

# Exact Solution for Stochastic Evaporation/Degradation Processes in a Chain/Ring Aggregate with Multiple Bonds

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## **Abstract**

Previously, important aspects determining the evolution of aggregate structures in physics and chemistry included size, mass, chemical decomposition amongst others. In this paper, we use a stochastic approach to describe degradation/fragmentation processes of aggregate structures with multiple bonds. The results of this approach revealed the importance of structure, bonding mechanism, and bonding configuration of an aggregate to its subsequent degradation.

## 0.1 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 polymer-like systems. These include kinetics of thermal and radiative polymer degradation [1–6], degradation of double-stranded polymers [1, 7, 8], fractals and polymer multi-chains [9, 10], biological macromolecules [11, 12], kinetics of self-arrangement and degradation/fragmentation of reversible polymer networks [13, 14], polymerization and aggregation of clusters (including sol-gel transitions) [10, 15–23], and thermal fragmentation of nano-particle clusters due to stochastic evaporation of bonding molecules [24–27], etc.

Methods of analysis of different types of degradation/fragmentation of polymer-like 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 [1–6]. The number of bonds between neighbouring primary elements may significantly affect the process of degradation/fragmentation. However, the current literature contains very limited consideration of degradation kinetics of polymer-like structures with multiple bonds. For example, papers by Gramotnev and Gramotnev [26, 27] used random graph theory representation for the analysis of stochastic degradation/evaporation processes in chain nano-particle aggregates with multiple bonds. Though the analysis was conducted on the example of fragmentation of aerosol nano-particle clusters resulting from combustion emissions, the obtained results and approaches are applicable for any type of polymer-like system (e.g., polymer networks with quadruple hydrogen bonds [13, 14]).

The analysis presented in [26, 27] was generalized to chain aggregates with arbitrary number of primary particles (primary elements) and/or bonds between them. However, the actual use of the developed approach for the analysis of large chain aggregates may be difficult. This is because the approach relies upon the knowledge of all possible evolutionary paths in the random graph representing stochastic evaporation of multiple bonds between the particles, whereas the number of such possible

paths rapidly increases with increasing number of particles and/or bonds in the chain [26, 27].

Random graphs have been used for quite a while to describe fragmenting and coagulating systems [18]. Recently, an interesting approach, based on time evolution of a random graph, was developed by Lushnikov [22] with the intension of applying it for the analysis of coagulation in finite systems with the sol-gel transition. 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 [22]) 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 Smoluchowskii equation with the coagulation kernel proportional to the product of masses of coagulating particles [22].

However, the approach described by Lushnikov [22] is not applicable for the consideration of stochastic degradation/evaporation of multiple bonds between the particles (aggregate primary elements).

Primarily, the complication with taking the approach described by Lushnikov [22] for coalescence/coagulation and applying it to bond fragmentation/degradation is initial structure. The model developed by Lushnikov [22] starts with a number of primary particles/monomers, each being identical. The uniformity of this initial condition allows for a description of the coagulating process by a combination of adding bonds inside an existing aggregate or joining two aggregates by a bond. This means that the final state may be described simply by a set of numbers describing the sizes of each aggregate and the number of total bonds inside each aggregate. When considering the fragmentation of such aggregates, these particular sets of numbers describing a state are not sufficient to find the subsequent states produced from bond degradation. This is because the structure of the internal bonds can significantly change the rate at which fragmentation will occur. This will be demonstrated in this paper. Finally, the model developed in [22] does not take into account the possibility of two or more bonds between a particular pair of monomers or the interaction between such bonds. In the case of multiple bonds, interaction would effectively change bonding energy per one bond [26, 27]

and therefore the rate at which degradation/evaporation of these bonds occur.

Therefore, the aim of this paper is to develop a new general approach for the analysis of degradation in polymer-like systems, based on a statistical consideration of degradation/evaporation of multiple bonds in chain-like and ring-like aggregates with arbitrary numbers of primary particles and bonds between them. Contrary to the paper by Lushnikov [22], this approach will consider the internal structure of a fragmenting aggregate and also introduce the possibility of multiple bonds with and without interaction. The presented approach, contrary to papers by Gramotnev and Gramotnev [26, 27], will also not require the knowledge of all possible evolutionary paths to total fragmentation, and thus it can immediately be applied to arbitrarily long aggregates with multiple bonds. Typical examples and comparison with the previous consideration presented in [26, 27] will also be conducted.

