

Exact solution for stochastic degradation and fragmentation processes in arbitrary chain and ring aggregates with multiple bonds

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This paper presents a statistical theory of stochastic evaporation and degradation processes in complex polymerlike ring and chain aggregates with multiple degrading bonds between the primary particles (monomers). The exact kinetic solution fully describing fragmentation processes is obtained for such aggregates with arbitrary number of primary particles (monomers) and bonds between them. The effects of additional interaction of multiple bonds with each other is shown to have a drastic impact on the predicted kinetic processes and time-dependent particle size distributions during aggregate degradation. Structural effects associated with different distributions of multiple bonds and bonding configurations in the aggregates are also investigated and shown to have a significant impact on typical fragmentation time and accumulation of fragmenting aggregates in intermediate modes. The developed theory and its results will be important for degradation of multistranded polymers, polymer networks, self-assembling structures, surface nanoclusters and nanotechnology, and formation and evolution of aerosol aggregates resulting from transport and industry emissions.

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I. INTRODUCTION

Statistical and probabilistic approaches play an essential role in the theoretical description of a wide range of complex processes in modern thermodynamics and statistical physics, chemical physics, physical and chemical kinetics, etc. In particular, a significant body of literature is available on statistical analysis of various stochastic evolutionary processes during aggregation and degradation of polymerlike systems. These include kinetics of thermal and radiative polymer degradation [1–7], degradation of double-stranded polymers [1,8,9], fractals and polymer multichains [10,11], biological macromolecules [12,13], kinetics of self-arrangement and degradation of reversible polymer networks [14,15], polymerization and aggregation of clusters (including sol-gel transitions) [11,16–24], and thermal fragmentation of nanoparticle clusters due to stochastic evaporation of bonding molecules [25–30].

Methods of analysis of different types of degradation and fragmentation processes in polymerlike systems (such as polymers, macromolecules, and particle aggregates) are based upon consideration of stochastic breakage (evaporation) of bonds between the primary elements (such as monomers, primary particles, etc.) in an aggregated system [1–7]. The analysis of such fragmentation (scission) is typically based upon direct solution of the kinetic equations of fragmentation (resembling the Smoluchowski equation for coagulation), or statistical methods [2,3]. However, direct solution of the fragmentation kinetic equations requires the knowledge of fragmentation rates (kernels in the fragmentation equation) for each of the links between the primary elements of the polymerlike aggregate [2,3]. These fragmentation rates are typically evaluated from a particular physical model and may be significantly different (leading to significantly different solutions), for example, for random scission and when the scission rate depends upon the length of the fragmenting chain aggregate [2,3].

Multiple bonds between neighboring primary elements in an aggregate may significantly affect the process of degradation and fragmentation and substantially complicate determination of fragmentation rates. For example, in the general situation where the number of bonds may vary from one link in a chain aggregate to another, the fragmentation kernels are difficult to evaluate, especially if these bonds interact with each other in every particular link. Similar complications arise when using the master equation for the analysis of fragmentation of chain aggregates with multiple bonds [23,31]. As a result, the current literature contains very limited consideration of degradation kinetics of polymerlike structures with multiple bonds. Even for identical number of bonds in each of the links in a chain aggregate, fragmentation rates (fragmentation kernels) have not been investigated so far.

Papers [27,28] used random graph theory representation for the analysis of stochastic degradation and evaporation processes in chain nanoparticle aggregates with multiple bonds. Though the analysis was conducted on the example of fragmentation of aerosol nanoparticle clusters resulting from combustion emissions, the obtained results and approaches are applicable for any type of polymerlike system (e.g., polymer networks with quadruple hydrogen bonds [14,15]).

The analysis was generalized to chain aggregates with arbitrary number of primary particles (primary elements) and/or bonds between them [27,28]. However, the actual application of the developed approach to large chain aggregates is difficult. This is because the approach relies upon the consideration of all possible evolutionary paths in the random graph representing stochastic evaporation of multiple bonds between the particles, and the number of such possible paths rapidly increases with increasing number of particles and/or bonds in the chain [27,28].

The relationship between coagulation/polymerization and random graphs was recognized long ago [19]. Recently, an interesting approach, based on time evolution of a random graph, was developed by Lushnikov [23] with the intention

of applying it for the analysis of coagulation in finite systems with the sol-gel transition [21–24]. The vertices of the graph represented particles, and edges between them represented bonds between the particles. Introducing new edges in such a graph is equivalent to increasing the number of bonds between the particles, i.e., formation of particle aggregates. New bonds between the particle aggregates (new edges between linked components of the graph [23]) are equivalent to their coagulation. Time-dependent probabilities of finding the coagulating system in particular states are then found as an exact solution within the proposed model. The resultant time-dependent mass spectrum for the particle aggregates is in exact agreement with that obtained from the Smoluchowski equation with the coagulation kernel proportional to the product of masses of coagulating particles [23].

However, this approach is not applicable for the consideration of stochastic evaporation of multiple bonds between the particles (aggregate primary elements). First, the model developed in Ref. [23] does not allow consideration of multiple bonds between the primary particles, because only a single edge (representing a single bond) was allowed to be formed between any two primary particles (represented by the graph vertices). Second, during fragmentation and degradation, the rate of removal of bonds (edges of the graph) is time dependent and has to be determined together with the probability distribution for different possible states. Third, the process of stochastically filling edges in a random graph is significantly different from stochastic removal of these edges from the random graph, which is what would be equivalent to the processes of degradation and evaporation of bonds. For example, the efficiency of coagulation of two particle aggregates is proportional to the product of the numbers of primary particles forming these aggregates, i.e., to the number of options for a bond between the two aggregates to be formed [23]. On the other hand, the efficiency of evaporation of one bond between two clusters is independent of the number of primary particles in them. Therefore, adding one edge to the graph results in coagulation with significantly larger probability than removing one edge results in fragmentation. Finally, the model developed in Ref. [23] does not take into account the possibility of additional interaction between two or more bonds, and such interaction would significantly change bonding energy per one bond in the case of multiple bonds [27,28].

