

# **EHRENFEST MODEL FOR THE CONDENSATION AND EVAPORATION PROCESSES IN DEGRADING AGGREGATES WITH MULTIPLE BONDS**

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## **Abstract**

In this paper, we present the explicit theory of degradation and thermal fragmentation kinetics of polymer-like systems and aggregates with multiple bonds in the presence of stochastic evaporation and condensation (restoration) of bonds. The analysis is conducted on the basis of the determination of the first passage time to state zero (fragmented state) in the Ehrenfest diffusion model in continuous time. The main approximations of the developed theory include the assumption that multiple bonds in any link between the primary elements in the aggregate do not interact with each other, and that coagulation rate after thermal fragmentation of the aggregates is negligible (which gives the absorbing zero state in the Ehrenfest model). In particular, it is demonstrated that even small condensation rates (of  $\sim 10$  times smaller than the rates of bond evaporation) may have a significant effect on typical evolution times for the degrading aggregates, and can result in strong accumulation of nano-aggregates in the intermediate fragmentation modes. Simple asymptotic (predominantly exponential) behavior of the obtained solution at large evolution times is analyzed and discussed. The results will be important for the investigation of degradation kinetics of a variety of polymer-like systems with multiple bonds, including self-arranged structures, polymer networks, different types of nano-clusters and their thermal fragmentation, etc.

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## 1. Introduction

The Ehrenfest model was introduced by Paul and Tatyana Ehrenfest [1] as a model for gas diffusion, to help explain why the entropy of a closed system must increase. This model considers a system with stochastic birth and death processes and describes the time evolution of probabilities for obtaining different possible states of the system, given an initial state. Typical mathematical treatments of the Ehrenfest model were developed in [2-4]. Since then the model has appeared in a multitude of physical and mathematical contexts involving stochastic death and birth processes [5-10]. For example, one of the important physical problems that could be described by the Ehrenfest model is related to fragmentation and degradation of polymer-like structures with multiple bonds and the possibility of stochastic scission (evaporation) and restoration (condensation) of bonds. This includes kinetics of thermal and radiative degradation and restoration of double-stranded polymers [11-13], evolution of fractals and polymer multi-chains [14,15], biological macromolecules [16,17], kinetics of self-arrangement and degradation of reversible polymer networks [18,19], polymerization and aggregation of clusters (including sol-gel transitions) [20-28], and thermal fragmentation of nano-particle clusters due to stochastic evaporation of bonding molecules [29-32].

In particular, our previous papers [29-32] were focused onto the detailed experimental and theoretical investigation of the fragmentation and degradation of airborne nano-particle clusters. These clusters were formed by primary particles held together by means of volatile molecules representing multiple bonds between them [29-31]. Stochastic evaporation of these volatile molecules is equivalent to random scission (degradation) of these bonds, with cluster fragmentation occurring when there are no bonding molecules left between the primary particles [29,31]. Two different methods of mathematical analysis of thermal degradation in such nano-clusters (and other polymer-like systems with multiple bonds) were proposed and developed, based on the graph representation of stochastic

evaporation of multiple bonds [31], and direct statistical analysis of Poisson processes of bond evaporation [32]. However, the presented analysis [31,32] did not involve the possibility of bond restoration, e.g., the possibility of condensation of bonding molecules in airborne nano-clusters. At the same time, such stochastic condensation or restoration processes are common in realistic situations involving evolution of airborne nano-clusters, self-arrangement and degradation of reversible polymer networks [18,19], degradation and restoration of biological macromolecules [16,17], etc.

The consideration of stochastic evaporation and condensation processes (representing death and birth processes) for multiple bonds in polymer-like structures, e.g., airborne nano-clusters with volatile bonding molecules, can be conducted using the Ehrenfest model. However, there are significant differences with specific applications of this model to particular physical systems. For example, for reversible polymer networks with quadruple hydrogen bonds between the primary elements of the network [18,19], this will be the standard Ehrenfest model with the maximum number of bonds between the elements equal to 4. The network will then evolve in time with the possibility of total fragmentation into separate primary elements (when all the hydrogen bonds are degraded and links between the primary elements are broken) and complete restoration when all the links between the primary elements are restored (having at least one bond in each). At the same time, dealing with degradation of airborne nano-clusters at low concentrations [29,30] should be treated differently. This is because, once fragmentation of a cluster has occurred, the probability of its restoration becomes negligible, because of typically much lower coagulation rates [33-35]. Therefore, the fragmented state with zero bonds in a link between the primary particles (the zero state) should be regarded as an absorbing state in the Ehrenfest model, and fragmentation of a link can only occur once (which corresponds to the first passage to the zero state in the Ehrenfest model). This situation will also be typical for the consideration of any other polymer-like systems with small coagulation or polymerization rates. The analysis

in this case is thus reduced to the determination of the first passage time for the system to the zero state in the standard Ehrenfest model.

The theory of hitting times that determines the probability density distribution for the random variable  $T$  (which can be regarded as the time that it takes for the link to fragment, i.e., to hit the zero absorbing state) has been well developed for the Ehrenfest model [4,6,36,37]. However, this analysis has so far been conducted primarily using the numerical approaches. There have only been a few analytical or semi-analytical attempts undertaken so far.

For example, a significant effort in developing analytical tools for the analysis of the two-urn and multi-urn Ehrenfest models have been undertaken by Karlin and McGregor [4], who derived explicit equations for the transition probabilities between an initial  $i$ -th state and a final  $j$ -th state in terms of generating functions and explicitly in terms Krawtchouk (orthogonal) polynomials. They also investigated the asymptotic behavior of the system at large moments of time and large values of the maximal number of births [4]. However, this theory is not applicable for the analysis of aggregate degradation and fragmentation, because it does not consider the absorbing (zero) state. In the earlier paper by Bellman and Harris [6], the authors derived the equations for the Laplace transforms of the probabilities to find the system in different states. This approach could potentially be used for the determination of the first passage time to the zero absorbing state during the degradation and fragmentation processes in a nano-particle aggregate. However, the required inverse Laplace transform is difficult to perform other than by means of numerical analysis.