## **0.2 Fragmentation of multiple bonds**

As mentioned above, Lushnikov used a random graph for the direct representation of a finite coagulating system with the graph vertices representing the primary particles (primary elements of the coagulating system), and edges representing the bonds between these particles or particle aggregates [22]. Degradation in such a representation would have corresponded to removal of edges from the graph. However, due to the mentioned shortcomings and difficulties of this approach (see the previous section), we tend towards an approach based on the assumptions in the papers by Gramotnev and Gramotnev [26, 27]. In this approach, the vertices of the random graph denote different possible states of the fragmenting aggregate/cluster, while the graph edges represent the processes of transformation between the neighbouring states (i.e., the processes of degradation/evaporation of bonds). Therefore, the edges are neither added to nor removed from the graph - they are always present representing the possibility of the corresponding degradation/evaporation processes. The actual relations discussed in the next section of this paper can be derived by using a simple generating function approach to the random graph suggested in [26, 27]. However, the results also can be easily understood by careful reasoning therefore the analysis of the generating function approach has been omitted, see [28] for more details pertaining to this approach.

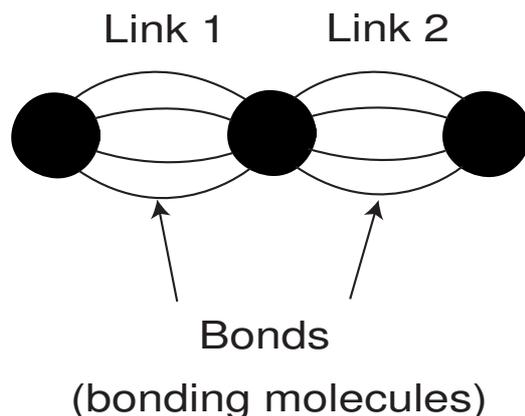


Figure 1: A sample chain 3-mer (consisting of three primary particles/monomers) with multiple bonds.

### 0.2.1 Non-interacting bonds

In this section, we consider the degradation and eventual fragmentation of a multiple bond linking two monomers. In order to distinguish between a single bond and a multiple bond we will refer to a single bond (the constituents of a multiple bond) with the word ‘bond’ and a multiple bond (which link two monomers) with the word ‘link’. The ‘order’ of the link will refer to the number of constituent bonds in the link. To demonstrate the difference, Figure 1 represents a 3-mer. The 3 monomers are connected in a chain structure, thus, it has 2 links. In this particular case, each link is of order 4, meaning, that each link consists of 4 bonds. A possible physical example of such a system is an aerosol cluster with three primary particles bonded together by 8 volatile molecules (8 bonds) [26,27]. The bonding volatile molecules may evaporate, eventually resulting in fragmentation of the cluster [26, 27]. Another example could be three monomers bonded by quadruple hydrogen bonds [13, 14].

The degradation/evaporation process works by stochastically reducing the number of bonds in a particular link. This stochastic process is taken to follow a Poisson distribution. The reason for this is that the process should not be effected by its history but rather its present state and conditions that it is in. The Poisson process is characterised by the rate constant,  $1/\tau$ , where  $\tau$  is the length of time that the probability, in which a particular bond has not been evaporated, will drop by a factor of  $e$ . This means that the probability for a particular bond to be evaporated, at time,  $t$ , given that it exists at time,  $t = 0$ , is given by

$$Pr(\text{evaporation}, t | \text{bond}, 0) = Pr_e(t) = 1 - e^{-t/\tau}. \quad (1)$$

This defines the probability there has been no evaporation in a particular bond and it is given by

$$Pr(\text{bond}, t | \text{bond}, 0) = Pr_b(t) = e^{-t/\tau}. \quad (2)$$

If we consider that each bond in a link of order,  $i_0$ , evaporates independantly of each other, then we can simply treat each bond as an binomial probability (evaporated or bonded) and use a binomial expansion to find the probability that at time,  $t$ , the number of existing bonds remaining in the link is  $i < i_0$ ,

$$Pr(i \text{ bonds}, t | i_0 \text{ bonds}, 0) = \Xi_i \left( (Pr_b(t) + Pr_e(t))^{i_0} \right) = \binom{i_0}{i} Pr_b^i(t) Pr_e^{i_0-i}(t), \quad (3)$$

where the operator  $\Xi_i$  finds the  $i$ th term in the expansion of  $(Pr_b(t) + Pr_e(t))^{i_0}$ . We consider the fragmentation effect to occur when all bonds have been evaporated ( $i = 0$ ) and therefore the probability that the link of order  $i_0$  has been broken/fragmented is given by

$$Pr(0 \text{ bonds}, t | i_0 \text{ bonds}, 0) = Pb_{i_0}(t) = Pr_e^{i_0}(t). \quad (4)$$