Therefore, the aim of this paper is to develop a general theoretical approach for the analysis of degradation in polymerlike systems, based on statistical consideration of stochastic evaporation of multiple bonds in chain and ring aggregates with arbitrary numbers of primary particles and arbitrary number of mutually interacting and noninteracting bonds between them. Contrary to Refs. [27,28], this developed approach will not require the knowledge of all possible evolutionary paths in the random graph representing the processes of evaporation and degradation of bonds, and thus it will be immediately applicable for arbitrarily large aggregates with multiple bonds. Typical examples demonstrating the effects of internal aggregate structure and additional interaction between multiple bonds are also presented and discussed. Comparison with the previously obtained results for fragmentation of chain aggregates with random scission of

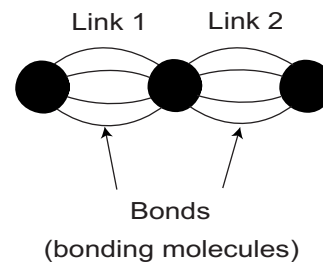


FIG. 1. A chain 3-mer (consisting of three primary particles/monomers) with quadruple bonds in the two links.

single bonds between the primary elements [2] will be conducted.

II. FRAGMENTATION OF MULTIPLE BONDS

A. Noninteracting indistinguishable bonds

Consider a cluster consisting of three monomers (primary particles) that are connected into a chain by two links, each link consisting of four indistinguishable bonds (Fig. 1). In general, we will use the term “ n -mer” to denote a cluster containing n linked monomers (primary particles), and the number of indistinguishable bonds in each link will be termed as the “order” of the link. A possible physical example of a chain 3-mer shown in Fig. 1 is an aerosol cluster with three primary particles bonded together by eight volatile molecules (eight bonds) [27,28]. The bonding volatile molecules may evaporate, eventually resulting in fragmentation of the cluster when the orders of one or both the links become zero [27,28]. Another example could be a quadruple hydrogen bonded 3-mer [14,15].

Stochastic evaporation (degradation) of bonds in any link is assumed to be a process governed by the Poisson distribution [32]. In other words, we assume that the process of evaporation of any bond (e.g., bonding molecule) from a link is not affected by the history of evolution and degradation of the link, but depends only on the current state of the link and external conditions (e.g., temperature). A Poisson process is characterized by a rate constant $1/\tau$, where τ is the time interval within which the probability for the process (bond evaporation) not to occur is reduced by a factor of e [32].

In this subsection, we also assume (more general case is considered below in this paper) that the multiple bonds in a link do not interact with each other (see also Refs. [27,28]). This means that the energy that should be given to one bond (e.g., a bonding molecule) to ensure its degradation evaporation is independent of the number of such bonds in a link [27,28]. In this case, the probability for any bond to evaporate from a link within a time interval t , given that this bond was present at the moment of time $t=0$, is given by [32]

$$P_e(t) = 1 - e^{-t/\tau}. \quad (1)$$

The probability that there has been no evaporation of the considered bond is then

$$P_b(t) = e^{-t/\tau}. \quad (2)$$

We also assume that each bond in a link of an arbitrary order i_0 evaporates independently of the other i_0 bonds. In this

case, evaporation of each of the bonds in the link can be considered using the binomial probability (evaporated or not evaporated). Then the probability that the order of the link is reduced from i_0 at the moment of time $t=0$ to $i < i_0$ within the period of time t is given as

$$P(i, t | i_0, 0) = \binom{i_0}{i} [P_b(t)]^i [P_e(t)]^{i_0-i}. \quad (3)$$

Fragmentation of the link occurs when all the bonds have evaporated, i.e., the order of the link becomes $i=0$. Therefore the probability that a link of the order i_0 fragments within the period of time t is

$$P(0, t | i_0, 0) = [P_e(t)]^{i_0} \equiv P_{f_{i_0}}(t). \quad (4)$$

The link does not fragment within the same period of time t if there is still at least one bond in it, i.e., its order is $i > 1$. The probability for this is given by

$$P(>0, t | i_0, 0) = 1 - P_{f_{i_0}}(t) \equiv P_{l_{i_0}}(t). \quad (5)$$

Because degradation and evaporation processes in different links in an arbitrary n -mer occurs independently, Eqs. (4) and (5) fully determine fragmentation of such an n -mer through the determination of fragmentation probabilities as functions of time for all the links. This fully determines time-dependent concentrations and numbers of all intermediate r -mers (with $r \leq n$) resulting from fragmentation of N_0 original n -mers—see Sec. III below.

B. Interacting indistinguishable bonds

In the previous section, we considered stochastic evaporation and degradation and fragmentation processes in a link with multiple indistinguishable bonds noninteracting with each other. As a result, the evaporation time τ for any of the bonds was independent of the number of these bonds (bonding molecules) in the link. However, multiple indistinguishable bonds in one link may interact with each other, resulting in increasing the overall energy of interaction per one bond [27,28,33]. For example, this may occur when multiple bonds between primary particles in an aerosol cluster are formed by volatile molecules [25–28] interacting with the particles and each other by means of van der Waals forces [27,28]. In this case, the energy that should be given to one molecule to ensure its evaporation from the link, which is the binding energy of evaporation, is larger than the energy that is required for evaporation of a single volatile molecule (single bond) from a link of the order $i=1$ [27,28]. We will assume that interaction between multiple bonds results in equal increase of binding energy of evaporation for all the bonds in a link [27] (which makes them indistinguishable even in the presence of their mutual interaction). This approximation can be regarded as reasonable only if the number of bonds in the link is small (e.g., less than 4 or 5), so that all of them can be assumed to have approximately the same probability of evaporation. If the number of bonding molecules is large, they effectively form a bonding droplet or cluster of molecules, in which surface effects (such as surface tension) may become significant, the internal molecules

will have smaller probability of evaporation. In this case, the approach developed in this paper will not be applicable.

If binding energy of evaporation increases with increasing order of the link, the characteristic evaporation time for a bond also depends on the link order [27,28]. The simple approach considered in Sec. II A is no longer applicable, and a different method of analysis based on the determination of the moment generating function (MGF) [32,34] is developed.

The characteristic evaporation time for any of the k indistinguishable bonds in a link is $\tau_k = \alpha_k \tau$, where τ is the typical evaporation time for a single bond in a first-order link, and α_k is a factor increasing the typical evaporation time for a bond, due to mutual interaction between multiple bonds in a multiorder link [27,28]. Because the strength of interaction between the bonds in the link increases with increasing number of bonds (order of the link), the α factors depend on (typically increase with) increasing order of the link. The actual values of the α factors depend upon the nature of interaction between the bonds. This particular problem is beyond the scope of this paper that is rather focused on the general consideration of degradation and fragmentation in general polymerlike systems.

