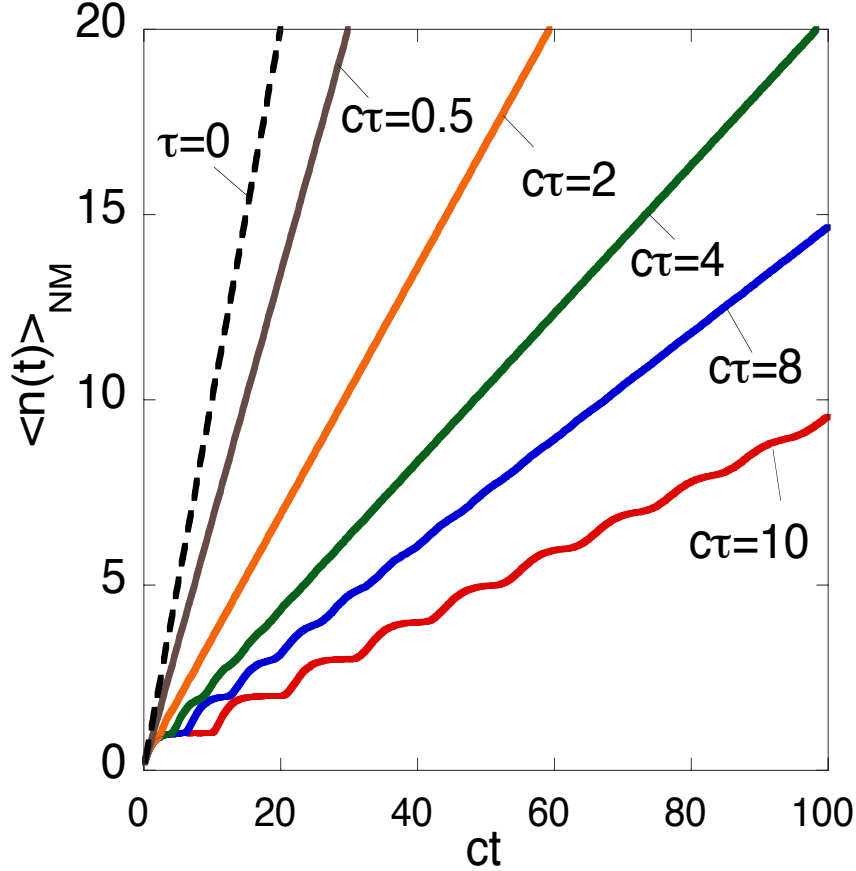


FIG. 1. (Color online) The mean length of the polymer chain vs. time for different values of the delay τ .

$ct \ll 1$, $\langle n(t, \tau) \rangle$ grows linearly at the rate close to c . In the opposite limit, $ct \gg 1$, the behaviour is more interesting with the curves showing a steplike variation at short times before settling into a linear behaviour later. This has a simple physical explanation. The time it takes the chain to add one monomer at a constant growth rate c , t_{add} , is approximately $1/c$. If $\tau/t_{eff} = c\tau \gg 1$, a monomer is added quickly, but then the system has to wait long until another one can be attached. Thus, for $t_{add} < t < \tau$, it behaves as if the delay were infinite, i.e. as if the only two possible outcomes were one or none monomers added, with the probabilities $P(one) = 1 - \exp(-ct)$ and $P(none) = \exp(-ct)$, respectively. The mean length

$$\langle n(t, \tau) \rangle_{NM} \approx 1 - \exp(-ct), \quad t_{add} < t < \tau \quad (23)$$

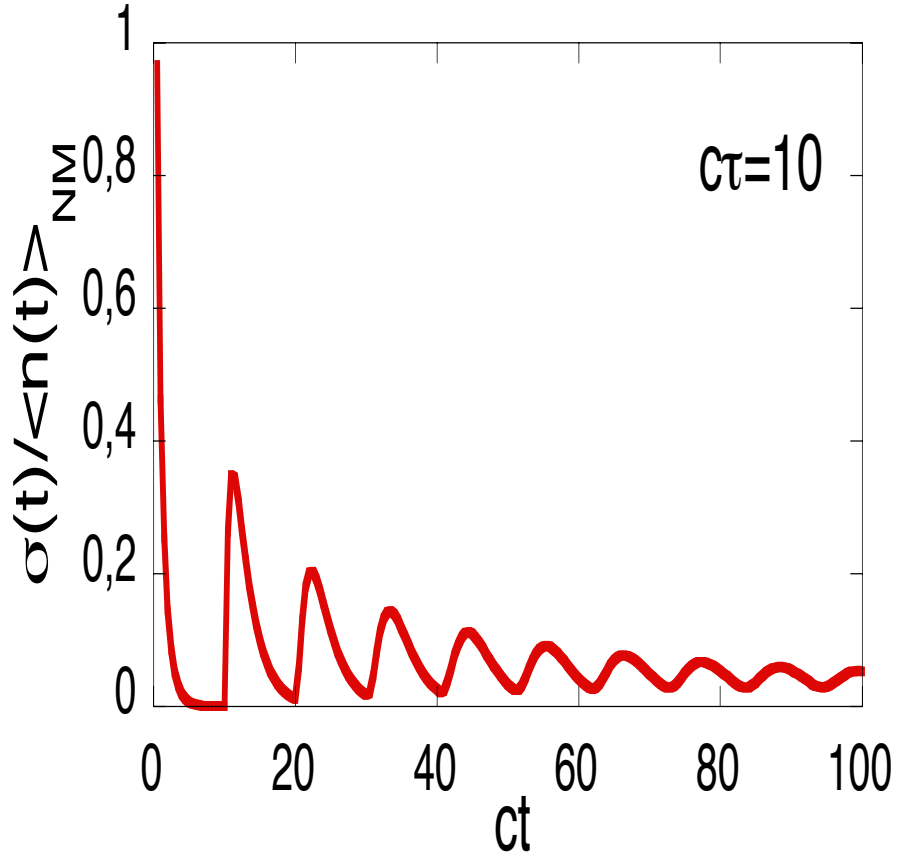


FIG. 2. (Color online) The standard deviation of the chain's length, $\sigma \equiv \sqrt{\langle n^2 \rangle_{NM} - \langle n \rangle_{NM}^2}$ vs. time for $c\tau = 10$.

reaches the value of 1, and remains unity until $t \approx \tau$, when the system 'recalls' that the delay is not infinite after all. A second monomer is added quickly, and $\langle n(t, \tau) \rangle_{NM}$ remains flat and close to 2 until $t \approx 2\tau$, and so on. This behaviour can be expected from the way we have constructed our model. Equivalently, it can be seen as an illustration of the ability of time delayed differential equations to produce rapid variations in their solutions after they seem to have reached an asymptotic limit [14].