Several other attempts of the explicit analytical analysis of the theory of hitting times in the Ehrenfest model have recently been undertaken by Di Crescenzo and colleagues [7-10,39]. For example, the evolution of the system and the first passage time to the central state with  $K/2$  number of births (where  $K$  is the maximal possible number of births in the link) has been analyzed in [9,10]. However, the obtained explicit equations are applicable for

the case with equal rates for the birth and death processes and large even values of  $K$ , which do not seem to be reasonable assumptions for the consideration of degradation and fragmentation of particle aggregates and other polymer-like systems.

Therefore, the aim of this paper is to develop a new approach for the explicit analytical analysis of the processes of degradation and fragmentation in the polymer-like systems with multiple bonds and the possibility of stochastic evaporation and restoration of bonds. Here, we will assume that the rates of bond degradation and restoration (death and birth processes) are independent of the number of bonds in a link, i.e. possible interaction between multiple bonds in a link [31,32] is neglected. The developed approach will be based on the direct solution of the Master equation, i.e. the Kolmogorov forward system. An exact analytical solution for the first time passage to the zero (absorbing) state in the Ehrenfest model will be derived. Detailed analysis of the effect of different evaporation and condensation rates on the evolution of the aggregates will be conducted, demonstrating high sensitivity of the kinetic fragmentation processes to small variations in the condensation rate.

## **2. Probability density for the first passage time**

Consider an aggregate formed by coagulated monomers (primary particles) with  $K$  being the maximum number of bonds (e.g., bonding molecules) in a link between any two monomers. That is, for any link between two monomers in the aggregate, there are  $K$  bonding sites ( $K$  possible birth processes in the Ehrenfest model). It is assumed that evaporation of each of the existing bonds in a link occurs independently of the other bonds at a rate  $\lambda_e > 0$ , and condensation (restoration) of bonds occurs at a rate  $\lambda_c > 0$  for each vacant site. In particular, this means that additional interaction between different bonds in a link [31,32] is neglected. If  $X(t)$  is the number of bonds at time  $t$ , then  $(X(t), t \geq 0)$  is assumed to be a continuous-time Markov chain taking values in  $S = \{0, 1, \dots, K\}$  with transition rates

$q_{n,n+1} = \lambda_c(K - n)$  and  $q_{n,n-1} = \lambda_e n$  for  $n = 1, 2, 3, \dots, K$ . However,  $q_{0n} = \delta_{0n}$ , because we assume that once there are no bonds in a link between two primary particles, these particles dissociate (fragment) and re-bonding does not occur because of the assumed negligible coagulation rates [33-35]. Thus we have an absorbing zero state. We are interested in the time  $T$  that it takes for the particles to fragment starting from an initial state with  $X(0) = N \leq K$  bonds.  $T$  is therefore the first passage time to state 0 in the standard Ehrenfest model.

Because degradation and condensation processes in the aggregate under the considered conditions occur independently in different links, fragmentation of each of such links can be considered separately. In this case, the Ehrenfest model with the absorbing zero state for one link gives the following rate equations for the probabilities of finding the considered link in the states with different numbers of bonds (the Kolmogorov forward scheme [42]):

$$\begin{aligned} \frac{dP_0}{dt} &= \lambda_e P_1, & \frac{dP_1}{dt} &= -[\lambda_c(K-1) + \lambda_e]P_1 + 2\lambda_e P_2, \\ \frac{dP_i}{dt} &= \lambda_c[K - (i-1)]P_{i-1} - [\lambda_c(K-i) + \lambda_e i]P_i + \lambda_e(i+1)P_{i+1}, & (i = 2, 3, \dots, K-1), & (1) \\ \frac{dP_K}{dt} &= \lambda_c P_{K-1} - \lambda_e K P_K, \end{aligned}$$

where  $P_0(t) \equiv P_{N0}(t) = P[X(t) = 0 | X(0) = N]$  is the probability to find the considered link with the initial number of bonds  $X(0) = N$  in the state 0 with the number of bonds  $X(t) = 0$  (fragmented state) at an arbitrary moment of time  $t$  (with the initial condition  $P_0(0) = \delta_{N0}$ ), and  $P_i(t) \equiv P_{Ni}(t) = P[X(t) = i | X(0) = N]$  is the probability for the transition from the initial state with  $X(0) = N$  bonds in a link to the state with  $X(t) = i$  bonds in the same link within the time interval  $t$ .

In terms of the probability generating function  $H(z, t) = \sum_{i=0}^K P_i(t) z^i$ , Eqs. (1) can be summarized into a single partial differential equation

$$\frac{\partial H}{\partial t} + (\lambda_c z + \lambda_e)(z-1) \frac{\partial H}{\partial z} - \lambda_c K(z-1)H = -\lambda_c K(z-1)P_0(t) \quad (2)$$

with the boundary conditions  $H(0,t) = P_0(t)$ ,  $H(1,t) = 1$ , and  $H(z,0) = z^N$ . In order to make the boundary conditions homogeneous, it will be convenient to work in terms of  $G = H + 1$ :

$$\frac{\partial G}{\partial t} + (\lambda_c z + \lambda_e)(z-1) \frac{\partial G}{\partial z} - \lambda_c K(z-1)G = -\lambda_c K(z-1)Q(t), \quad (3)$$

where  $Q(t) = P_0(t) - 1$ , with the boundary conditions  $G(0,t) = Q(t)$ ,  $G(1,t) = 0$ , and

$G(z,0) = z^N - 1$ . Our aim is to evaluate  $Q(t)$  and thus determine  $P_0(t) = P[X(t) = 0 | X(0) = N]$ , which is the probability for the considered link with the initial number of bonds  $N$  at  $t = 0$  to reach the fragmented state before the moment of time  $t > 0$ .

