Cluster size distribution in the autocatalytic growth model

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We generalize the model of transition-metal nanocluster growth in aqueous solution, proposed recently [Phys. Rev. E 87, 022132 (2013)]. In order to model time evolution of the system, kinetic equations describing time dependence of the rate of chemical reactions are combined with Smoluchowski coagulation equation. In the absence of coagulation and fragmentation processes, the model equations are solved in two steps. First, for any injective functional dependence of the autocatalytic reaction rate constant on the cluster size, we obtain explicit analytical form of the $i$-mer concentration, $\xi_i$, as a function of $\xi_1$. This result allows us to reduce considerably the number of time-evolution equations. In the simplest situation, the remaining single kinetic equation for $\xi_1(t)$ is solved in quadratures. In a general case, we obtain small system of time-evolution equations, which, although rarely analytically tractable, can be relatively easily solved by using numerical methods.

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I. INTRODUCTION

Colloid formation, as well as polymerization processes of various kind, usually involve chemical reactions. Consequently, theoretical description of such phenomena should take into account both the chemical reactions and purely physical processes of coagulation and fragmentation. In particular, within the rate equation approach, time-evolution equations which are a generalization of both the rate equations, describing kinetics of chemical reactions, and the Smoluchowski coagulation equation, a standard tool used by physicists to describe various aggregation phenomena [1–19], are obtained.

Such ‘reaction-aggregation’ equations [16–19] usually defy analytical solutions unless the model parameters are chosen in a very special way - suffice to say that even the standard Smoluchowski coagulation equation without terms related to chemical reactions can be solved analytically only in few cases, cf. [4].

In a recent paper [19] we have introduced reaction-aggregation model, which reduces to the model of autocatalytic reaction in absence of coagulation. In such a situation, we were able to find analytical solution of the model equations in two nontrivial cases. In the present work we consider a more general form of this model. Its detailed analysis is provided, and new analytical results are presented. In particular, in the absence of coagulation, analytical form of the $k$-mer (cluster consisting of $k$ atoms or monomers) concentration as a function of the monomer concentration has been found for essentially arbitrary values of the model parameters.

This result has two important consequences. First, it greatly reduces a number of time-evolution equations. The remaining ones are to be solved either analytically (which is possible only in very special cases), or in general, numerically. In the simplest situation, only one ordinary differential equation remains, and typically we are left with a system consisting of 2-4 such equations, which makes the numerical analysis of the model feasible.

Second, it provides us with complete information about the structure of the cluster size distribution. In particular, we are able to determine all $k$-mer concentrations in the $t \to \infty$ limit by solving one additional algebraic equation, but without solving any of the time evolution equations. It should be noted here that in many applications, the asymptotic cluster size distribution is far more important than details of the time evolution of the system.

Our original goal was to provide a rigorous mathematical description of a transition metal nanocluster nucleation and growth kinetics in aqueous solution according to mechanism proposed by Watzky and Finke. [20–24]. Mathematical modelling of nanocluster nucleation and growth is a subject of considerable practical importance, due to the fact that solution route synthesis still remains one of the most convenient methods of producing transition-metal nanoparticles [25], which find numerous applications due to their unique optical, electronic, catalytic and biological properties. However, the Watzky-Finke (WF) mechanism, both in its basic and one of its extended forms, is applicable to other experimental situations, particularly to certain cases of transition metal oxides or sulfides (e.g. CdS) nanocluster formation, and some polymerization phenomena, including protein aggregation [24]. Therefore, it is expected that the results presented here will find useful applications outside the field of colloidal science.

This paper is organized as follows: we start in Sec. II by listing chemical reactions and physical processes included in the present model. In Sec. III we provide time evolution rate equations of the model, being generalization of those introduced and analyzed in Ref. [19]. In Sec. IV we analyze in detail the situation when coagulation is absent. This Section contains the central results of the present paper, i.e., universal relations between $k$-mer and monomer concentrations.
In Sec. VII we show how to solve the time-evolution equations by using the results of Section VI. However, because analytical solutions of kinetic equations of the present model are not available in a general case, we concentrate on numerical analysis of these equations. We do not present any numerical results, but rather make some comments of a general character. In Sec. VII we provide the Reader with some simple special cases of the model, for which analytical solutions of the time-evolution equations can be easily obtained.

Section VII contains summary and discussion. Some generalizations of the present model are briefly discussed in the Appendices.