As $t/\tau \rightarrow \infty$ the steps are smoothed out, and the mean length of the polymer grows linearly with time (K is a constant),

$$\langle n(t, \tau) \rangle_{NM} \approx \tilde{c}t + K, \quad t \rightarrow \infty \quad (24)$$

at a constant rate \tilde{c} , $1/\tau \leq \tilde{c} \leq c$. The value of \tilde{c} is found by recalling that in our model adding $\langle n(t) \rangle$ monomers is accompanied by switching off the growth for a duration of ap-

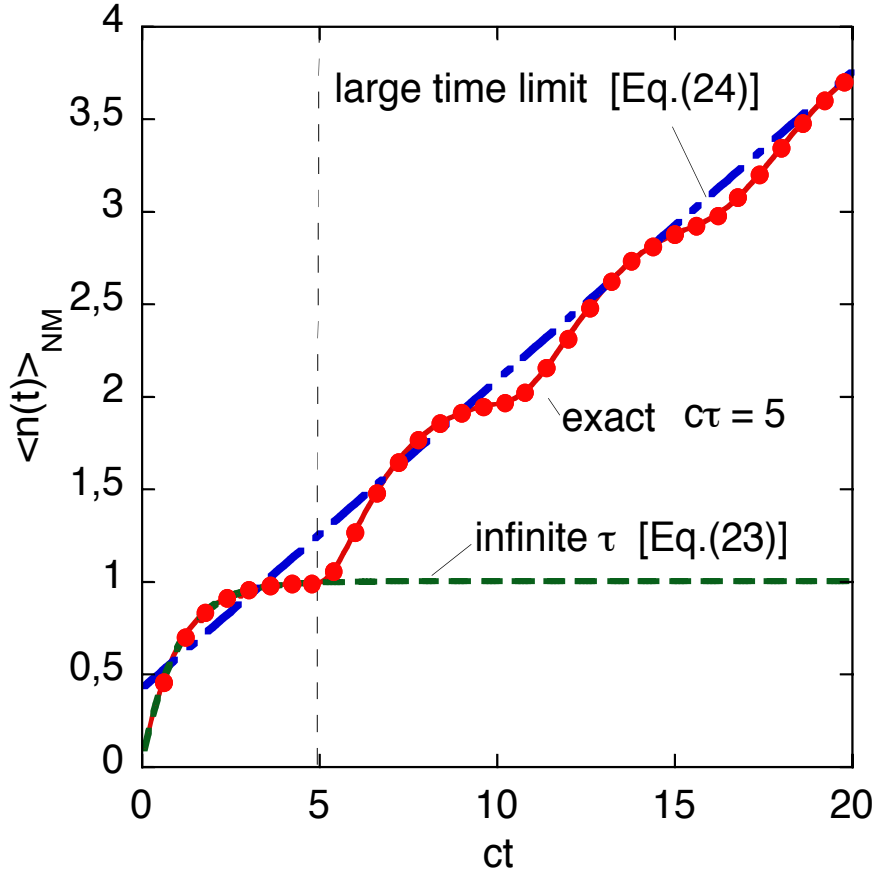


FIG. 3. The mean length of the polymer chain vs. time for $c\tau = 5$ (solid). Also shown are the short time limit (23) (dashed) and the long time limit (24) (dot-dashed). The filled dots are the results of stochastic simulation with the PDF (18) described in Sect. VII.

proximately $[\langle n(t) \rangle - 1]\tau - \tau/2$. (The last addition may occur close to t , so its delay is, on average, shorter.) Thus, the growth is similar to the growth without delay over a time $\langle n(t) \rangle \tau - \tau/2$ at the rate c . Equating $\langle n(t) \rangle$ to $c[t - \langle n(t) \rangle \tau + \tau/2]$ yields

$$\tilde{c} = \frac{c}{1 + c\tau}, \quad K = \frac{c\tau}{2(1 + c\tau)}. \quad (25)$$

The two limiting cases, (23) and (24), are illustrated in Fig.3.

VI. LINEAR GROWTH WITH BRANCHING. GROWTH-INDUCED DELAY

Next we consider the delay in backbiting, caused by the fact that in order to form the six-membered ring required for the backbiting reaction, a minimum of three monomer units

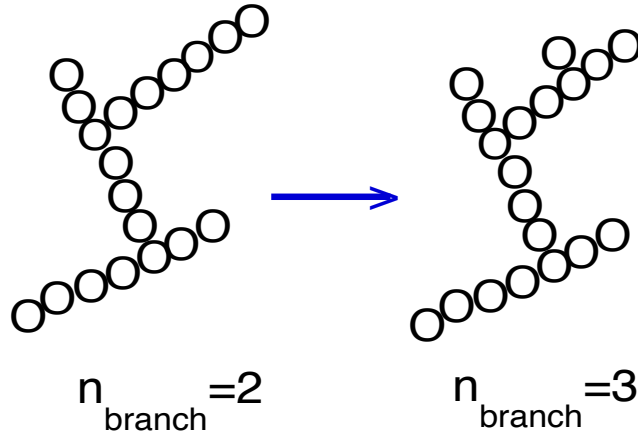


FIG. 4. (Color online) A polymer chain grows by adding monomers to its right hand side end at a constant rate c_{add} . The chain also forms branches, at a constant rate c_{branch} . After a branching event the chain needs to acquire at least three more monomers until next branching can occur.