Thus, the probability that the link still holds is given by

$$Pr(\text{not } 0 \text{ bonds}, t | i_0 \text{ bonds}, 0) = Pc_{i_0}(t) = 1 - Pr_e^{i_0}(t). \quad (5)$$

## 0.2.2 Interacting bonds

Often, it is the case, where the characteristic evaporation time,  $\tau$ , for a single bond to evaporate is dependant on the number of bonds present in the link. This is certainly the situation for thermal fragmentation described by Gramotnev and Gramotnev [26,27]. The dependance, in this case, comes from the interaction of the weak dispersion forces representing the bonds. The interaction of bonds resulting from dispersion forces is often neglected as an approximation [29], however, although the effect on the binding energy (and hence the characteristic evaporation time) due to the presence of

other bonds is usually small it can be important [30]. For completeness, we discuss the forms of  $Pb_{i_0}(t)$  and  $Pc_{i_0}(t)$  in the presence of interacting bonds.

The characteristic evaporation time for a single bond in a link of order  $i$  can be represented by  $\tau_i = \alpha_i \tau$ , where  $\alpha_i$  is some factor depending on the order of the link.

Calculation of these factors can be complex and the mathematical discussion in this section leaves them general. A brief discussion of these factors is presented in the paper by Gramotnev and Gramotnev [26].

We consider the same problem as in the last section, however, the characteristic time depends on the number of bonds in the link. We define the Poisson rate at which the number of bonds in a particular link of order,  $i_0$ , decreases from  $i$  to  $i - 1$ . This rate is given by  $\Lambda_i = i/\tau_i = i/(\alpha_i \tau)$ . Multiplying the rate by  $i$  in this definition is due to the fact that any one of the  $i$  bonds may evaporate to decrease the number of bonds by one. We define a set of random variables denoted by  $T_i$ . This random variable is defined as the length of time a given link will remain with  $i$  bonds before one evaporates. Due to the Poisson nature of each evaporation, We can easily show that the probability density function (PDF) for this time is given by

$$f_i(t) = \Lambda_i e^{-\Lambda_i t}. \quad (6)$$

We wish to find the PDF for the time it takes to evolve from  $i_0$  bonds to  $i$  bonds. In which case, this will be denoted by a new random variable  $\Psi_i = \sum_{n=i+1}^{i_0} T_n$ . To find the distribution function for  $\Psi_i$ , we will need to find the ‘‘Moment Generating Function’’ (MGF) for  $T_i$ . We then take the product of these functions over all terms in the sum for  $\Psi_i$ , to find the MGF for  $\Psi_i$ . The MGF for  $T_i$  is found by taking the Laplace transform of Equation (6). Here  $E$  represents the MGF of the random variable.

$$E(T_i) = \frac{\Lambda_i}{\Lambda_i + s} \quad (7)$$

$$E(\Psi_i) = \prod_{n=i+1}^{i_0} \frac{\Lambda_n}{\Lambda_n + s}. \quad (8)$$

To find the PDF of  $\Psi_i$  we require the inverse Laplace transform of  $E(\Psi_i)$ .

$$PDF(\Psi_i) = \mathcal{L}^{-1}E(\Psi_i) = \mathcal{L}^{-1} \left[ \prod_{n=i+1}^{i_0} \frac{\Lambda_n}{\Lambda_n + s} \right]. \quad (9)$$

We note that this does not equate to  $\Pr(i \text{ bonds}, t | i_0 \text{ bonds}, 0)$ . To find  $\Pr(i \text{ bonds}, t | i_0 \text{ bonds}, 0)$  we need to integrate Equation (9) from 0 to  $t$  to find the probability that the system has reached the case where there is only  $i$  bonds left, then take away the probability that the system has reached the case where there is only  $i-1$  bonds left. This leaves us with the expression for  $\Pr(i \text{ bonds}, t | i_0 \text{ bonds}, 0)$ ,

$$\Pr(i \text{ bonds}, t | i_0 \text{ bonds}, 0) = \int_0^t \left[ \mathcal{L}^{-1} \left[ \prod_{n=i+1}^{i_0} \frac{\Lambda_n}{\Lambda_n + s} \right] - \mathcal{L}^{-1} \left[ \prod_{n=i}^{i_0} \frac{\Lambda_n}{\Lambda_n + s} \right] \right] dt. \quad (10)$$