The Poisson rate at which the number of bonds in a link decreases from k to $k-1$ is given by $\Lambda_k = k / \tau_k = k / (\alpha_k \tau)$ [27]. The k factor in this equation appears because the reduction of the link order by 1 can be achieved by evaporation of any of the k indistinguishable bonds, which occurs within the time interval τ_k/k .

We define the random variable T_k as the time interval within which the order of the link remains k , before decaying into the state with $(k-1)$ bonds. For the Poisson evaporation and degradation process with the rate Λ_k , it can be shown that the probability density function (PDF) for the random variable T_k is given as [32,34]

$$f_{T_k}(t) = \Lambda_k \exp(-\Lambda_k t), \quad (6)$$

where the origin of time is taken at the moment when the order of the link is reduced from $k+1$ to k .

We wish to find the PDF for the interval of time that it takes for the link to evolve from the initial state with i_0 indistinguishable interacting bonds to the state with i indistinguishable interacting bonds. Such a degradation process is associated with the random variable

$$\Psi_i = \sum_{k=i+1}^{i_0} T_k, \quad (7)$$

which represents the actual time interval that it takes for a link with the initial order i_0 to reach the state with the order i .

To find the PDF for Ψ_i , we use the method based on the moment generating function (MGF), which is defined for the T_k random variables as $M_{T_k}(s) = E[\exp(sT_k)]$, where $E(\dots)$ means expectation value of the function in brackets [34]. It follows from this definition that the MGF is the Laplace transformation of the respective PDF [see Eq. (6)] [32,34]: $M_{T_k}(s) = \Lambda_k / (\Lambda_k + s)$. According to the theorem for a sum of

random variables [33], the MGF for the random variable Ψ_i is the product of MGFs for the random variables in the sum (7):

$$M_{\Psi_i}(s) = \prod_{k=i+1}^{i_0} M_{T_k}(s) = \prod_{k=i+1}^{i_0} \frac{\Lambda_k}{\Lambda_k + s}. \quad (8)$$

The required PDF of Ψ_i is then obtained by applying the inverse Laplace transform to $M_{\Psi_i}(s)$:

$$f_{\Psi_i}(t) = L^{-1}[M_{\Psi_i}(s)] = L^{-1}\left(\prod_{k=i+1}^{i_0} \frac{\Lambda_k}{\Lambda_k + s}\right). \quad (9)$$

The expression $f_{\Psi_i}(t)dt$ gives the probability that the considered link in the initial state with i_0 bonds at the moment of time $t=0$ reaches the state with i bonds within the time interval between t and $t+dt$. The probability $P(i, t|i_0, 0)$ that the considered link can be found in the state with i bonds at the moment of time t is then given as

$$P(i, t|i_0, 0) = \int_0^t \left[L^{-1}\left(\prod_{k=i+1}^{i_0} \frac{\Lambda_k}{\Lambda_k + s}\right) - L^{-1}\left(\prod_{k=i}^{i_0} \frac{\Lambda_k}{\Lambda_k + s}\right) \right] dt, \quad (10)$$

where the first term in the integrand represents the probability that the state with i bonds is reached within the time interval $(0, t]$, while the second term (with negative sign) gives the probability that the link has reached and already left the state with i bonds (i.e., further decayed into states with lower order). In other words, the second term in the integrand in Eq. (10) gives the probability that the state with $i-1$ bonds is reached within the time interval $(0, t]$.

If $\Lambda_k \neq \Lambda_q$ for all positive integers k and q such that $k \neq q$, then every pole in the inverse Laplace transform in Eq. (10) is simple. Taking into account the above definition of Λ_k , we see that this occurs when $k\alpha_q \neq q\alpha_k$ for all positive integers k and q such that $k \neq q$. In this case, finding the inverse Laplace transforms and taking the integrals in Eq. (10), we obtain

$$P(i, t|i_0, 0) = \left(\prod_{k=i+1}^{i_0} \Lambda_k\right) \sum_{k=1}^{i_0} \left[e^{-\Lambda_k t} \prod_{q=1(q \neq k)}^{i_0} (\Lambda_q - \Lambda_k)^{-1} \right]. \quad (11)$$

As mentioned above, this equation has been derived under the assumption that $\Lambda_k \neq \Lambda_m$ for all positive integer k and m between 1 and i_0 , such that $k \neq m$. If $\Lambda_k \rightarrow \Lambda_m$, then the sum in Eq. (11) contains the two terms

$$e^{-\Lambda_k t} (\Lambda_m - \Lambda_k)^{-1} \prod_{\substack{q=1 \\ (q \neq k, m)}}^{i_0} (\Lambda_q - \Lambda_k)^{-1} \\ + e^{-\Lambda_m t} (\Lambda_k - \Lambda_m)^{-1} \prod_{\substack{q=1 \\ (q \neq k, m)}}^{i_0} (\Lambda_q - \Lambda_m)^{-1}$$

each of which tend to infinity. However, it can be seen that their sum has a finite limit at $\Lambda_k \rightarrow \Lambda_m$, which suggests that

Eq. (11) can still be used (if the limit is taken) even if $\Lambda_k = \Lambda_m$. This has also been confirmed by the numerical analysis demonstrating that Eq. (11) gives a finite limit at $\Lambda_k \rightarrow \Lambda_m$.

If we assume that $\alpha_m = 1$ (i.e., $\Lambda_k = k/\tau$), then Eq. (11) yields

$$\begin{aligned} P(i, t|i_0, 0) &= \frac{i_0!}{i!} \tau^{i_0-i} \sum_{k=i}^{i_0} \frac{e^{-tk/\tau}}{\tau^{i_0-i} (i_0-k)! (k-i)!} (-1)^{k-i} \\ &= \sum_{k=i}^{i_0} \frac{i_0!}{k! (i_0-k)! i! (k-i)!} (-1)^{k-i} e^{-tk/\tau} \\ &= \sum_{\beta=i}^{i_0} \binom{i_0}{\beta} \binom{\beta}{i} (-1)^{\beta-i} e^{-t\beta/\tau} \\ &= \binom{i_0}{i} \sum_{\beta=i}^{i_0} \binom{i_0-i}{\beta-i} (-1)^{\beta-i} e^{-t\beta/\tau} \\ &= \binom{i_0}{i} [P_b(t)] [P_e(t)]^{i_0-i} \end{aligned}$$

which is identical (as expected) to Eq. (3). The last step in this derivation is done by changing the index of summation and using the binomial theorem.