and needed in a linear segment of the chain. It is assumed that the polymer chain grows at a constant rate c_{add} , without any delay, its full length at a time t being $c_{add}t$. It can, however, form branches [15], [16] as illustrated in Fig.4. The branching occurs with a rate c_{branch} , but can only happen after a linear segment contains at least three monomers [17]. In other words, a branching event should be preceded by at least $n_0 = 3$ attachments of monomers [18]. It is the number of branchings, n_{branch} , we are interested in. To make the problem tractable, we assume that the growth is deterministic, i.e., that exactly one monomer is added to the chain at $t_{add} = 1/c_{add}$. This makes branching a delayed reaction of the type considered in the Sections IV-V, and the delay time is now given by

$$\tau = n_0/c_{add} = n_0 t_{add}. \quad (26)$$

The model, which should work well for a large n_0 , since a branching event can occur just before or just after attachment of an extra monomer, so that the actual delay may lie between $(n_0 - 1)t_{add}$ and $n_0 t_{add}$. We will address this issue shortly. For now, the mean number of branchings in the chain, $\langle n_{branch}(t) \rangle$ is given by a formula similar to Eq.(23), but shifted by τ , since already the first branching may occur only after at least n_0 growth events,

$$\langle n_{branch}(t) \rangle = \langle n(t - n_0 t_{add}, n_0 t_{add}) \rangle_{NM}. \quad (27)$$

The mean number of branchings in the chain, and the mean length of its linear segment,

$$\langle N(t) \rangle \equiv \frac{c_{add}t}{\langle n_{branch}(t) \rangle + 1}, \quad (28)$$

depend on the ratio

$$\gamma \equiv n_0 \frac{c_{branch}}{c_{add}}. \quad (29)$$

For $\gamma \gg 1$ and $n_0/c_{add} + 1/c_{branch} < t < 2n_0/c_{add}$ there is exactly one branching, the second one appearing approximately after $t = 2n_0/c_{add} + 1/c_{branch}$.

For $\gamma \gg 1$ and $t \rightarrow \infty$ the number of branches grows linearly at the rate obtained from Eqs.(25) and (26):

$$\tilde{c}_{branch} = \frac{c_{branch}c_{add}}{c_{add} + n_0c_{branch}}, \quad (30)$$

and

$$\langle N(t) \rangle = c_{add}/\tilde{c}_{branch} = n_0 + \frac{c_{add}}{c_{branch}}. \quad (31)$$

For $c_{branch} \gg c_{add}$ a branching event occurs just after a linear segment has grown to contain n_0 monomers, so that $\tilde{c}_{branch} = c_{add}/n_0$ and $\langle N(t) \rangle = n_0$. In the opposite limit $\gamma \ll 1$ growth outpaces branching. After an initial delay of n_0/c_{add} , branching proceeds at a rate $\approx c_{branch}$, and the mean length of the linear segment, $\langle N(t) \rangle$, is approximately c_{add}/c_{branch} .

Figure 5 shows the dependence of $\langle N(t) \rangle$ on t , for $n_0 = 3$ and different values of γ in Eq.(29). Figure 6 shows a related quantity, the ratio of the mean number of the branchings to the mean total length of the chain, $\langle n_{branch}(t) \rangle / c_{add}t$. We note that for $\gamma \ll 1$ the curved part of the graph in Fig. 6 is due to the fact that branching is delayed relative to growth by about n_0/c_{add} , after which it proceeds at a constant rate of $\langle n_{branch}(t) \rangle \approx \tilde{c}_{branch}(t - n_0/c_{add})$. The total length of the chain grows as $c_{add}t$. For the ratio we, therefore, have

$$\langle n_{branch}(t) \rangle / c_{add}t \approx \frac{\tilde{c}_{branch}}{c_{add}} - n_0 \frac{\tilde{c}_{branch}}{c_{add}^2 t}. \quad (32)$$

The ratio is 20% below its large-time value $\tilde{c}_{branch}/c_{add}$ at $t \approx 5n_0/c_{add}$, as can be seen from Fig.7. This approximates the range of times in which the initial delay in building a branchable chain leads to non-constant behaviour of the ratio $\frac{\text{number of branches}}{\text{chain length}}$.

VII. STOCHASTIC SIMULATION OF DELAYED GROWTH

If the growth of the chain does not occur at regular times, but is itself a Poisson process, we need to take into account the small probability that three monomers can be added also

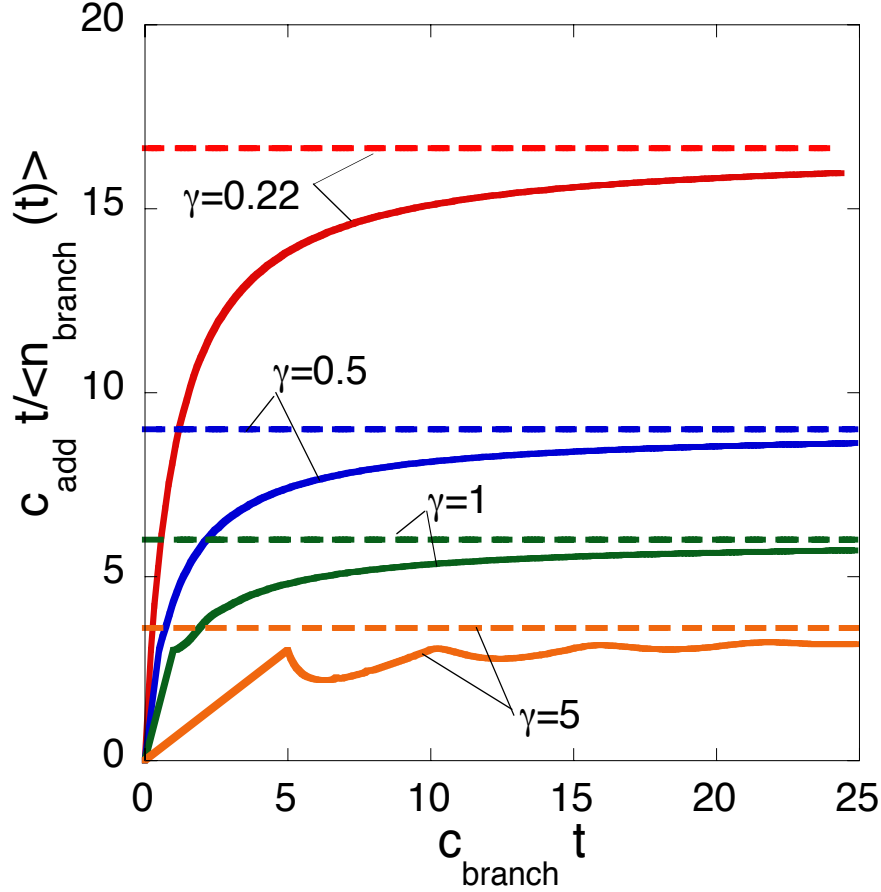


FIG. 5. The mean length of the linear segment, $\langle N(t) \rangle$, vs. time, for different values of the parameter $\gamma = n_0 \frac{c_{branch}}{c_{add}}$ and $n_0 = 3$. Also shown by the dashed lines are the large time values, as given by Eq.(31).