We assume that every pole is a simple pole (i.e. we impose the condition that  $nq \neq \alpha_n \alpha_q, \forall \{n, q | n \neq q\}$ ). This is a reasonable assumption as the values for  $\alpha_n$  are not constricted to integers, and as such, a contradiction to this assumption is a very unlikely scenario. With the use of complex analysis, we can find the inverse Laplace transforms and subsequently integrate the exponential terms that result in the expression for  $\Pr(i \text{ bonds}, t | i_0 \text{ bonds}, 0)$ . That is,

$$\Pr(i \text{ bonds}, t | i_0 \text{ bonds}, 0) = \prod_{n=i+1}^{i_0} \{\Lambda_n\} \sum_{n=i}^{i_0} e^{-\Lambda_n t} \prod_{\substack{q=1 \\ q \neq n}}^{i_0} \{\Lambda_q - \Lambda_n\}^{-1}. \quad (11)$$

In order to show this result agrees with the result obtained in Section 0.2.1, we make the simplification that  $\alpha_n = 1$  ( $\Lambda_n = n/\tau$ ). This yields,

$$\Pr(i \text{ bonds}, t | i_0 \text{ bonds}, 0) = \tau^{i_0-i} \frac{i_0!}{i!} \sum_{n=i}^{i_0} \frac{e^{-tn/\tau}}{\tau^{i_0-i} (i_0 - n)! (n - i)!} (-1)^{n-i} \quad (12)$$

$$= \sum_{n=i}^{i_0} \frac{i_0!}{n! (i_0 - n)! i! (n - i)!} (-1)^{n-i} e^{-tn/\tau} \quad (13)$$

$$= \sum_{\beta=i}^{i_0} \binom{i_0}{\beta} \binom{\beta}{i} (-1)^{\beta-i} e^{-\beta t/\tau} \quad (14)$$

$$= \binom{i_0}{i} \sum_{\beta=i}^{i_0} \binom{i_0 - i}{\beta - i} (-1)^{\beta-i} e^{-\beta t/\tau} \quad (15)$$

$$= \binom{i_0}{i} Pr_b^i(t) Pr_e^{i_0-i}(t). \quad (16)$$

The last step is done by changing the index of summation and using binomial theorem. This indicates that the analytic methods are in agreement.

It is important to find the more general forms of  $Pb_{i_0}(t)$  and  $Pc_{i_0}(t)$  under the assumption of bond interaction. This is done by substituting in  $i = 0$  into Equation (11) as was done in the previous section. It can be shown that,

$$Pb_{i_0}(t) = 1 - \sum_{n=1}^{i_0} \exp\left(\frac{-nt}{\tau\alpha_n}\right) \prod_{\substack{q=1 \\ q \neq n}}^{i_0} \left(1 - \frac{n\alpha_q}{q\alpha_n}\right)^{-1}, \quad (17)$$

$$Pc_{i_0}(t) = \sum_{n=1}^{i_0} \exp\left(\frac{-nt}{\tau\alpha_n}\right) \prod_{\substack{q=1 \\ q \neq n}}^{i_0} \left(1 - \frac{n\alpha_q}{q\alpha_n}\right)^{-1}. \quad (18)$$

Using these results, we can now analyse the degradation of different chain and ring type structures with multiple bonds.

### 0.3 Degradation of Rings and Chains

Using the expressions for the probability of a link to break or stay linked, we will start this section with a discussion of the degradation of a ring aggregate system and then further discuss the degradation of a chain aggregate system.

For notational purposes, a sample ring aggregate diagram has been presented in Figure 2. In Figure 2, each link is labelled by a greek letter, which not only defines its position in the ring but also represents the defining characteristic of the link, its order.

We now define a Fragmentation State Vector,  $|\Psi_b(t)\rangle$ , for  $\Psi$  given by,

$$|\Psi_b(t)\rangle = \begin{pmatrix} Pb_\alpha(t) \\ Pb_\beta(t) \\ Pb_\gamma(t) \\ \vdots \\ Pb_\omega(t) \end{pmatrix}.$$

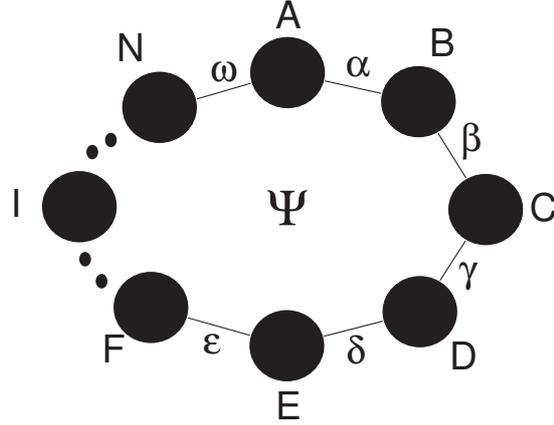


Figure 2: Diagram of an  $N$ -mer ring structure, labelled  $\Psi$ . The alpha-numeric labelling represents the monomer constituents and the greek labelling represent the order of each link.