Using the procedure of separation of variables, the solution to Eq. (3) is sought in the form

$$G(z,t) = \sum_{i=1}^K A_i(t) (\lambda_c z + \lambda_e)^{K-i} (z-1)^i, \quad (4)$$

where functions  $A_i(t)$  do not depend on  $z$ . Notice that  $G$  given by (4) satisfies the boundary condition  $G(1,t) = 0$ . Substituting (4) into (3) we obtain

$$\sum_{i=1}^K [A_i'(t) + iA_i(t)(\lambda_c + \lambda_e)] (\lambda_c z + \lambda_e)^{K-i} (z-1)^i = -\lambda_c K(z-1)Q(t).$$

Thus, if we can find constants  $C_i$  such that  $\sum_{i=1}^K C_i (\lambda_c z + \lambda_e)^{K-i} (z-1)^i = -\lambda_c K(z-1)Q(t)$ , then

$$A_i'(t) + iA_i(t)(\lambda_c + \lambda_e) = C_i Q(t), \quad (i = 1, 2, 3, \dots, K). \quad (5)$$

The following lemma shows that this is possible, and at the same time establishes the existence of functions  $A_i(t)$  satisfying (5).

**Lemma.** Let  $K \geq 1$  and  $f$  be a polynomial with real coefficients that satisfies the condition  $f(1) = 0$  and has degree no greater than  $K$ . Then,  $\forall a, b > 0, \exists$  unique set of constants  $B_i$  such that

$$f(z) = \sum_{i=1}^K B_i (az + b)^{K-i} (z-1)^i \quad (6)$$

and  $B_i = g_i(1)$ , where

$$g_i(z) = \frac{1}{i!} \frac{d^{i-1}}{dz^{i-1}} (az+b)^{i-K} \left( \frac{d}{dz} - \frac{aK}{az+b} \right) f(z). \quad (7)$$

To prove this lemma, we first observe that

$$(az+b)^{i-K} \left( \frac{d}{dz} - \frac{aK}{az+b} \right) f(z) = \sum_{j=1}^K B_j (a+b)^j (az+b)^{i-j-1} (z-1)^{j-1}.$$

Then, differentiation  $i-1$  times by the Leibniz theorem gives,

$$\begin{aligned} g_i(z) &= \frac{1}{i!} \frac{d^{i-1}}{dz^{i-1}} (az+b)^{i-K} \left( \frac{d}{dz} - \frac{aK}{az+b} \right) f(z) \\ &= \sum_{k=0}^{i-1} \sum_{j=1}^K B_j \frac{j}{i!} (a+b) \binom{i-1}{k} \frac{d^{i-k-1}}{dz^{i-k-1}} (az+b)^{i-j-1} \frac{d^k}{dz^k} (z-1)^{j-1}. \end{aligned}$$

Because  $(d^k/dz^k)(z-1)^{j-1}|_{z=1} = (j-1)! \delta_{k,j-1}$  for  $j \geq 1$ , and

$$[(d^{i-j}/dz^{i-j})(az+b)^{i-j-1}]_{z=1} = (a+b)^{-1} \delta_{ij},$$

we get

$$g_i(1) = \sum_{j=1}^i B_j \frac{j!}{i!} (a+b) \binom{i-1}{j-1} \frac{d^{i-j}}{dz^{i-j}} (az+b)^{i-j-1} \Big|_{z=1} = B_i,$$

This proves the Lemma.

Using this lemma, we can evaluate  $C_i$  in Eq. (5) explicitly. Putting  $a = \lambda_c$  and  $b = \lambda_e$ , setting  $f(z) = -\lambda_c K(z-1)$ , and evaluating the derivatives in Eq.(7), we find that

$$C_i = -\lambda_c K \binom{K-1}{i-1} \frac{(-\lambda_c)^{i-1}}{(\lambda_c + \lambda_e)^{K-1}} \quad (i = 1, 2, \dots, K) \quad (8)$$

Taking the Laplace transformation of Eq. (5), we find:

$$s\tilde{A}_i(s) - A_i(0) + i(\lambda_c + \lambda_e)\tilde{A}_i(s) = C_i\tilde{Q}(s),$$

which gives

$$\tilde{A}_i(s) = \frac{C_i\tilde{Q}(s) + A_i(0)}{s + i(\lambda_c + \lambda_e)},$$

where  $\tilde{Q}(s)$  and  $\tilde{A}_i(s)$  are the Laplace transforms of the functions  $Q(t)$  and  $A_i(t)$ ,

respectively.

Since one of the boundary conditions requires that  $G(0,t) = Q(t)$ , Eq. (4) yields

$\tilde{Q}(s) = \sum_{i=1}^K \tilde{A}_i(s) \lambda_e^{K-i} (-1)^i$ . Therefore,

$$\tilde{Q}(s) = \left( 1 - \frac{\sum_{i=1}^K C_i (-1)^i \lambda_e^{K-i}}{\sum_{i=1}^K s + i(\lambda_c + \lambda_e)} \right)^{-1} \frac{\sum_{i=1}^K A_i(0) (-1)^i \lambda_e^{K-i}}{\sum_{i=1}^K s + i(\lambda_c + \lambda_e)} \quad (9)$$

The third boundary condition for Eq. (3) [ $G(z,0) = z^N - 1$ ] entails

$z^N - 1 = \sum_{i=1}^K A_i(0) (\lambda_c z + \lambda_e)^{K-i} (z-1)^i$ , and the constants  $A_i(0)$  can be determined from the

above Lemma. Putting  $a = \lambda_c$ ,  $b = \lambda_e$ , and setting  $f(z) = z^N - 1$ , we find:

$$A_i(0) = \frac{\sum_{j=1}^{\min(i,N)} \binom{N}{j} \binom{K-j}{i-j} \frac{(-\lambda_c)^{i-j}}{(\lambda_c + \lambda_e)^{K-j}}}{\sum_{j=1}^{\min(i,N)} \binom{N}{j} \binom{K-j}{i-j} \frac{(-\lambda_c)^{i-j}}{(\lambda_c + \lambda_e)^{K-j}}} \quad (i=1,2,\dots,K) \quad (10)$$

We therefore have an explicit expression for  $\tilde{Q}(s)$  – see Eq. (9). Thus inverse Laplace

transformation of Eq. (9) will give  $Q(t)$  and thus the sought probability  $P_0(t) = P[X(t) =$

$0|X(0) = N]$  (see Eq. (3)).