within a short time. For growth occurring at a constant rate c_{add} the probability to add n_0 monomers within a time τ is

$$w_{n_0}(\tau) = \int_0^\tau d\tau_{n_0-1} \dots \int_0^{\tau_2} d\tau_1 f_{add}(\tau - \tau_{n_0-1}) \dots f_{add}(\tau_1) = c_{add}^n \frac{\tau^{n_0-1}}{(n_0-1)!} \exp(-c_{add}\tau) \quad (33)$$

where we have used $f_{add}(t) = c_{add} \exp[-c_{add}t]$. Next we average the delayed PDF for branching,

$$f_{branch}(t, \tau) \equiv c_{branch} \theta(t - \tau) \exp[-c_{branch}(t - \tau)],$$

over all possible delays, thus obtaining

$$\bar{f}_{branch}(t, n_0) \equiv \int_0^\infty w_{n_0}(\tau) f_{branch}(t, \tau) d\tau = \quad (34)$$

$$\frac{c_{branch} c_{add}^{n_0}}{(n_0-1)!} \exp(-c_{branch}t) \frac{d^{n_0-1}}{d\beta^{n_0-1}} \left[\frac{\exp(\beta t) - 1}{\beta} \right]_{\beta=c_{branch}-c_{add}}$$

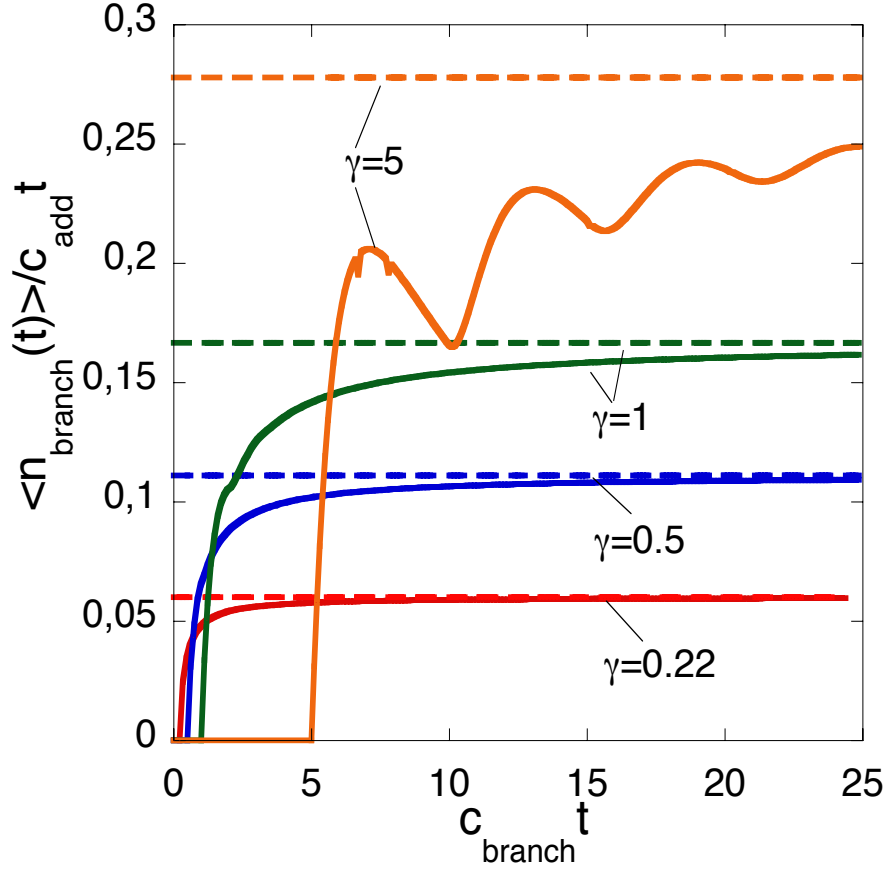


FIG. 6. (Color online) The ratio of the mean number of branching to the mean total length of the chain, $\langle n_{branch}(t) \rangle / c_{add} t$ vs. time, for different values of the parameter $\gamma = n_0 \frac{c_{branch}}{c_{add}}$ and $n_0 = 3$. Also shown by the dashed lines are the large time values as follow from Eq.(31).

The shapes of $\bar{f}_{branch}(t, n_0)$ for various values of n_0 are shown in Fig.8. Then we replace f in Eqs.(5) with \bar{f}_{branch} , and use them to generate the statistics for branching events. Since we no longer have a simple analytic solution for the resulting non-Markovian equations, we employ a numerical stochastic algorithm similar to that developed by Gillespie [12]. There are two ways to simulate delayed branching of a polymer chain using the method similar to that of [12] and [19]. A rigorous proof of their equivalence is given in Appendix A.

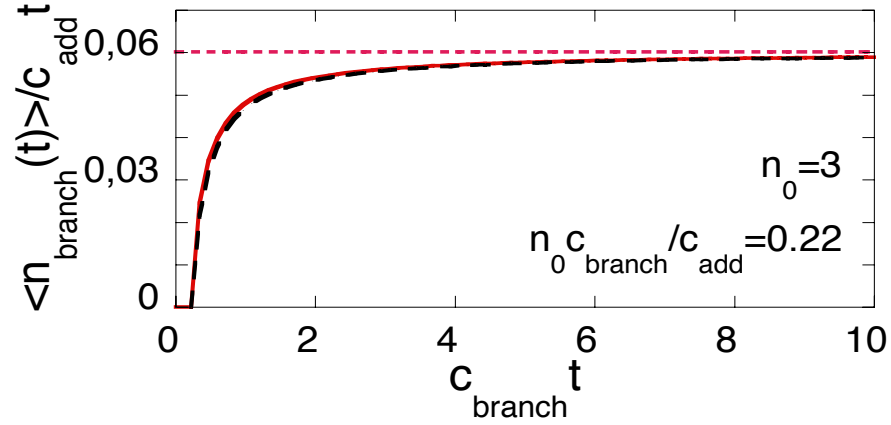


FIG. 7. (Color online) The ratio of the mean number of branches to the mean total length of the chain, $\langle n_{branch}(t) \rangle / c_{add} t$, for $\gamma = 0.22$: exact (solid) and as given by Eq.(32) (dashed). Also shown is the large time limit of the ratio (short dashed).