Equations similar to Eqs. (4) and (5) in the presence of bond interaction can be found by substituting $i=0$ into Eq. (11):

$$P(0, t|i_0, 0) \equiv P_{f_{i_0}}(t) = 1 - \sum_{k=1}^{i_0} \exp\left(-\frac{kt}{\tau\alpha_k}\right) \prod_{\substack{q=1 \\ q \neq k}}^{i_0} \left(1 - \frac{k\alpha_q}{q\alpha_k}\right)^{-1}, \quad (12)$$

which is the probability that the link fragments within the period of time t , and

$$P(>0, t|i_0, 0) \equiv P_{l_{i_0}}(t) = 1 - P_{f_{i_0}}(t), \quad (13)$$

which is the probability that the link does not fragment within the period of time t , i.e., there is still at least one bond in it ($i > 0$).

III. DEGRADATION OF RINGS AND CHAINS

In this section, we consider fragmentation kinetics of chain and ring polymerlike structures (particle aggregates), based on the derived Eqs. (4) and (12) determining the probability for a link to break within an arbitrary time interval t . A typical ring aggregate Ψ is shown in Fig. 2 with n links labeled by Greek letters ($\alpha, \beta, \gamma, \dots$) with the initial number of bonds $i_\alpha, i_\beta, i_\gamma, \dots$, respectively.

We define a column and a row n -dimensional fragmentation state vectors for the Ψ cluster:

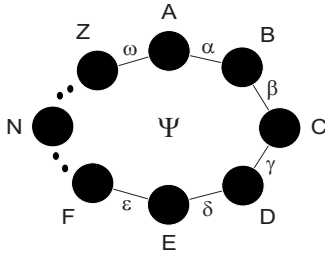


FIG. 2. Diagram of a ring cluster (n -mer) Ψ with n primary particles (monomers) denoted by the black circles and capital letters; the links in the ring are identified by Greek letters ($\alpha, \beta, \gamma, \dots$) with the initial number of bonds $i_\alpha, i_\beta, i_\gamma, \dots$, respectively.

$$|\Psi(t)\rangle = \begin{pmatrix} P_{f_{i_\alpha}}(t) \\ P_{f_{i_\beta}}(t) \\ \vdots \\ P_{f_{i_\omega}}(t) \end{pmatrix}, \quad \langle\Psi(t)| = [P_{f_{i_\alpha}}(t) \ P_{f_{i_\beta}}(t) \ \cdots \ P_{f_{i_\omega}}(t)], \quad (14)$$

whose components are the probabilities for the respective link to fragment within the time interval t . We also define the diagonal $n \times n$ linking matrix $D_\Psi(t)$ and $n \times n$ permutation matrix ρ as follows:

$$D_\Psi(t) = \begin{pmatrix} P_{l_{i_\alpha}}(t) & & & 0 \\ & P_{l_{i_\beta}}(t) & & \\ & & \ddots & \\ 0 & & & P_{l_{i_\omega}}(t) \end{pmatrix}; \quad (15)$$

$$\rho = \begin{pmatrix} 0 & \cdots & 0 & 1 \\ 1 & 0 & \cdots & 0 \\ 0 & \ddots & \ddots & \vdots \\ \vdots & \ddots & \ddots & \ddots \\ 0 & \cdots & 0 & 1 & 0 \end{pmatrix}.$$

Note that each of the two matrices have only one nonzero element in each row and column. The diagonal elements of the linking matrix are the probabilities for the links in the ring not to fragment within the time interval t [e.g., $P_{l_{i_\alpha}}(t) = 1 - P_{f_{i_\alpha}}(t)$].

When the column $|\Psi(t)\rangle$ vector is multiplied by the permutation matrix from the left [or the row vector $\langle\Psi(t)|$ from the right], the components of this vector experience cyclic permutations, i.e., the last component $P_{f_{i_\omega}}(t)$ in the column vector in Eq. (14) is shifted into the first place [or the first component $P_{f_{i_\alpha}}(t)$ of the row vector is shifted to the last place]. This operation is equivalent to the rotation of the ring in Fig. 2 clockwise through one link for the column vector (or counterclockwise for the row vector).

To find the probability of obtaining an r -mer (with $r < n$) from the initial ring aggregate Ψ within a time interval t , we start from the monomer labeled A in Fig. 2 and calculate the

probability $P_{f_{i_\alpha}}(t)$ that by the moment of time t the link labeled α has disappeared (fragmented). Then, starting from link ω , find the probabilities for each of the $r-1$ links on the left of monomer A not to fragment within the same time interval t [e.g., for the ω th link, this will be the probability $P_{l_{i_\omega}}(t)$]. Calculate the probability for the r th link on the left of monomer A to fragment within the same period of time. Because the degradation and evaporation processes in different links are independent, multiplying all these probabilities gives the probability of getting the r -mer aggregate within the period of time t . However, this would only be the probability of getting the r -mer from a particular section of the initial ring, i.e., consisting of r monomers starting from monomer A to the left (counterclockwise along the ring in Fig. 2). To take into account also the probabilities of getting r -mers from different sections of the ring Ψ , we conduct the same procedure starting from all other monomers in the Ψ ring (but not just from monomer A as discussed above), and then sum over all the obtained probabilities.

Similarly, to calculate the probability to obtain a n -mer chain aggregate from the original n -mer ring aggregate Ψ , start from link α and multiply the probability $P_{f_{i_\alpha}}(t)$ for this link to fragment (break) by the respective probabilities for all other links not to fragment within the same time interval t . This gives the probability to obtain an n -mer chain aggregate, under the condition that the break of the initial ring occurs at link α . Conduct the same procedure starting from all other links in the initial n -mer ring aggregate Ψ and sum over all resultant \mathfrak{J} different probabilities. This gives the final overall probability to obtain a n -mer chain aggregate from the original n -mer ring aggregate Ψ within the time interval t . The probability of getting a ring n -mer aggregate from the original n -mer ring aggregate Ψ within the time interval t (i.e., the probability that the original ring does not break into a chain) is calculated simply by multiplying the probabilities for all the links not to fragment within the time interval t . The sum of the two probabilities to obtain n -mer chain and ring aggregates will then give the overall probability of getting a n -mer aggregate (chain or ring) from the original n -mer ring aggregate Ψ .