To simplify the calculations the change of variable  $s \rightarrow s/(\lambda_c + \lambda_e)$  makes the calculations more manageable. Using the new variable, if  $\tilde{R}(s) = (\lambda_c + \lambda_e) \tilde{Q}[(\lambda_c + \lambda_e)s]$ ,

then  $\tilde{R}(s)$  is the Laplace transform of the function  $R(t) = Q[t/(\lambda_c + \lambda_e)]$ . Introducing the

notations  $g = \lambda_e/(\lambda_c + \lambda_e)$  and  $q = \lambda_c/\lambda_e$ , and substituting Eqs. (8) and (10) into Eq. (9), we

find:  $\tilde{R}(s) = \sum_{i=1}^K a_i \tilde{U}_i(s)$ , where

$$a_i = g^K q^i \sum_{j=1}^{\min(i,N)} \binom{N}{j} \binom{K-j}{i-j} (-1)^j (1-\rho)^{-j} \quad (11)$$

and

$$\tilde{U}_i(s) = \frac{1}{(s+i) \left( 1 - g^K \sum_{j=1}^K \binom{K}{j} q^i \frac{j}{s+j} \right)}. \quad (12)$$

Note that there is no singularity in  $\tilde{U}_i(s)$  at  $s = -i$ . This is because of the term  $(s+i)$

in the denominator of the sum (when  $j = i$ ). At the same time, it is possible to see that the function  $\tilde{U}_i(s)$  has  $K$  first-order singularities at  $s = r_1, \dots, r_K$ , such that  $-i < r_i < -i + 1$ , where  $i = 1, 2, \dots, K$ . Indeed, the expression in the denominator in Eq. (12) can be reduced as

$$1 - g^K \sum_{j=1}^K \binom{K}{j} q^j \left( \frac{j}{s+j} \right) = g^K \sum_{j=0}^K \binom{K}{j} q^j \left( \frac{s}{s+j} \right) = \frac{\tilde{\phi}(s)}{\prod_{k=1}^K (s+k)},$$

where

$$\tilde{\phi}(s) = g^K \sum_{j=0}^K \binom{K}{j} q^j \prod_{\substack{k=0 \\ k \neq j}}^K (s+k)$$

is the polynomial of the order of  $K$ . Its  $K$  roots,  $s = r_1, \dots, r_K$ , lie within the intervals  $-i < r_i < -i + 1$ , because  $\tilde{\phi}(-j) = K! g^K (-q)^j$  (with  $j = 0, 1, \dots, K$ ) are  $K + 1$  non-zero values of  $\tilde{\phi}$  that alternate in sign when  $j$  is changed by an integer. Therefore, we can write

$\tilde{\phi}(s) = \prod_{m=1}^K (s - r_m)$ , and  $\tilde{U}_i(s) = \tilde{V}_i(s) / \prod_{m=1}^K (s - r_m)$ , where  $\tilde{V}_i(s) = \prod_{k=1, k \neq i}^K (s + k)$  is the polynomial of the order of  $K - 1$ , and it is non-zero at any of values of  $s = r_1, \dots, r_K$  (which means that  $r_1, \dots, r_K$  are all the singularities of the Laplace transform  $\tilde{U}_i(s)$ ). Using partial fractions we get

$$\tilde{U}_i(s) = \sum_{m=1}^K \left( \frac{1}{s - r_m} \right) \frac{V_i(r_m)}{\prod_{k \neq m} (r_m - r_k)}.$$

In this case, the inverse Laplace transform of and so the inversion of  $\tilde{R}(s)$  becomes straightforward:

$$R(t) = \sum_{m=1}^K e^{r_m t} \sum_{i=1}^K a_i \frac{V_i(r_m)}{\prod_{k \neq m} (r_m - r_k)} = \sum_{m=1}^K e^{r_m t} \frac{1}{\prod_{k \neq m} (r_m - r_k)} \sum_{i=1}^K a_i \prod_{k \neq i} (r_m + k).$$

(Both products in this equation are taken over  $k = 1, 2, \dots, K$ .) Finally, because  $Q(t) = R[(\lambda_c + \lambda_e)t]$ , we obtain

$$P_0(t) = 1 + Q(t) = 1 + \sum_{m=1}^K \frac{\exp[r_m(\lambda_c + \lambda_e)t]}{\prod_{k \neq m} (r_m - r_k)} \sum_{i=1}^K a_i \prod_{k \neq i} (r_m + k). \quad (13)$$

Substituting here Eq. (11), introducing the notations  $s_m = -r_m$ , so that  $s_m > 0$  for all values of  $m$ , and differentiating with respect to  $t$ , we arrive at the main result that is formulated as the following theorem.

**Theorem:** The probability density function  $f(t)$  of the first passage time to 0 state (fragmented link) starting from the state with  $N$  bonds in the link is given by

$$f(t) = \sum_{m=1}^K \frac{s_m(\lambda_c + \lambda_e) \exp[-s_m(\lambda_c + \lambda_e)t]}{\prod_{k \neq m} (s_k - s_m)} \sum_{i=1}^K g^{K-i} \prod_{k \neq i} (k - s_m) \times \\ \times \sum_{j=1}^{\min(i, N)} \binom{N}{j} \binom{K-j}{i-j} (-1)^{j-1} (1-g)^{i-j}, \quad (14)$$

where  $\rho = \lambda_e/(\lambda_c + \lambda_e)$ , and  $s_1, \dots, s_K$  are the roots of the polynomial

$$\sum_{j=0}^K \binom{K}{j} \left( \frac{\lambda_c}{\lambda_e} \right)^j \prod_{\substack{k=0 \\ k \neq j}}^K (s - k) = 0 \quad (15)$$

arranged so that  $m-1 < s_m < m$  for  $m = 1, 2, \dots, K$ .