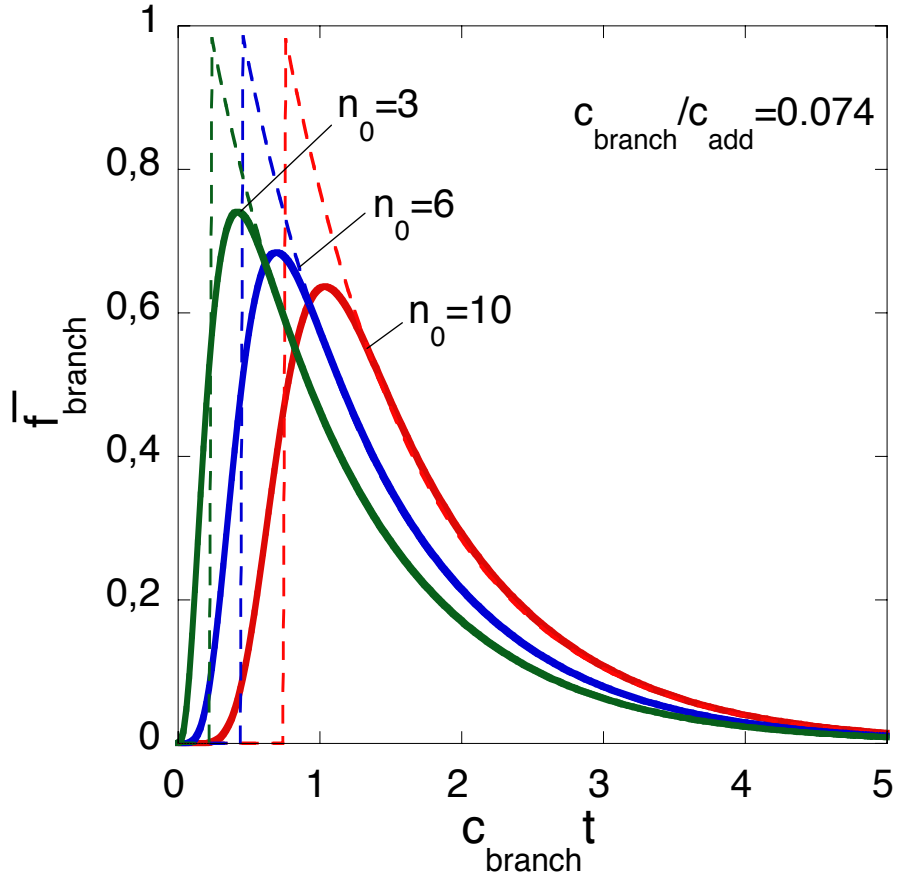


FIG. 8. (Color online) The PDF \bar{f}_{branch} for $c_{branch} / c_{add} = 0.074$ for various values of n_0 . Also shown by the dashed lines are the PDFs (18).

A. Stochastic simulation of a single delayed process, with the delay built into the corresponding PDF

A random number generator is prepared, so that it 'draws' a random number t_j , $j = 1, 2, \dots, K$ with a probability

$$\omega_j = f(t_j)dt, \quad (35)$$

where $f(t)$ is the PDF given by Eq. (34). The number of branches is set to zero, and then the first value t_1 is drawn. If it lies between 0 and the time t at which the growth is stopped, the number of branches is increased by 1, and t_1 becomes the new starting time. This step is repeated until the k -th step yields $t_k > t$, at which point the drawing stops, and the vector $\hat{t} = (t_1, t_2, \dots, t_{k-1})$ corresponding to this particular realisation of the system's history is stored. Repeating the simulation a large number of times N , one obtains a collection of histories, from which the probability of any particular property can be obtained as the relative frequency with which the property occurs. For example, the probability to have n branches by a time t is given by

$$P(n, t) = N_n/N, \quad (36)$$

where N_n the number of realisations with exactly n events.

The results of a stochastic simulation with the PDF (18), shown in Fig.3, are in full agreement with the analytical results (19)-(20). The results for the PDF (34) are presented in Fig.9.

B. Stochastic simulation of two Poisson processes with an additional constraint

Alternatively, one can perform a simulation of two simultaneous Poisson processes with their respective PDFs defined as follows

$$f_{add}(t) = c_{add} \exp(-c_{add}t), \quad f_{branch}(t) = c_{branch} \exp(-c_{branch}t), \quad (37)$$

and impose an additional constraint that a branching can only occur after n_0 monomers have been added previously. (Note that without such a constraint the processes are independent, and the ratio of the mean number of branchings to the mean length of a polymer in Fig.6 is a constant equal to c_{branch}/c_{add} at all times.)

Now in each step of the simulation one draws random values of t_k^{add} and t_k^{branch} from the probability distributions f_{add} and f_{branch} in Eqs. (37), respectively. If $t_k^{add} < t_k^{branch}$, a growth event is recorded at $t_k = t_{k-1} + t_k^{add}$. Otherwise the recorded event is the branching of the chain appearing at $t_k = t_{k-1} + t_k^{branch}$. The step is repeated until t_k is found to be greater than t , and a history consisting of branching events interspersed among acts of growth is stored. With many histories collected, average values of observables are evaluated as in the previous Subsection.

A comparison demonstrates a good agreement between the single- and two-processes simulations of branching events. The results are shown in Fig.9 for various values of γ . For growth events distributed in time, the sharp features present in the time dependence of observables in the model of Sect. IV, are smoothed over, yet there remain significant non-Markovian effects.

Note also that computationally the approach of Subsection A is more efficient than the straightforward algorithm described in B (Figure 10), since it reduces a number of simulated processes to one.