Furthermore, we define the Linking Matrix,  $\Psi_c(t)$ , for  $\Psi$  and the Rotation Matrix (or Permutation Matrix),  $\rho$ , by the forms

$$\Psi_c(t) = \begin{pmatrix} Pc_\alpha(t) & & & \mathbf{0} \\ & Pc_\beta(t) & & \\ & & \ddots & \\ \mathbf{0} & & & Pc_\omega(t) \end{pmatrix} \quad \rho = \begin{pmatrix} 0 & \dots & 0 & 1 \\ 1 & 0 & \dots & 0 \\ & \ddots & \ddots & \vdots \\ \mathbf{0} & & 1 & 0 \end{pmatrix},$$

where  $\mathbf{0}$  represents a region of 0's and  $\ddots$  represents a logical repetition. Note that each of the two matrices have only one non-zero element in each row and column and both are  $N \times N$  in dimension.

Consider, now, a sample of  $n$  ring aggregates,  $\Psi$ , as shown in Figure 2. We may find the number of ( $R \leq N$ )-mers that can be expected,  $Q_R$ , as a result of fragmentation of this sample by considering the probability of obtaining any possible  $R$ -mer and multiplying this by the number of initial  $N$ -mer rings,  $n$ . In order to find the probability of obtaining any possible  $R$ -mer we start from the monomer labelled  $A$  in Figure 2 and consider the probability of a break at  $\alpha$ . We then proceed to rotate the ring clockwise and multiply by the probability of a link/connection in the place where the  $\alpha$  link used to be, which is the probability that the  $N$  monomer and the  $A$  monomer are connected. We continue to rotate and multiply by the probability of successive links before we finally multiply by the probability of a break after  $R$  monomers in the ring have been considered to be linked. We then sum the contribution of the same probability of obtaining an  $R$ -mer beginning with the monomer  $B$

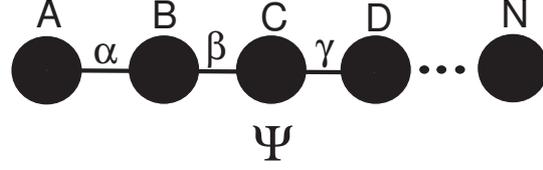


Figure 3: Diagram of an  $N$ -mer chain structure, labelled  $\Psi$ . The alpha-numeric labelling represents the monomer constituents and the greek labelling represent the order of each link.

rather than A, then beginning with C and so on.

The calculation of the expected  $N$ -mers resulting from the original  $N$ -mer,  $Q_N$ , is a little different because it does not include two breaks in the link but rather the probability of total connectedness plus the probability of only one break. This being the case, however, a similar approach has been used in order to find the probability of obtaining an  $N$ -mer.

The expected number of  $R$ -mers can therefore be represented mathematically for a given,  $n$ ,  $N$ -mers,  $\Psi$ , using the following relation

$$Q_R(\Psi, t) = \left\{ \begin{array}{ll} \frac{n}{N} \langle 1 | [\rho \Psi_c(t)]^{N-1} \rho | (N-1) \Psi_b(t) + 1 \rangle & , N = R \\ n \langle \Psi_b(t) | [\rho \Psi_c(t)]^{R-1} \rho | \Psi_b(t) \rangle & , 1 \leq R < N \end{array} \right\}, \quad (19)$$

where the notation  $\langle 1 |$  is a row vector of order  $N$  with every element equal to unity and intuitively

$$|(N-1) \Psi_b(t) + 1 \rangle \equiv (N-1) |\Psi_b(t)\rangle + |1\rangle.$$

Degradation of the chain shown in Figure 3 can be found quite easily from Equation 19.