In particular, this Theorem provides an explicit solution to the kinetic problem of fragmentation of aggregates with multiple bonds with the possibility of their stochastic degradation and restoration, and at condition of negligible coagulation rate. At the same time, this Theorem is applicable for any other types of stochastic death and birth processes described by the Ehrenfest model with the absorbing zero state. It is also important to note that the above analytical consideration is only applicable if the additional interaction between multiple bonds in a link between the primary elements can be neglected, which means that death and birth processes (degradation and restoration of bonds) occur at rates that are independent of the number of bonds in a link (see the beginning of this section).

Notice also that in the limit  $\lambda_c \rightarrow 0$ , we have  $r_m \rightarrow m$  and  $P_0(t) \rightarrow (1 - e^{-\lambda_e t})^N$ . This can also be obtained from Eq. (13) as an exact equation  $P_0(t) = (1 - e^{-\lambda_e t})^N$  if  $\lambda_c = 0$ . This

equation is quite obvious because, when  $\lambda_c = 0$ , the  $N$  bonds evaporate independently at the same rate  $\lambda_e$ , and each bond lasts for an exponentially distributed amount of time. Thus the above equation for  $P_0(t)$  is simply the product of  $N$  independent (and equal in the case of non-interacting bonds [31,32]) probabilities for evaporation of all  $N$  bonds from the link by the moment of time  $t$ . This is in obvious agreement with the previous results obtained in [32].

### 3. Numerical results and discussion

In this section, the above Theorem is used for the analysis of thermal fragmentation of polymer-like systems with the absorbing zero states and stochastic evaporation and condensation of bonds. This is done on the example of airborne nano-particle aggregates resulting from combustion emissions [29-31]. For this purpose, the Theorem from section 2 is combined with the approach developed in [32] for the analysis of thermal fragmentation (without bond restoration) in a ring or chain aggregates,  $\Psi$  and  $\Psi'$  (Fig. 1), with multiple bonds (e.g., bonding molecules between the primary particles in combustion nano-aggregates [29-31]). Paper [32] determined the expectation numbers  $Q_r(\Psi, t)$  for  $r$ -mers (aggregates with  $r$  primary particles) at an arbitrary moment of time  $t$ , given  $M_0$  identical  $n$ -mer aggregates in the same initial state at  $t = 0$  ( $r \leq n$ ). The state of the initial identical  $n$ -mer aggregates is determined by the initial number of links ( $n + 1$  for a ring and  $n$  for a chain) and the initial numbers of bonds  $i_\alpha, i_\beta, i_\gamma, \dots$  in each of these links (Fig. 1).

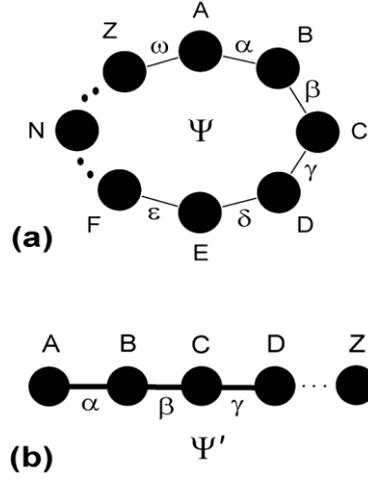


Figure 1. The diagrams of a ring  $n$ -mer  $\Psi$  (a) and a chain  $n$ -mer  $\Psi'$  (b) with  $n$  primary particles (monomers) denoted by the black circles; the links in the aggregates are identified by the Greek letters ( $\alpha, \beta, \gamma, \dots$ ) with the initial number of bonds  $i_\alpha, i_\beta, i_\gamma, \dots$ , respectively.

For example, for a ring cluster  $\Psi$  (Fig. 1a) without bond restoration (condensation), we have [32]:

$$Q_r(\Psi, t) = \begin{cases} M_0 n \langle 1 | p [D_\Psi(t) p]^{n-1} | (n-1) \Psi(t) + 1 \rangle, & \text{for } r = n; \\ M_0 \langle \Psi(t) | p [D_\Psi(t) p]^{r-1} | \Psi(t) \rangle, & \text{for } r < n; \end{cases} \quad (16)$$

where  $|\Psi(t)\rangle$  and  $\langle \Psi(t)|$  are the column and row  $n$ -dimensional fragmentation state vectors [32]:

$$|\Psi(t)\rangle = \begin{pmatrix} P_{f_{i_\alpha}}(t) \\ P_{f_{i_\beta}}(t) \\ \vdots \\ P_{f_{i_\omega}}(t) \end{pmatrix}; \quad \langle \Psi(t)| = \left( P_{f_{i_\alpha}}(t) \quad P_{f_{i_\beta}}(t) \quad \cdots \quad P_{f_{i_\omega}}(t) \right), \quad (17)$$

whose components are the probabilities for the respective link to fragment within the time interval  $t$ ,

$$D_\Psi(t) = \begin{pmatrix} P_{l_{i_\alpha}}(t) & & & 0 \\ & P_{l_{i_\beta}}(t) & & \\ & & \ddots & \\ 0 & & & P_{l_{i_\omega}}(t) \end{pmatrix}; \quad p = \begin{pmatrix} 0 & \cdots & 0 & 1 \\ 1 & 0 & \cdots & 0 \\ 0 & \ddots & \ddots & \vdots \\ \vdots & \ddots & \ddots & \ddots \\ 0 & \cdots & 0 & 1 & 0 \end{pmatrix}, \quad (18)$$

$P_{l_{i_\alpha}}(t) = 1 - P_{f_{i_\alpha}}(t)$  are the probabilities for the links in the ring not to fragment within the time interval  $t$ ,  $\langle 1|$  and  $|1\rangle$  are the row and column  $n$ -dimensional vectors with all their components equal to 1, and

$$|(n-1)\Psi(t)+1\rangle \equiv (n-1)|\Psi(t)\rangle + |1\rangle. \quad (19)$$

Similar equations can be written for a chain aggregate with multiple bonds [32].