Mathematically, the resultant overall probabilities of getting different r -mers from the original Ψ ring (ring n -mer) can be conveniently represented using the introduced link and permutation matrices. Multiplying these probabilities by the initial number N_0 of identical ring aggregates Ψ , we obtain the expectation numbers $Q_r(\Psi, t)$ of r -mers at the moment of time t :

$$Q_r(\Psi, t) = \begin{cases} N_0 n \langle 1 | \rho [D_\Psi(t) \rho]^{n-1} | (n-1) \Psi(t) + 1 \rangle, & \text{for } r = n, \\ N_0 \langle \Psi(t) | \rho [D_\Psi(t) \rho]^{r-1} | \Psi(t) \rangle, & \text{for } r < n, \end{cases} \quad (16)$$

where $\langle 1 |$ is a row n -dimensional vector with all its components equal to 1,

$$|(n-1)\Psi(t) + 1\rangle \equiv (n-1)|\Psi(t)\rangle + |1\rangle, \quad (17)$$

and $|1\rangle$ is a column n -dimensional vector whose components are all equal to 1.

The origin of Eq. (16) could be understood from the following consideration. For example, for $r < n$, application of ρ and then $D_\Psi(t)$ to the column vector $|\Psi(t)\rangle$ results in the vector

$$D_\Psi(t)\rho \begin{pmatrix} P_{f_{i_\alpha}}(t) \\ P_{f_{i_\beta}}(t) \\ \vdots \\ P_{f_{i_\omega}}(t) \end{pmatrix} = \begin{pmatrix} P_{f_{i_\omega}}(t)P_{l_{i_\alpha}}(t) \\ P_{f_{i_\alpha}}(t)P_{l_{i_\beta}}(t) \\ \vdots \\ P_{f_{i_{\omega-1}}}(t)P_{l_{i_\omega}}(t) \end{pmatrix}. \quad (18)$$

The components of this vector are the probabilities for all possible states with one link fragmented and the next link on the right not fragmented. Different vector components correspond to all possible positions of the fragmented link in the initial ring Ψ . The second application [in accordance with Eq. (16)] of ρ and then $D_\Psi(t)$ to vector (18) gives

$$D_\Psi(t)\rho \begin{pmatrix} P_{f_{i_\omega}}(t)P_{l_{i_\alpha}}(t) \\ P_{f_{i_\alpha}}(t)P_{l_{i_\beta}}(t) \\ \vdots \\ P_{f_{i_{\omega-1}}}(t)P_{l_{i_\omega}}(t) \end{pmatrix} = \begin{pmatrix} P_{f_{i_{\omega-1}}}(t)P_{l_{i_\omega}}(t)P_{l_{i_\alpha}}(t) \\ P_{f_{i_\omega}}(t)P_{l_{i_\alpha}}(t)P_{l_{i_\beta}}(t) \\ \vdots \\ P_{f_{i_{\omega-2}}}(t)P_{l_{i_{\omega-1}}}(t)P_{l_{i_\omega}}(t) \end{pmatrix}. \quad (19)$$

The components of this new vector are the probabilities for the states with one link fragmented and the next two links on the right not fragmented. Different vector components again correspond to all possible different positions of the fragmented link in the initial ring Ψ . Repeating this procedure $r-1$ times [see Eq. (16)] gives a vector whose components are the probabilities for all possible states with one link fragmented and the next $r-1$ links on the right not fragmented. Multiplying this vector by $\langle\Psi(t)|\rho$ from the left [see Eq. (16)] gives the sum of all the probabilities to have one link in the initial ring Ψ fragmented, $r-1$ links on the right not fragmented, and the r th link on the right also fragmented (which gives the r -mer) for all possible positions of the first fragmented link in the initial ring Ψ . Multiplying this sum by the initial number of identical clusters Ψ gives the overall expected number of r -mers (with $r < n$) at an arbitrary moment of time t —Eq. (16).

Expectation numbers of r -mers at the moment of time t , resulting from degradation of an arbitrary initial chain aggregate Ψ' (Fig. 3) can easily be found from Eq. (16). Indeed, an arbitrary chain aggregate (Fig. 3) is equivalent to the ring aggregate (Fig. 2) with $i_\omega=0$. Therefore, the equations for the expectation numbers of r -mers at the moment of time t , resulting from degradation of an arbitrary chain aggregate Ψ' , immediately follow from Eq. (16) with $i_\omega=0$:

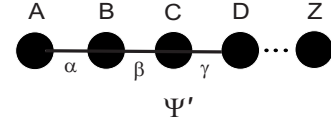


FIG. 3. Diagram of a chain cluster (n -mer) Ψ' with n primary particles (monomers) denoted by the black circles and capital letters; the links in the chain are identified by Greek letters ($\alpha, \beta, \gamma, \dots$) with the initial number of bonds $i_\alpha, i_\beta, i_\gamma, \dots$, respectively.

$$\begin{aligned} Q_r(\Psi', t) &= \begin{cases} N_0 n \langle 1 | \rho [D'_{\Psi'}(t)\rho]^{n-1} | (n-1)\Psi'(t) + 1 \rangle, & \text{for } r = n, \\ N_0 \langle \Psi'(t) | \rho [D'_{\Psi'}(t)\rho]^{r-1} | \Psi'(t) \rangle, & \text{for } r < n, \end{cases} \end{aligned} \quad (20)$$

where

$$D'_{\Psi'}(t) = \begin{pmatrix} P_{l_{i_\alpha}}(t) & & & 0 \\ & \ddots & & \\ & & P_{l_{i_\mu}}(t) & \\ 0 & & & 0 \end{pmatrix}, \quad |\Psi'(t)\rangle = \begin{pmatrix} P_{f_{i_\alpha}}(t) \\ \vdots \\ P_{f_{i_\mu}}(t) \\ 1 \end{pmatrix}. \quad (21)$$

Significant simplifications can be made for the expectation numbers Q_r for both chain and ring aggregate structures when all the links have uniform order. It can be shown that for a n -mer ring Ψ in which every link is of the order i_0

$$Q_r(\Psi, t) = \begin{cases} N_0 P_{l_{i_0}}^{n-1} (P_{l_{i_0}} + n P_{f_{i_0}}), & \text{for } r = n, \\ N_0 n P_{l_{i_0}}^{r-1} P_{f_{i_0}}^2, & \text{for } r < n, \end{cases} \quad (22)$$

and for a n -mer chain Ψ' in which every link is of the order i_0

$$Q_r(\Psi', t) = \begin{cases} N_0 P_{l_{i_0}}^{n-1}, & \text{for } r = n, \\ N_0 P_{l_{i_0}}^{r-1} [2P_{f_{i_0}} + (n-r-1)P_{f_{i_0}}^2], & \text{for } r < n. \end{cases} \quad (23)$$

This simplification is also useful as it allows analysis of even more complex structures, such as combinations of rings and chains. This could be done through the consideration of all possible positions of r -mers inside the complex structure.