C. A simpler choice of the delayed PDF

The algorithm outlined in section A suggests an efficient way of simulating delayed processes if the amount of delay is known *a priori*. In practice, however, it is often not the case. If so, one may use a set of experimental data to tune parameters of PDFs taking an appropriate optimisation route [11]. Optimisation is most easily achieved for a PDF having a simple analytical representation and depending only on a small number of parameters. A simple two-parametric analytical form broadly similar to Eq.(34) is the linear-exponential (LE) one, used in [11]

$$\bar{f}_{branch}^{LE}(t) = kt \quad \text{for } 0 \leq t \leq b, \quad kb \exp[-(t-b)/\tau] \quad \text{for } t > b, \text{ and } 0 \text{ otherwise.} \quad (38)$$

where $t = b$ corresponds to the maximum of $\bar{f}_{branch}(t, n_0)$ in (34), $k = \bar{f}_{branch}(b, n_0)/b$, and $\tau = (1 - kb^2/2)/kb$. Figure 11 compares the PDF (34) with its LE approximation (38), while Figure 12 illustrates the level of accuracy achieved by the approximate PDF in computation of a branching fraction (32). The LE approximation accurately reproduces the short time behaviour of the branching fraction curve, while in the long time limit it underestimates its

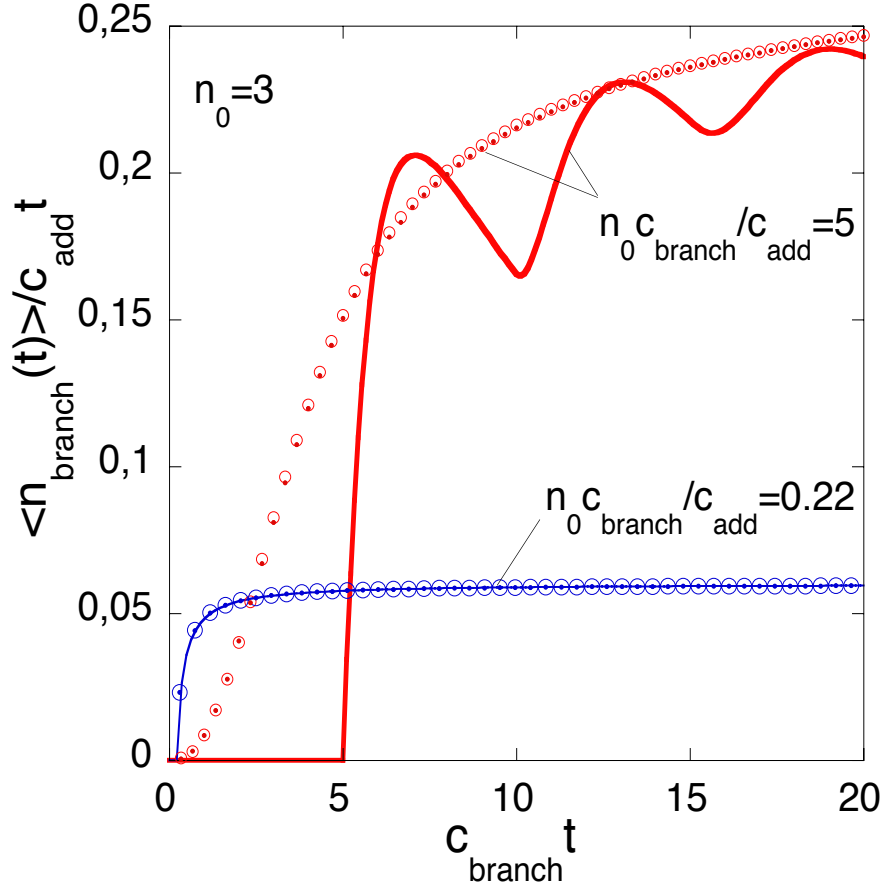


FIG. 9. (Color online) The ratio of the mean number of branches to the mean total length of the chain, $\langle n_{branch}(t) \rangle / c_{add} t$ vs. time, for $n_0 = 3$ and different values of c_{branch}/c_{add} . The results for a smooth PDF of Eq.(34) are obtained by the stochastic simulations described in the Subsecs. A (closed circles) and B (large open circles). The results for PDFs with a uniquely defined delay (18) are shown by solid lines for comparison.

value by less than 8%. This justifies the use of approximation (38) as an initial guess for a delayed PDF used to fit the experimental data [11]. Finally, the comparison of computational efficiency of simulated approaches suggested in A, B and C is presented in Figure 13. The approach of C outperforms the methods A and B by up to two orders of magnitude, which will become more dramatic with increasing size and complexity of simulated processes.

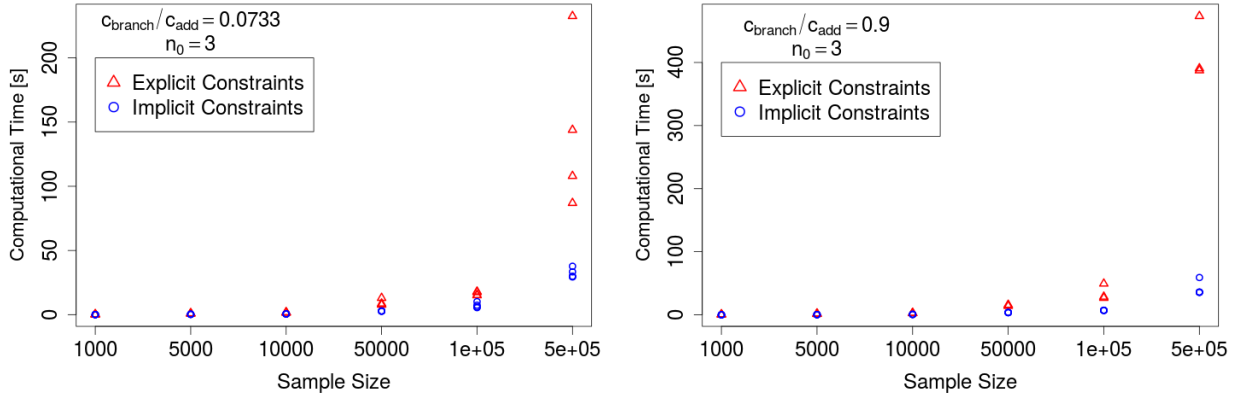


FIG. 10. Computational cost of simulation approaches A (circles) and B (triangles) for two values of the ratio c_{branch}/c_{add} and $n_0 = 3$. The approach A draws realizations more efficiently.