As indicated above, Eqs. (16) – (19) have been derived [32] for the situation where restoration of bonds (e.g., condensation of bonding molecules) can be neglected. Nevertheless, because Eqs. (16) – (19) contain only probabilities for each link in the cluster to fragment, it is clear that these equations do not depend on whether we take the possibility of bond condensation into account or not. The only parameters that must be affected by bond restoration are the fragmentation probabilities themselves, and they are determined by the Theorem in Section 2. Therefore, Eqs. (16) – (19) are also applicable in the case with bond restoration (condensation) if we assume that the respective probabilities in Eqs. (17) and (18) are determined by Eq. (13) which, for example, for the link  $\alpha$  can be written as:

$$P_{f_{i_\alpha}}(t) \equiv P_0(t; i_\alpha, \lambda_c, \lambda_e, K) = 1 + \sum_{m=1}^K \frac{\exp[-s_m(\lambda_c + \lambda_e)t]}{\prod_{k \neq m} (s_k - s_m)} \sum_{j=1}^K a_j \prod_{k \neq j} (k - s_m). \quad (13a)$$

Recall that  $a_j$  are determined by Eq. (11) where instead of  $N$  we use the respective initial number of bonds in any particular link (e.g.,  $i_\alpha$  for the link  $\alpha$  – see Fig. 1a), and  $K$  is the maximum possible number of bonds (i.e., the number of bond sites) in a link:  $K \geq i_\alpha$ . This means that the condensation process has the upper limit on the number of bonds that can condense into a single link, and this limit is  $K$ . Here,  $s_1, s_2, \dots, s_K$  are the roots of the polynomial (15).

To demonstrate the effect of bond restoration (condensation of bonding molecules [29-31]) on fragmentation kinetics of aggregates with multiple bonds, consider fragmentation of identical 2-mers with multiple bonds. The probability of fragmentation of

the initial 2-mer within a period of time  $t$  is given by Eq. (13a). Therefore, the probability that the initial 2-mer does not fragment is  $1 - P_0(t; i_\alpha, \lambda_c, \lambda_e, K)$ . Then the period of time  $T_{90}$  within which the probability that the initial 2-mer does not fragment is reduced to 0.1 is the time interval for 90% fragmentation of the initial 2-mers. Fig. 2 presents the typical dependencies of  $T_{90}$  normalized to the characteristic time of evaporation of one bond  $\lambda_e^{-1}$  on ratio of the rates of condensation  $\lambda_c$  and evaporation  $\lambda_e$  for different numbers  $K$  of bonding sites between the primary particles and different initial numbers of bonds  $i_\alpha \leq K$  (shown by numbers next to the respective curves in Fig. 2).

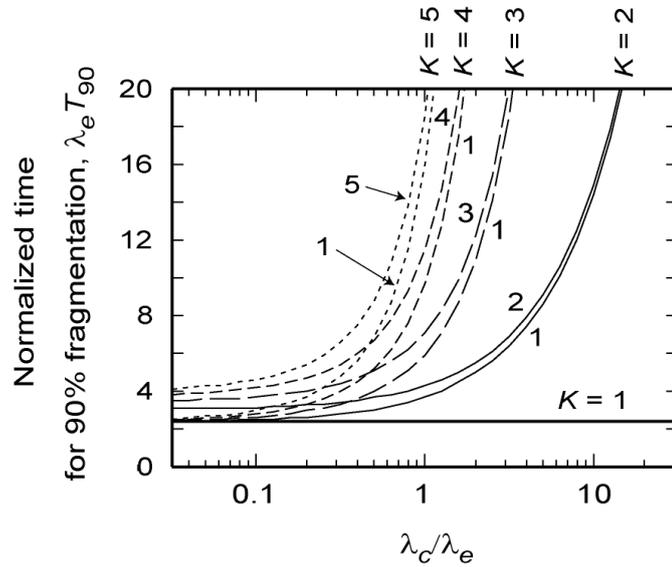


Figure 2. The dependencies of time  $T_{90}$  for 90% fragmentation of the initial 2-mer clusters with multiple bonds on ratio  $\lambda_c/\lambda_e$  of condensation and evaporation rates at different numbers  $K$  of bonding sites (which are also the maximum possible numbers of bonds) in the 2-mers. All the time intervals are normalized to the characteristic time  $\lambda_e^{-1}$  of evaporation of a single bond. Different initial numbers of bonds are indicated by integers ( $1 \leq i_\alpha \leq K$ ) next to the respective curves. The lowest straight line corresponds to  $K = i_\alpha = 1$ .

In particular, it can be seen that all the curves corresponding to  $i_\alpha = 1$  asymptotically tend to the same value of  $T_{90}$  at small condensation rates (when  $\lambda_c/\lambda_e \rightarrow 0$ ) – Fig. 2. This is expected, because at small values of  $\lambda_c$  condensation does not play a significant role, and if

the initial number of bonds in a link is equal to 1, fragmentation of this link occurs irrespectively of the maximal possible number  $K$  of bonds (bonding sites) in the link. However, if the initial number of bonds in the 2-mers are different (the curves indicated by numbers 2, 3, 4, and 5 in Fig. 2), then the fragmentation time appears to be different even if condensation rate is negligible (which is in agreement with the previous results of [31,32]).

Expectedly, increasing condensation rate  $\lambda_c$  results in a substantial increase of the typical fragmentation times. As can be seen from Fig. 2, condensation rate can only be neglected when it is more than  $\sim 5$  times less than the evaporation rate. At larger condensation rates, restoration of bonds noticeably increases fragmentation times. As a result, bond restoration may play a significant role in the evolution of airborne combustion aerosol clusters near the source, especially if the saturated pressure of the bonding volatile molecules is relatively high. On the other hand, as shown in [29-31], the typical evaporation time for bonding molecules in combustion aerosol clusters is  $\sim 10$  s with the typical binding energy of  $\sim 10^{-19}$  J [31], which gives  $\lambda_e \sim 0.1$  s $^{-1}$ . Such low evaporation rates mean low pressures of the saturated vapor of the volatile compounds responsible for bonding in aerosol clusters, which also mean low probability of condensation (restoration) of bonds. Therefore, more experimental evidence is needed, together with their comparison with the theoretical results of this paper, to determine whether condensation of bonding molecules (restoration of bonds) plays a significant role in the evolution of combustion aerosol clusters.