It can be seen that Eq. (23) has exactly the same form as Eq. (50) from the paper by Ziff and McGrady [2]. This is expected, because Eq. (23) has been derived under the condition of identical links (having equal number of bonds) between the primary elements in the chain aggregate. Therefore, the probability to break within any chosen period of time is the same for all of these links. This is equivalent to the situation of random scission considered in Ref. [2]. The difference is that the actual values of $P_{f_{i_0}}$ and $P_{l_{i_0}}$ in Eq. (23) are different from those in Ref. [2]—see Eqs. (4), (5), (12), and (13). This is because Ref. [2] analyzed fragmentation of chain aggregates with single bonds between the primary elements of the chain, while we consider multiple noninteract-

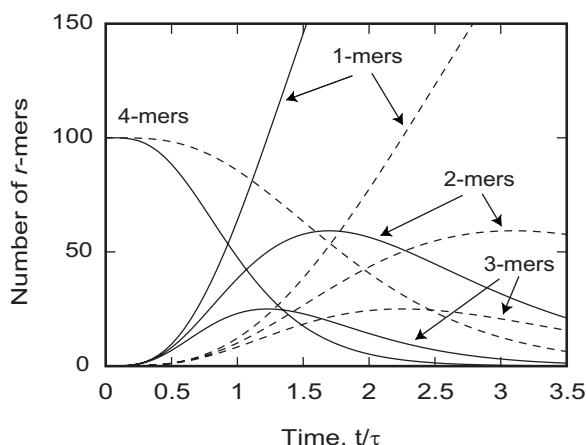


FIG. 4. Time-dependent numbers of r -mers during thermal degradation and fragmentation of $N_0=100$ identical ring aggregates with $n=4$ primary particles and the initial number of bonds, $i_0=2$ bonds, in each of the four links; τ is the evaporation time for a single bond in a first-order link (e.g., for combustion aerosol aggregates $\tau \sim 10$ s [26,27]). Solid curves: noninteracting identical bonds in the link ($\alpha_1=\alpha_2=1$). Dashed curves: interacting identical bonds in the links ($\alpha_1=1$, $\alpha_2=2.69$ which correspond to the 4% increase of binding energy of evaporation for two bonds in a link [27]).

ing [Eqs. (4) and (5)] and interacting [Eqs. (12) and (13)] bonds between any two primary elements of the chain. It is obvious that for single bonds between primary elements in a chain aggregate, Eq. (23) is fully identical to Eq. (50) from Ref. [2].

Note that the developed general theoretical approach to stochastic degradation and fragmentation of polymerlike clusters with multiple bonds is fully consistent with the method developed in Refs. [27,28]. However, the current approach appears to be significantly more general and provides the exact analytical solution for significantly more complex aggregated structures with arbitrary numbers of primary particles and interacting bonds between them.

IV. NUMERICAL RESULTS AND DISCUSSIONS

Using the obtained general exact solution for the stochastic degradation and fragmentation processes in complex ringlike and chainlike aggregates with arbitrary number of multiple bonds, we can now consider specific examples of such aggregates, and investigate the effect of structural parameters and number of bonds in the initial aggregates on their thermal fragmentation. This will be demonstrated on the examples of different types of ring and chain 4-mers.

Figure 4 shows the effect of interaction between multiple bonds in a link on the evolution of $N_0=100$ identical 4-mer ring aggregates Ψ with second-order links. The dependencies of aggregate numbers are plotted as functions of time which is normalized to the evaporation time τ for a single bond in a first-order link. Such normalization makes the presented figure (as well as other dependencies below) applicable for any possible values of evaporation time. The actual values for τ should be determined by the nature of bonds between the primary particles (monomers). For example, for

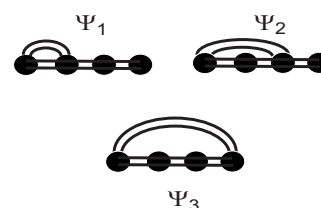


FIG. 5. Three different structures of the initial 4-mers: a chain with quadruple bonds in the first link (Ψ_1), a ring of three primary particles and one extra primary particle attached to it (Ψ_2), and a ring of 4 primary particles (Ψ_3). Solid lines indicate bonds between the particles.

combustion aerosol aggregates, where multiple bonds may be formed by volatile molecules, it was found that typically $t \sim 10$ s [26,27] (which certainly depends on ambient temperature, particle dimensions and composition, type of volatile molecules, vapor pressure of volatile compounds in the air, etc. [27].)

The set of solid curves in Fig. 4 demonstrates typical time-dependent numbers of 3-mers, 2-mers, and 1-mers obtained as a result of thermal fragmentation of the initial $N_0=100$ identical ring aggregates Ψ with four primary particles each, if there is no interaction between the double bonds in each of the links (i.e., $\alpha_1=\alpha_2=1$). The set of the dashed curves gives the same dependencies but in the presence of additional interaction between the double bonds in each of the links. We assume that such interaction results in the 4% increase of binding energy of evaporation per one bond in a pair of bonds, compared to a single bond in a first-order link. This results in $\alpha_1=1$ and $\alpha_2=2.69$ [27].

Although the maximum numbers (concentrations) of the 2-mers and 3-mers are hardly affected by the interaction of double bonds in each of the links in the Ψ aggregates, there is a significant delay with the fragmentation processes (compare solid and dashed curves in Fig. 4). This is due to higher stability of links with additional interaction between the multiple bonds. The reasons why there is no accumulation of aggregates in the intermediate fragmentation modes (2-mer and 3-mer modes in Fig. 4), despite fragmentation delays associated with bond interaction, were discussed in Ref. [27]. One of the outcomes demonstrated by Fig. 4 is that fragmentation processes are highly sensitive to any additional interactions between multiple bonds in a link, which should thus be carefully taken into account when considering kinetics of fragmentation and degradation processes in polymerlike systems with multiple bonds.