It is easily noticeable that the chain structure is indistinguishable from the ring structure given in Figure 2, with the small change that  $\omega = 0$ . Therefore, it is easy to write the expected number of  $R$ -mers due to fragmentation of the chain structure as

$$Q_R(\Psi, t) = \left\{ \begin{array}{ll} \frac{n}{N} \langle 1 | [\rho \Psi'_c(t)]^{N-1} \rho | (N-1) \Psi'_b(t) + 1 \rangle & , N = R \\ n \langle \Psi'_b(t) | [\rho \Psi'_c(t)]^{R-1} \rho | \Psi'_b(t) \rangle & , 1 \leq R < N \end{array} \right\}, \quad (20)$$

where

$$|\Psi'_b(t)\rangle = \begin{pmatrix} Pb_\alpha(t) \\ Pb_\beta(t) \\ Pb_\gamma(t) \\ \vdots \\ 1 \end{pmatrix} \quad \text{and} \quad \Psi'_c(t) = \begin{pmatrix} Pc_\alpha(t) & & \mathbf{0} \\ & \ddots & \\ & & Pc_\psi(t) \\ \mathbf{0} & & & 0 \end{pmatrix}.$$

Simplifications due to symmetry and uniformity can be made in the cases of both chain and ring aggregate structures quite easily when all the links have uniform order. The simplifications can be done because the vectors and matrices ( $|\Psi_b(t)\rangle$ ,  $\Psi_c(t)$  etc) now have common factors. It can be shown that for an  $N$ -mer ring in which every link is of the order  $i_0$

$$Q_R(\Psi, t) = \begin{cases} nPc_{i_0}^{N-1} (Pc_{i_0} + NPb_{i_0}) & , N = R \\ nNPc_{i_0}^{R-1} Pb_{i_0}^2 & , N > R \end{cases} \quad (21)$$

and for an  $N$ -mer chain in which every link is of the order  $i_0$

$$Q_R(\Psi, t) = \begin{cases} nPc_{i_0}^{N-1} & , N = R \\ nPc_{i_0}^{R-1} Pb_{i_0} (N - R + 1 - (N - R - 1)Pc_{i_0}) & , N > R \end{cases} \quad (22)$$

This simplification of uniform order make it possible to analyse even more complex structures, such as combinations of rings and chains, numerically. This is done by a simple consideration of all the possible positions of  $R$ -mers inside the complex structures. This must be done, however, using this approach, case by case.

The comparison of the results presented here to the results obtained by Gramotnev and Gramotnev [26,27] were absolutely identical. The advantage of this study lies in its ability to be extended to more complex structures with simplicity of calculations.

## 0.4 Results

In this section, initial conditions and the nature of the bonds themselves will be shown to play a vital role in the evolution of a degradation/fragmentation process. The analysis of the evolution of aggregates in the literature, usually, consider all  $N$ -mers to be indistinguishable by placing them all

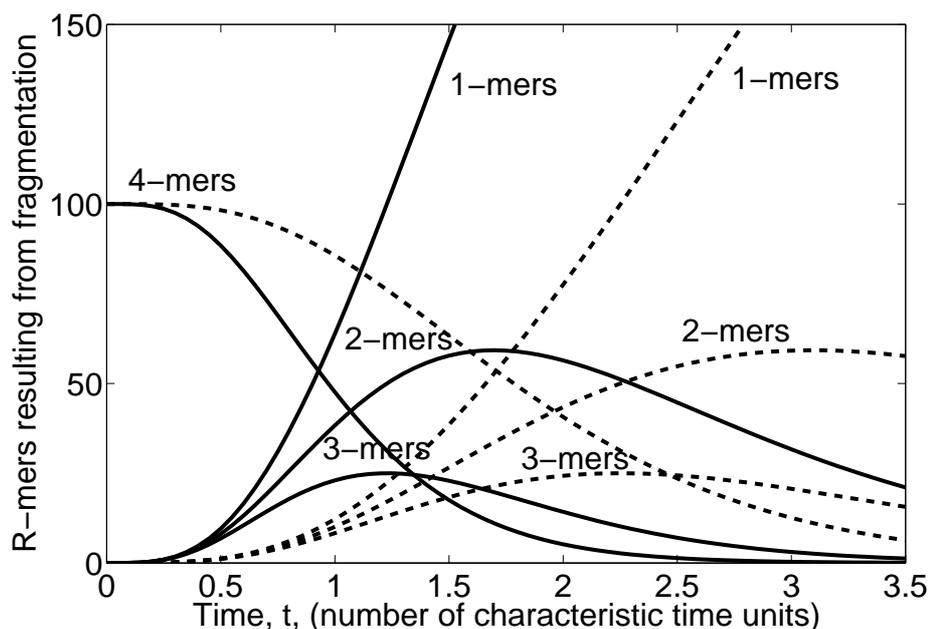


Figure 4: Fragmentation of 100 4-mer ring aggregates with (dashed) and without (solid) bond interaction.

in a class by the same name. In order to demonstrate that  $N$ -mers, in general, degrade/fragment differently depending on their structure and bonding mechanism all the following results are given using different 4-mers. When non-unity values for  $\alpha_i$  are used, they are calculated in the same way as in the paper by Gramotnev and Gramotnev [26, 27].