It can also be seen that increasing number of bonding sites ( $K$ ) and/or bonds ( $i_\alpha$ ) between the primary particles in the aggregate also results in a significant increase of fragmentation time (Fig. 2). This is because increasing  $K$  leads to increasing probability for condensation (restoration) of bonds and thus decreasing probability of fragmentation. Increasing  $i_\alpha$  results in increasing time that it takes for all these bonds to evaporate and fragmentation to occur. Nevertheless, because the probability of fragmentation is non-zero for any number of bonds between the primary particles, and coagulation is neglected (we

have zero absorbing state), all the initial aggregates eventually experience fragmentation, and the effect of condensation is only in increasing fragmentation time, rather than preventing it altogether – eventually all the initial aggregates will fragment.

Further demonstration of the impact of bond restoration on the evolution of particle numbers during the fragmentation kinetics is illustrated on the example of a ring aggregate with four links between four primary particles with the initial bond numbers:  $i_\alpha = 1$ ,  $i_\beta = 2$ ,  $i_\gamma = 1$ , and  $i_\delta = 2$  (the 1-2-1-2 cluster [32]). Fig. 3 shows the evolution of normalized  $r$ -mer numbers resulting from degradation and fragmentation of the initial 1-2-1-2 clusters. The normalization was done with respect to the initial number of the clusters at  $t = 0$ .

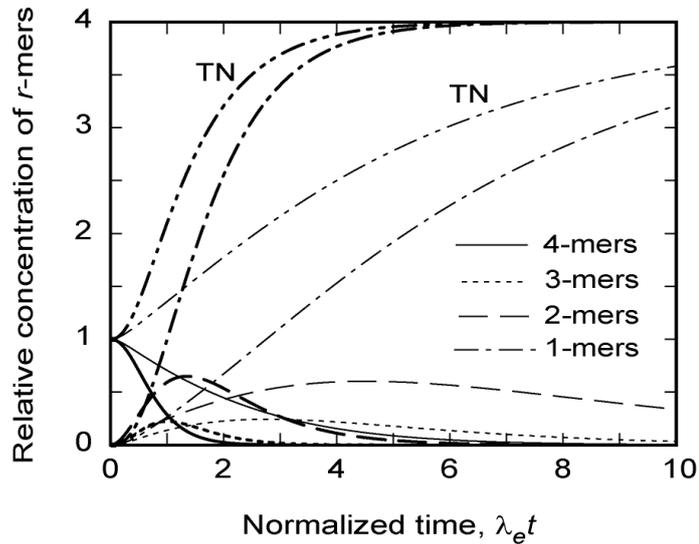


Figure 3. The time-dependent relative (normalized to the initial number of aggregates) numbers of different  $r$ -mers resulting from fragmentation of the initial ring 1-2-1-2 aggregates. The thick curves correspond to thermal fragmentation of the initial ring 1-2-1-2 aggregates with no bond restoration (condensation). The thin curves correspond to the evolution in the presence of bond restoration with  $\lambda_c/\lambda_e = 1$  and the number of bond sites  $K = 4$  in each of the four links in the initial ring aggregate. The TN curves represent the evolution of the normalized total number of all the  $r$ -mer aggregates.

As can clearly be seen from Fig. 3, restoration of bonds may lead to a substantial modification of the evolution pattern for thermal fragmentation of nano-clusters. It can also

be seen that restoration (condensation) of bonds may lead to a significant accumulation of aggregates in the intermediate fragmentation modes. For example, the numbers of the 2-mers and 3-mers at relatively large evolution times is drastically increased in the presence of bond restoration (see dotted and dashed curves in Fig. 3). At the same time, the typical numbers of the primary particles are, on the contrary, may be significantly reduced by bond restoration (compare the thick and thin dash-and-dot curves in Fig. 3).

Interestingly, Eq. (13a) allows significant simplification in the asymptotic regime at large  $t$  and relatively large numbers  $K$ . Eq. (13a) contains  $K$  exponential terms with positive roots  $s_m$  of the polynomial (15). Therefore, the term with the smallest root (which is always  $s_1$ , according to Eq. (15)) will be dominant in the sum in Eq. (13a), and all other terms can be neglected at sufficiently large values of  $t$ . Assuming that  $s_1$  is small (i.e.,  $s_1 \ll 1$  – the conditions for that will be discussed below), we can write:

$$\prod_{k \neq m} (s_k - s_1) = \prod_{k \neq m} s_k + O(s_1), \quad \prod_{k \neq j} (k - s_1) = \frac{K!}{j} + O(s_1).$$

Using these equations, and neglecting the terms with all  $s_m$  except for the one with  $s_1$ , Eq. (13a) can be reduced as (for  $s_1 \ll 1$ ):

$$P_{f_{i_\alpha}}(t) \equiv P_0(t; i_\alpha, \lambda_c, \lambda_e, K) \approx 1 + \frac{\exp[-s_1(\lambda_c + \lambda_e)t]}{\prod_{k \neq 1} s_k} \sum_{j=1}^K a_j \frac{K!}{j}$$

Using Eq. (15), it can be shown that the product of all the roots  $\prod_k s_k = K!(1 + \lambda_c / \lambda_e)^{-K}$ .