The effects of structural variations of initial aggregates on their degradation and fragmentation are demonstrated on the example of the three different types of the initial 4-mers: $\Psi_{1,2,3}$ —Fig. 5. Aggregates Ψ_1 and Ψ_3 are immediately described by the general solutions obtained in the previous section [Eqs. (16) and (20)], while the analysis of degradation of aggregates Ψ_2 is based upon separate consideration of fragmentation probabilities for every link in the initial aggregate. Here, we also assume that there is no interaction between multiple bonds in a link (i.e., all the α coefficients are assumed to equal 1). As a result any differences between the resultant time-dependent numbers of intermediate aggregates

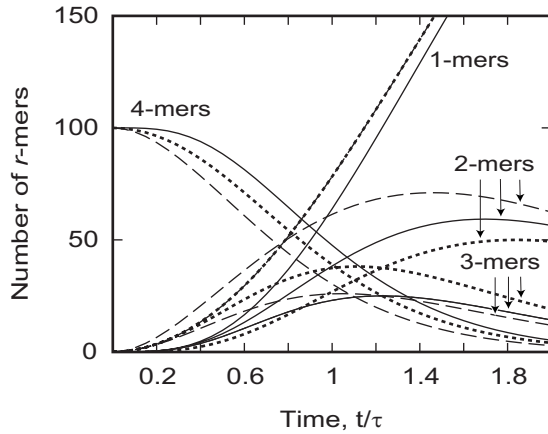


FIG. 6. Time-dependent numbers of r -mers during thermal degradation and fragmentation of $N_0=100$ identical aggregates of types Ψ_1 (dashed curves), Ψ_2 (dotted curves), and Ψ_3 (solid curves); τ is the evaporation time for a single bond in a first-order link. No interaction between multiple bonds in a link is assumed (i.e., the α coefficients are all equal to 1).

should be attributed solely to structural differences between the three different types of initial 4-mers (Fig. 5).

It can be seen that in this case for the aggregates Ψ_2 , we have

$$Q_r(\Psi_2, t) = \begin{cases} N_0 P_{l_2}^3 (P_{l_2} + 3P_{f_2}), & \text{for } r = 4, \\ N_0 P_{f_2} P_{l_2}^2 (P_{l_2} + 5P_{f_2}), & \text{for } r = 3, \\ 2N_0 P_{l_2} P_{f_2}^2 (1 + P_{f_2}), & \text{for } r = 2, \\ N_0 P_{f_2} (1 + P_{f_2})^2, & \text{for } r = 1. \end{cases} \quad (24)$$

Notice that each of the three initial aggregates (Fig. 5) has the same number of primary particles (four) and the same total number of bonds (eight). Nevertheless, they display significantly different fragmentation kinetics (see Fig. 6) which is related to their different internal structures.

For example, the largest maximum of the number (concentration) of 2-mers during fragmentation of the Ψ_1 aggregates is related to the fact that the first links in the initial state of this aggregate contains four bonds (Fig. 5). Therefore, fragmentation of this link is delayed (until all four bonds have evaporated), which leads to a significant accumulation of aggregates in the intermediate 2-mer state (Fig. 6). The typical structure-induced variations in numbers (concentrations) of the intermediate aggregates could be as high as $\sim 50\%$ (Fig. 6). The more complex the initial aggregates, the stronger could be the differences in their degradation and fragmentation, caused by their different internal structures.

On the other hand, the curves for 1-mers for the initial aggregates Ψ_1 and Ψ_2 are identical in Fig. 6. This is because for each primary particle in the initial aggregate Ψ_1 there is an equivalent particle in the aggregate Ψ_2 that is bonded to the rest of the aggregate by the same number of bonds. For example, the first and second particles in aggregate Ψ_1 are equivalent to the first and third particles in aggregate Ψ_2 , the third particle in Ψ_1 is equivalent to the second particle in Ψ_2 , and the fourth particle in Ψ_1 is equivalent to the fourth par-

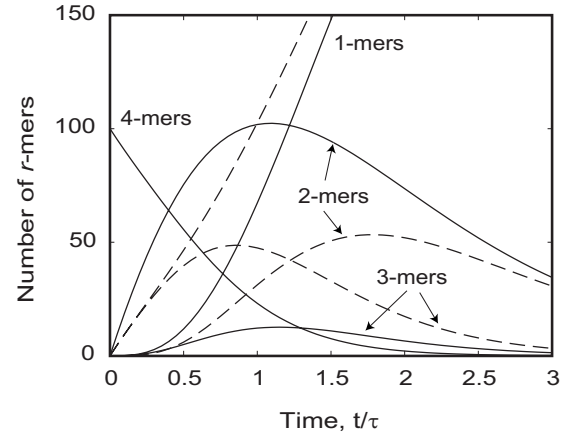


FIG. 7. Time-dependent numbers of r -mers during thermal degradation and fragmentation of $N_0=100$ identical 4-mer chain aggregates of types Φ_1 with the sequence of the link orders 4-1-3 (dashed curves), and chain aggregates Φ_2 with the sequence of the link orders 3-4-1 (dashed curves). Decrease of number of the 4-mers occurs in the same way for both the initial aggregates (see the solid curve for 4-mers). τ is the evaporation time for a single bond in a first-order link. No interaction between multiple bonds in a link is assumed (i.e., the α coefficients are all equal to 1).

ticle in Ψ_2 . Because degradation of all the links occurs independently, this means that the rate of detaching primary particles from both these initial aggregates is the same, which results in identical curves for 1-mers for Ψ_1 and Ψ_2 in Fig. 6. This provides a simple rule for the determination of similar features in evolutionary kinetics for structurally different initial aggregates (this rule could also be extended to 2-mers and r -mers, though in these cases it will be significantly more complicated).