Figure 4 shows the effect bond interaction can have on the evolution of 100 fragmenting 4-mers. The first set of data show the number of expected 4-mers, 3-mers etc as a function of time as a result of bond interaction as described by Gramotnev and Gramotnev [26, 27] and the second set of data assumes that there is no interaction of bonds. As this comparison has been done by Gramotnev and Gramotnev for chain aggregates we compare here the fragmentation of 4-mer ring aggregates. All links are of order 2.

Although the maximum concentrations are unaltered, there is a significant delay at which the fragmentation occurs. This is essentially due to the stability of the bonds brought about by their interaction, whilst the actual structure and hence the mechanics of the evolution do not change. This demonstrates the fact that for timing of a fragmentation process it is important to understand the bonding mechanism and investigate the bond interaction contributions to binding energy.

Figure 6 shows the importance of initial internal structure to the fragmentation process. It shows

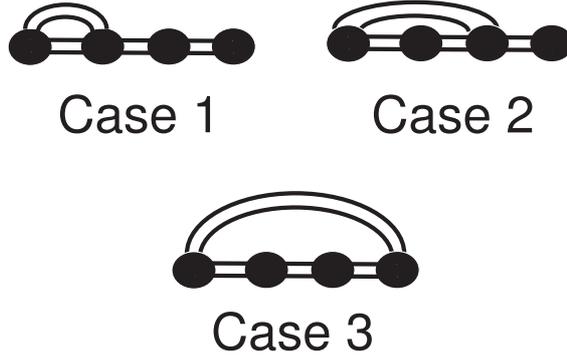


Figure 5: 3 different cases of 4-mers with the same number of bonds.

the fragmentation of the 3 different cases of 4-mers. The 3 cases are shown in Figure 5. We have not considered bond interaction in Figure 6 in order to show discrepancies between a reversal of Lushnikovs model [22] and a real fragmentation/degradation mechanism. Cases 1 and 3 have been analysed using Equations 20 and 21 respectively whilst the convenience that all the links of case 2 have an order of 2 was used to intuitively derive

$$Q_R(\text{case } 2, t) = \left\{ \begin{array}{l} nPc_2^3(Pc_2 + 3Pb_2) \quad , R = 4 \\ nPb_2Pc_2^2(Pc_2 + 5Pb_2) \quad , R = 3 \\ 2nPc_2Pb_2^2(1 + Pb_2) \quad , R = 2 \\ nPb_2(Pb_2 + 1)^2 \quad , R = 1 \end{array} \right\}, \quad (23)$$

based on consideration of every possible outcome of link breakages.

Notice that each of the three cases have the same number of monomers (4) and each have the same number of bonds (8). This means that they would be indistinguishable according to most current models involving evolution of aggregates, including that of Lushnikov [22]. However the way in which they fragment does not indicate equality.

It is clear that although the evolution of the three different cases do not vary a great deal they certainly do not fragment as though they were indistinguishable aggregates. Not only is there a slight time delay between the fragmentation processes on the whole but there is also a difference in the time-dependent mass spectrum. It can be seen from Figure 6 that for some aggregate size categories at some moments the mass spectrum can vary up to about 50% due to structural differences of initial 4-mers. For larger aggregates, this may vary even more due to the larger number of structural