Therefore,

$$P_{f_{i_\alpha}}(t) \approx 1 + (1 + \lambda_c / \lambda_e)^K s_1 \exp[-s_1(\lambda_c + \lambda_e)t] \sum_{j=1}^K \frac{a_j}{j} \quad (20)$$

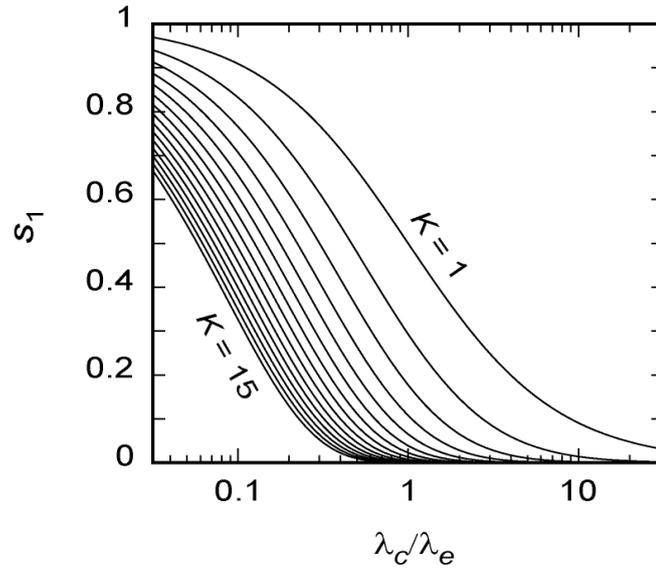


Figure 4. The dependencies of the smallest root  $s_1$  of the polynomial (15) on ratio of the condensation rate and evaporation rate. The 15 different curves correspond to 15 consecutive numbers  $K$  of bond sites in the considered link.

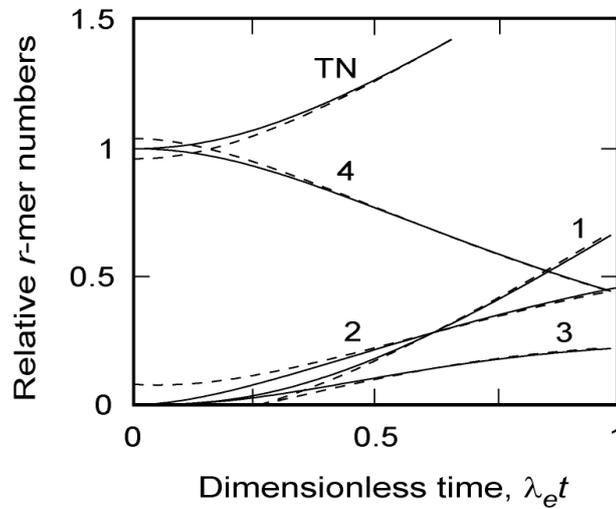


Figure 5. The comparison of the evolutionary curves for time-dependent  $r$ -mers numbers obtained using the full analytical solution Eq. (13a) (solid curves), and its approximate version in the form of Eq. (20) (dashed curves) for thermal fragmentation of the 1-2-1-2 ring aggregates at  $\lambda_c/\lambda_e = 1.1$  and  $K = 2$  (the solid curves are the same as thin curves in Fig. 3 in the presence of bond condensation).

Eq. (20) suggests that the root  $s_1$  determines the rate of changing probability of fragmentation of the considered link. The typical dependencies of  $s_1$  of the polynomial (15)

on ratio  $\lambda_c/\lambda_e$  are shown in Fig. 4 for different numbers of bonding sites  $K$  in the link. In particular, this figure demonstrates that increasing  $K$  results in decreasing  $s_1$ , i.e., in improving applicability of the asymptotic equation (20). Similar situation occurs when the ratio  $\lambda_c/\lambda_e$  is increased. For example, as can be seen from Fig. 4, Eq. (20) is approximately applicable at all values of  $K$ , if the condensation rate is larger than the evaporation rate.

Importantly, the actual applicability of Eq. (20) extends beyond the asymptotic behavior of the fragmentation probability at large values of  $t$ . For example, Fig. 5 presents the comparison between the evolutionary curves for time-dependent numbers of the  $r$ -mers resulting from fragmentation of the initial 1-2-1-2 clusters, which were obtained using the full analytical solution for fragmentation probability (Eq. (13a)) and using the asymptotic equation (20). Note that both the ratio  $\lambda_c/\lambda_e = 1.1$  and  $K = 2$  are not particularly large – yet the obtained dependencies (dashed and solid curves in Fig. 5) are in very good agreement. Thus the asymptotic solution (Eq. (20)) seems to work reasonably good well when  $K$  and  $\lambda_c/\lambda_e$  are of the order of one even at small time intervals (Fig. 5).

#### 4. Conclusions

This paper has developed the analytical theory of thermal degradation and fragmentation of polymer-like systems and aggregates with multiple bonds in the presence of stochastic evaporation and condensation (restoration) of bonds. In particular, it has been demonstrated that bond restoration (condensation) may have a significant impact on the fragmentation kinetics, when its rate exceeds  $\sim 10\%$  of the rate of bond evaporation (rate of thermal degradation). For example, if the ratio of the condensation rate to the evaporation rate is equal to 0.2, the typical time for 90% fragmentation of the initial clusters can easily be increased by up to  $\sim 50\%$  or more, compared to the case with no bond condensation.

It has also been shown that bond restoration may lead to substantial accumulation of clusters (products of fragmentation) in the intermediate fragmentation modes. Particle

numbers in such intermediate modes resulting from fragmentation in the presence of bond restoration may be dozens of times larger than those for fragmentation in the absence of bond restoration at the same evolution times. This may also lead to major fragmentation delays and increase of typical evolutionary times. In particular, this will be important for the detailed explanation the behavior and evolution of particle modes in the size distribution in combustion aerosols [29,40,41], or any other polymer-like aggregates and networks. Taking into account thermal fragmentation of nano-particle aggregates with multiple bonds and bond restoration will also be useful for the theoretical description of the previously observed maximum of the total number concentration of airborne combustion nano-particles at an “optimal” distance from the source [29,30].

It is also important to note that the developed theory of aggregate degradation is applicable for the special case of multiple bonds that do not interact with each other. If the multiple bonds (e.g., bonding molecules [31,32]) interact with each other, e.g., due to additional van der Waals interaction between the bonding molecules in a link between the primary particles [31,32], then the developed analytical theory is no longer applicable. At this stage, it seems difficult to derive analytical solution for particle degradation in the presence of bond restoration and additional interaction between multiple bonds in a link. Therefore, such an analysis should rather involve numerical methods of solution of the respective kinetic equations. However, this is beyond the scope of the current paper.

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