Degradation and fragmentation processes of an aggregate with multiple bonds also significantly depends upon permutations of the links in the initial aggregate. For example, Fig. 7 shows the fragmentation curves for the two initial chain aggregates, both consisting of four primary particles connected by three links with the following orders: 4-1-3 (initial aggregate Φ_1) and 3-4-1 (initial aggregate Φ_2). Substantial (more than 50%) differences, especially for the 2-mer and 3-mer intermediate states, are demonstrated for fragmentation of the aggregates Φ_1 and Φ_2 (Fig. 7). This once again demonstrates the importance of the initial structure and composition of the aggregate for its stochastic degradation and fragmentation kinetics. Introducing additional (weak) interaction between multiple bonds in a link results in the possibility of even stronger structural effects on degradation kinetics.

V. CONCLUSIONS

The exact analytical solution for stochastic degradation and fragmentation of polymerlike systems (aggregates) with multiple bonds has been obtained in the general case of chain and ring aggregates with arbitrary number of primary particles (monomers) and arbitrary number of interacting and noninteracting bonds between them. The obtained solution

allows determination of evolutionary kinetics of the aggregates, typical fragmentation times, time-dependent aggregate numbers (concentrations) in intermediate fragmentation modes, analysis of possible particle accumulation in these intermediate modes due to fragmentation delays, and investigation of the effects of additional interaction between multiple bonds on fragmentation kinetics.

In particular, it has been demonstrated that the distribution of multiple bonds within an aggregate and its initial internal structure may have a drastic impact on the fragmentation kinetics and the related time-dependent particle size distribu-

tions. Additional interaction between multiple bonds (e.g., bonding molecules) is also shown to have a very substantial impact on aggregate fragmentation.

The obtained results will be important in a wide range of areas in physics, physical chemistry, and interdisciplinary science, including degradation of polymers, polymer networks, large biological molecules, formation and evolution of particle modes in combustion aerosols caused by transport and industry emissions, formation and degradation of surface nanostructures, self-assembling systems, etc.

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- [1] N. S. Allen and M. Edge, *Fundamentals of Polymer Degradation and Stabilisation* (Elsevier, London, 1992).
- [2] R. M. Ziff and E. D. McGrady, *J. Phys. A* **18**, 3027 (1985).
- [3] R. M. Ziff and E. D. McGrady, *Macromolecules* **19**, 2513 (1986).
- [4] S. Wang, J. M. Smith, and B. J. McCoy, *AIChE J.* **41**, 1521 (1995).
- [5] G. Madras, J. M. Smith, and B. J. McCoy, *Ind. Eng. Chem. Res.* **35**, 1795 (1996).
- [6] G. Madras and B. J. McCoy, *AIChE J.* **44**, 647 (1998).
- [7] M. Kostoglou, *Chem. Eng. Sci.* **55**, 2507 (2000).
- [8] W. V. Metanowski, R. E. Bareiss, J. Kahovec, K. L. Loening, L. Shi, and V. P. Shibaev, *Pure Appl. Chem.* **65**, 1561 (1993).
- [9] *Ladder and Spiro Polymers, Encyclopedia of Polymer Science and Engineering*, edited by H. F. Mark, N. M. Bikales, C. G. Overberger, G. Menges, and J. I. Kroschwitz, 2nd ed. (Wiley-Interscience, New York, 1990).
- [10] Z. Guan, P. M. Cotts, E. F. McCord, and S. J. McLain, *Science* **393**, 445 (1999).
- [11] H. H. Wickman and J. N. Korley, *Nature (London)* **393**, 445 (1998).
- [12] T. Lindahl, *Nature (London)* **362**, 709 (1993).
- [13] R. P. Sinha and D.-P. Hader, *Photochem. Photobiol. Sci.* **1**, 225 (2002).
- [14] R. P. Sijbesma, F. H. Beijer, L. Brunsveld, B. J. B. Folmer, J. H. K. K. Hirschberg, R. F. Lange, J. K. L. Lowe, and E. W. Meijer, *Science* **278**, 1601 (1997).
- [15] R. P. Sijbesma and E. W. Meijer, *Chem. Commun.* **1**, 5 (2003).
- [16] R. Mezzenga, J. Ruokolainen, G. H. Fredrickson, E. J. Kramer, D. Moses, A. J. Heeger, and O. Ikkala, *Science* **299**, 1872 (2003).
- [17] H. Y. Fan, K. Yang, D. M. Boye, T. Sigmon, K. J. Malloy, H. Xu, G. P. Lopez, and C. J. Brinker, *Science* **304**, 567 (2004).
- [18] F. Leyvraz, *Phys. Rep.* **183**, 95 (2003).
- [19] J. L. Spouge, *J. Stat. Phys.* **38**, 573 (1985).
- [20] A. A. Lushnikov, *J. Colloid Interface Sci.* **65**, 276 (1978).
- [21] A. A. Lushnikov, *Phys. Rev. Lett.* **93**, 198302 (2004).
- [22] A. A. Lushnikov, *Phys. Rev. E* **71**, 046129 (2005).
- [23] A. A. Lushnikov, *J. Phys. A* **38**, L777 (2005).
- [24] A. A. Lushnikov, *Phys. Rev. E* **73**, 036111 (2006).
- [25] D. K. Gramotnev and G. Gramotnev, *J. Aerosol Sci.* **36**, 323 (2005).
- [26] D. K. Gramotnev and G. Gramotnev, *J. Appl. Meteorol.* **44**, 888 (2005).
- [27] D. K. Gramotnev and G. Gramotnev, *J. Appl. Phys.* **101**, 084902 (2007).
- [28] G. Gramotnev and D. K. Gramotnev, in *Biannual Congress of the Australian Institute of Physics, Canberra, Australia* (2005), p. 210; D. K. Gramotnev and G. Gramotnev, in *European Aerosol Conference (EAC 2005), Ghent, Belgium* (2005), p. 690.
- [29] G. Gramotnev and D. K. Gramotnev, *Atmos. Environ.* **41**, 3521 (2007).
- [30] D. K. Gramotnev and G. Gramotnev, *Atmos. Environ.* **41**, 3535 (2007).
- [31] N. G. Van Kampen, *Stochastic Processes in Physics and Chemistry* (Elsevier, Burlington, 2007).
- [32] D. R. Cox and H. D. Miller, *The Theory of Stochastic Processes* (Chapman and Hall, London, 1977).
- [33] J. Israelachvili, *Intermolecular and Surface Forces*, 2nd ed. (Academic Press, New York, 1991).
- [34] R. J. Larsen and M. L. Marx, *An Introduction to Mathematical Statistics and Its Applications*, 2nd ed. (Prentice Hall, N.J., 1986).