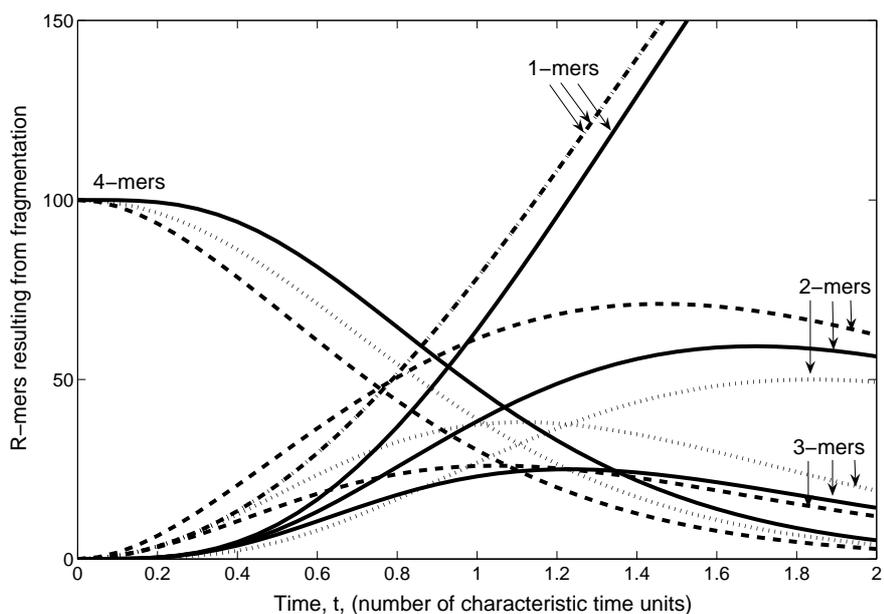


Figure 6: Fragmentation of 100 4-mer aggregates with structure of case 1 (dashed), with structure of case 2 (dotted) and structure of case 3 (solid).

possibilities.

Furthermore, Figure 7 shows that the degradation process of an aggregate can change simply by permuting the orders of the links and keeping the structure constant. Compared in the Figure is two different chain 4-mers. The first has links of order 4, 1, 3, in sequence and the second has links of order 3, 4, 1, in sequence. Once again, we demonstrate the importance of the initial structure/composition of the aggregate on its degradation. The time-dependent mass spectrum in these cases is vastly different from each other. This is mainly due to the larger likelihood that the link of order 1 will be the first to break. In the first case this will result in two 2-mers and in the second case this will result in 1 1-mer and 1 3-mer. Bond interaction has also been neglected in this comparison.

## 0.5 Conclusion

The majority of analysis into fragmenting or coagulating systems in the literature have considered, using graph theory, all  $N$ -mers to be equal and all bonds/links to be equal. In this paper we have relaxed this assumption and shown the importance of not oversimplifying a complex process like degradation/fragmentation of aggregates with multiple bonds. We have derived a stochastic method

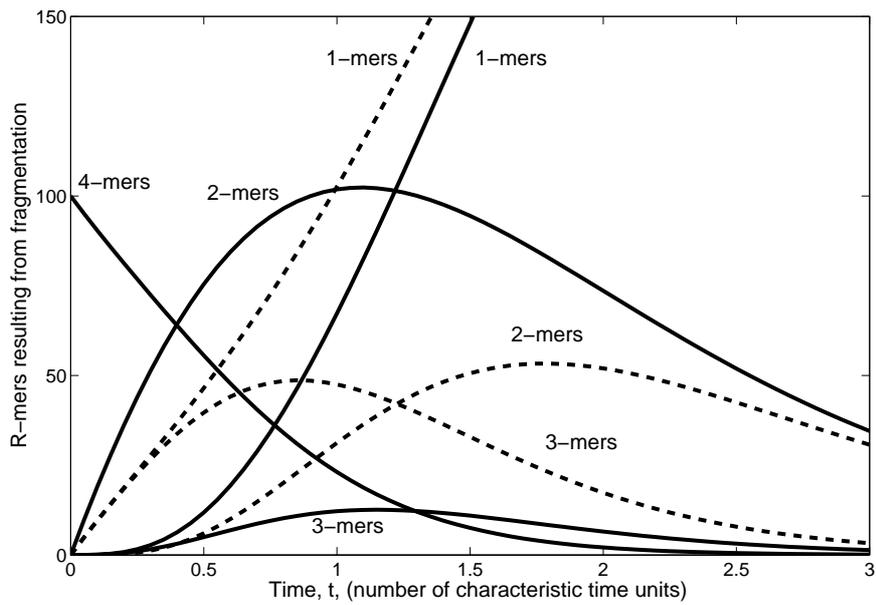


Figure 7: Fragmentation of 100 4-mer chain aggregates with links of order 4, 1, 3, in sequence (solid) and 3, 4, 1, in sequence (dashed).

for calculating time-dependent mass spectrums for simple aggregate structures including chains and rings. Using this method we were able to demonstrate the way in which the mass spectrum can be altered under different conditions that are usually neglected as not important. These conditions include the possibility of multiple bonds, the possibility of interaction of these bonds with each other and different initial structures.

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