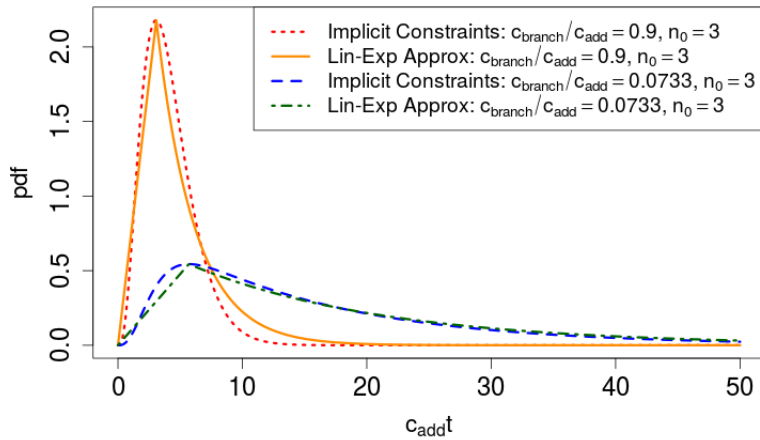


FIG. 11. Comparison of the delayed PDF (34) with its linear-exponential approximation (38) for two values of the ratio c_{branch}/c_{add} and $n_0 = 3$.

VIII. CONCLUSIONS AND DISCUSSION

In summary, introduction of a delay after each growth event significantly changes the statistics of polymer chain growth. The process is governed by the ratio τ/t_{add} , where τ is the length of the delay, and t_{add} is the time it takes, on average, to add a monomer to the chain. For $\tau/t_{add} \ll 1$ the growth remain essentially Markovian, with the mean chain length growing as t/t_{add} , except at very short times. For $\tau/t_{add} \gg 1$ the growth at short

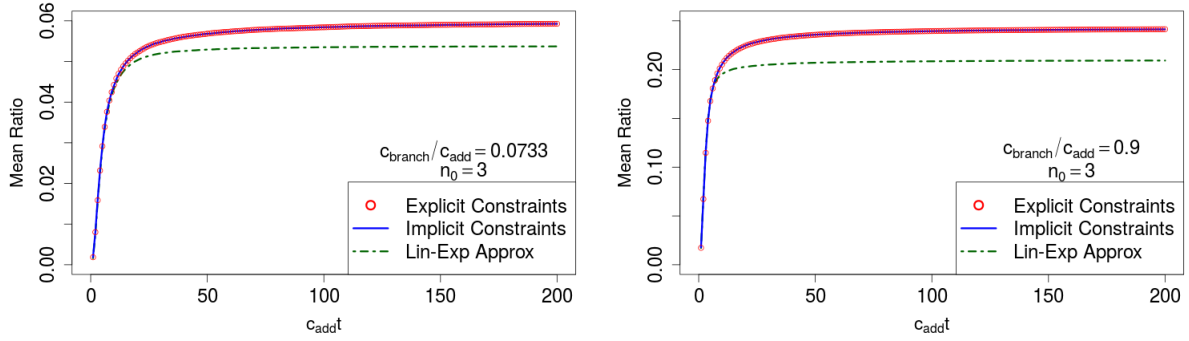


FIG. 12. The ratio of the mean number of branches to the mean total length of the chain (the branching fraction) simulated using the algorithms presented in A (solid line), B (circles) and C (dashed line) for two values of the ratio c_{branch}/c_{add} and $n_0 = 3$.

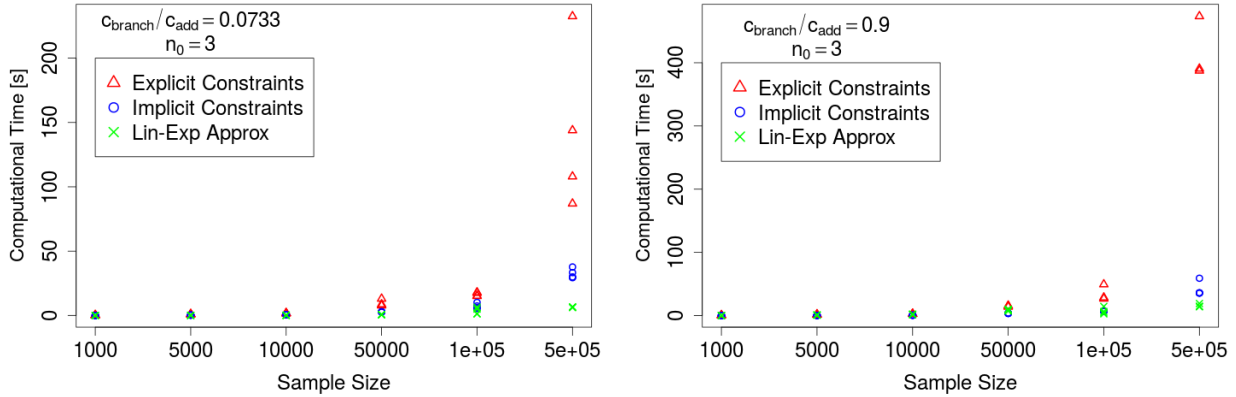


FIG. 13. Computational cost of simulation approaches A (circles), B (triangles) and C (crosses) for two values of the ratio c_{branch}/c_{add} and $n_0 = 3$. The approach C draws realizations more efficiently than A and B.

times proceeds by rapid attachments of single monomers, separated by long 'waiting periods' in which nothing happens. As time progresses, the step-like variations of the mean polymer chain become less pronounced, and a growth with a renormalised constant growth rate \tilde{c} [cf. Eq.(25)] is achieved.

In the simple model of Sect. VI, formation of branches in the chain is a delayed process, whose delay is determined by the growth rate of the polymer chain. The growth itself is unaltered by the branching rate c_{branch} which, in turn, depends on the structural properties

of the chain and not on the rate at which the monomers are added. The behaviour of the mean number of branches is, therefore, similar to that of the mean chain length in a linear growth with delay, described in the preceding paragraph. The ratio of the mean number of branchings to the mean length of the chain, $\langle n_{branch}(t) \rangle / c_{add}t$, has a constant value c_{branch}/c_{add} in the Markovian case. In the presence of a delay, at short times $t \lesssim 10n_0/c_{add}$ it rises from zero to reach the steady value of $c_{branch}/(c_{add} + n_0c_{branch})$ as shown in Fig.6. In general, the presence of a delay is best visible for $c_{branch}t_{add} \gtrsim 1$.

The growth rate $c_{add} = 1/t_{add}$ is proportional to the concentration of monomers, and, is therefore, variable. Our analysis suggests a way of checking whether there are possible time delays of order τ in the growth of a particular polymer. One way is to examine the mean number of branches occurring at growth times $t \lesssim 5\tau$, in order to see whether the ratio of mean number of branchings to the mean chain length is flat. Admittedly, its experimental realization may be difficult. Alternatively, one might try adjusting c_{add} . If for $c_{add}\tau \gtrsim 1$ there are visible deviations from the Poisson statistics of Sect. III, some kind of a time delay is the likely reason.

Apart from time delays, there may be various complex processes accompanying growth of a polymer. Yet, the delayed nature of the growth is one possible reason for observed deviations from the predictions of the Poisson law.

Finally, we note that computer simulation of the phenomenon can be achieved by different methods, whose accuracy and efficiency have been discussed in detail.

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**X. APPENDIX A. PROOF OF THE EQUIVALENCE BETWEEN THE
METHODS OF SECTS. VII A AND VII B**

The aim of this section is to prove that stochastic simulation of two explicitly constrained Poisson processes (VII B) is equivalent to simulating stochastically a single delayed process (VII A), with the delay built into the correspondent PDF given by Eq.(34).

Let us consider two competing Poisson processes, an addition and a branching, which occur at constant rates c_{add} and c_{branch} respectively, with a branching event possible only after at least n_0 additions. We are interested in the time \bar{T}_{branch} needed for the next branching event to happen, distributed with the PDF $\bar{f}_{branch}(t, n_0)$, whose form we want to establish. With n_0 initial additions required, \bar{T}_{branch} has the form

$$\bar{T}_{branch} = \sum_{i=1}^{n_0} T_{add}^i + T_{branch}, \quad (39)$$

where $T_{add}^1, T_{add}^2, \dots, T_{add}^{n_0}$ are the times required for the 1st, 2nd, ..., n_0^{th} addition respectively and T_{branch} is a time for the next branching event to occur if no delay is imposed.

First, we derive the corresponding PDFs for each term of the r.h.s of (39) and then find the resulting PDF for the sum of random variables in Eq.(39). Since addition is a Poisson process, its PDF is

$$f_{add}^{T_{add}^i}(t) = c_{add} \exp(-c_{add}t) \mathbb{I}_{[0;+\infty)}(t) = g(t; 1, c_{add}), \quad (40)$$

where $g(t; \alpha, \beta) = \frac{\beta^\alpha}{\Gamma(\alpha)} t^{\alpha-1} \exp(-\beta t) \mathbb{I}_{[0;+\infty)}(t)$ is the PDF of the Gamma distribution, $\Gamma(\alpha, \beta)$, $\Gamma(\alpha)$ is the gamma function ($\Gamma(\alpha) = (\alpha - 1)!$ if $\alpha \in \mathbb{N}$) and $\mathbb{I}_{[0;+\infty)}(t)$ is 1 if $t \geq 0$, and 0 otherwise. From the Appendix B it follows that that the PDF for $\sum_{i=1}^{n_0} T_{add}^i$ is given by

$$f_{add}^{\sum_{i=0}^{n_0} T_{add}^i}(t) = g(t; \sum_{i=0}^{n_0} 1, c_{add}) = g(t; n_0, c_{add}) = \frac{c_{add}^{n_0}}{(n_0 - 1)!} t^{n_0-1} \exp(-c_{add}t) \mathbb{I}_{[0;+\infty)}(t). \quad (41)$$

Once the required minimal length of n_0 monomers is achieved, branching is also a Poisson process, and T_{branch} is distributed with the PDF

$$f_{branch}(t) = c_{branch} \exp(-c_{branch}t) \mathbb{I}_{[0;+\infty)}(t). \quad (42)$$

The PDF of \bar{T}_{branch} in Eq.(39) can now be found as a convolution of the PDFs of its constituent parts, $\bar{f}_{branch}(t, n_0) = \int f_{add}^{\sum_{i=0}^{n_0} T_i}(\tau) f_{branch}(t - \tau) d\tau$. Explicitly we have

$$\begin{aligned} \bar{f}_{branch}(t, n_0) &= \int_0^{+\infty} \frac{c_{add}^{n_0}}{(n_0 - 1)!} \tau^{n_0-1} \exp(-c_{add}\tau) c_{branch} \exp(-c_{branch}(t - \tau)) \mathbb{I}_{[0;+\infty)}(t - \tau) d\tau = \\ &= \frac{c_{branch} c_{add}^{n_0}}{(n_0 - 1)!} \exp(-c_{branch}t) \int_0^t \tau^{n_0-1} \exp[(c_{branch} - c_{add})\tau] d\tau = \\ &= \frac{c_{branch} c_{add}^{n_0}}{(n_0 - 1)!} e^{-c_{branch}t} \frac{d^{n_0-1}}{d\beta^{n_0-1}} \left[\frac{e^{\beta t} - 1}{\beta} \right]_{\beta=c_{branch}-c_{add}}, \end{aligned} \quad (43)$$

which is equivalent to (34).

XI. APPENDIX B. A USEFUL RELATION

Consider m independent random variables T_i , $i = 1, \dots, m$ which are sampled from the Gamma distribution defined in the Appendix A, $T_1, \dots, T_m \sim \text{Gamma}(\alpha_i, \beta)$. Then their sum, $T \equiv \sum_{i=1}^m T_i$, is a random variable sampled from $\text{Gamma}(\sum_{i=1}^m \alpha_i, \beta)$. To show that this is the case, we write the moment generating functions (mgf) for each T_i ,

$$\psi_{T_i}(\lambda_i) = \int_0^{+\infty} e^{\lambda_i t_i} \frac{\beta^{\alpha_i}}{\Gamma(\alpha_i)} t_i^{\alpha_i-1} e^{-\beta t_i} dt_i = \left(1 - \frac{\lambda_i}{\beta}\right)^{-\alpha_i}. \quad (44)$$

The product $\prod_{i=1}^m \psi_{T_i}(\lambda_i)$ and putting $\lambda_1 = \lambda_2 = \dots = \lambda_m = \lambda$ yields the mgf for the sum T , $\psi_T(\lambda)$. By (44) we have $\psi_T(\lambda) = (1 - \lambda/\beta)^{-\sum \alpha_i}$. Comparing again with (44) shows that

$$T \sim \text{Gamma}\left(\sum_{i=1}^m \alpha_i, \beta\right). \quad (45)$$

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