II. MODEL

The basic transition-metal colloidal nanoparticle formation mechanism, as proposed by Watzky and Finke [20], cf. [21]–[24], consists of two steps. The first is production of a monomer, i.e., zerovalent transition-metal atom (B1) due to reaction of a metal precursor (A), which is usually a transition-metal coordination compound, with the reducing agent (R)

\[ A + R \rightarrow B_1 + X_1. \]  

(1)

The second is a parallel autocatalytic reduction reaction taking place on the surface of an \( i \)-mer (B\(_i\)), i.e., the zerovalent metal cluster consisting of \( i \) atoms,

\[ A + R + B_i \rightarrow B_{i+1} + X_2. \]  

(2)

The remaining (apart from \( B_i \)) products of reactions [11] and [2] are collectively denoted \( X_1 \) and \( X_2 \).

In contrast to our previous treatment [19] of the WF mechanism in its original formulation [20]–[23], here the presence of the reducing agent has been explicitly taken into account in both [11] and [2]. Usually, as an excess of the reducing agent is used, we may assume that its concentration is time-independent. Consequently, both [11] and [2] are frequently treated as pseudo-first and pseudo-second order reactions, respectively [20]–[23]–[26]–[29]. However, in the present paper this assumption is abandoned [37].

Two basic steps [11] and [2] may be supplemented with the coagulation process

\[ B_i + B_j \rightarrow B_{i+j}, \]  

(3)
cf. Ref. [21]. In addition, although chemical reactions [11] and [2] are assumed to be irreversible due to the presence of large amount of the reducing agent, this does not need to be the case for the physical processes, and [20] is generalized to include fragmentation [11].

Various extensions of the original WF scheme [11]–[19] are possible, and frequently required, depending on the experimental situation at hand. First, in many cases of practical importance, transition metal (e.g. Au) has more than one possible oxidation state. In such situation at least one additional preliminary step

\[ P + R \rightarrow A + X_3, \]  

(4)

should be introduced [20]–[29], see also [11]. For example, P may be an Au(III) chloride complex ion [AuCl\(_4\)]\(^-\), resulting from dissociation of tetrachloroauric acid (HAuCl\(_4\)). According to [4], Au(III) is reduced first to Au(I) [28], appearing in a form of [AuCl\(_2\)]\(^-\) \( \equiv \) A complex ion, and subsequently reduced to zerovalent gold forming nanoclusters of various sizes (Au\(_0\)) [29].

Next, analogously to the case of \( A \rightarrow B \) reduction reaction, [4] can also have its catalytic counterpart [27]

\[ P + R + B_i \rightarrow A + B_i + X_4. \]  

(5)

Again, additional products (\( X_3, X_4 \)) of both [11] and [19] reactions have been explicitly written. Also, in open systems the supply of \( R, P \) or \( A \) molecules or \( B_i \) clusters (\( i \geq 1 \)) by an external source (injection mechanism) may be present.

Many other generalizations of the above defined model are obtained if Eqs. [11]–[19] are augmented by additional chemical reactions, or if more complex mechanisms of [11], [2], [11], or [3] reactions are considered, i.e., by taking into account more elementary reactions steps. Some of such extensions will be discussed in Appendices [A] and [B].

III. TIME EVOLUTION EQUATIONS

We assume here that the system we wish to describe may be treated as spatially homogeneous (‘perfect mixing’ assumption), i.e., concentration or temperature gradients are sufficiently small. Consequently, diffusion and convection can be neglected. Also, we assume that temperature is time-independent (isothermal process). Under such conditions description making use of kinetic rate equations is adequate, and concentrations of \( R, P, A \) and \( B_i, i \in \mathbb{N} \), denoted here by \( c_\rho, c_\pi, c_\alpha, \) and \( \xi_\ell, \) respectively, are the state variables of the present model [39].

Kinetics of chemical reactions [11], [2], [11], and [3] is modeled here in a way usual for the rate equation approach, whereas in order to describe kinetics of reversible aggregation [38], an approach based on Smoluchowski coagulation equation [36]–[39] is employed. In effect, we obtain the following set of time-evolution equations for \( c_\rho, c_\pi, c_\alpha, \xi_1, \) and \( \xi_k, k > 1, \)

\[ \dot{c}_\rho = \tilde{w}_\rho - \tilde{k}_\pi c_\pi \sum_{j=1}^{\infty} \tilde{R}_j^{(\pi)} \xi_j c_\pi \]

\[ - \tilde{c}_\alpha c_\alpha - \sum_{j=1}^{\infty} \tilde{R}_j^{(\alpha)} \xi_j c_\alpha, \]  

(6)

\[ \dot{c}_\pi = \tilde{w}_\pi - \tilde{k}_\alpha c_\alpha \sum_{j=1}^{\infty} \tilde{R}_j^{(\alpha)} \xi_j c_\pi \]  

(7)
\[ \dot{c}_\alpha = \dot{w}_\alpha + \tilde{k}_\alpha c_\alpha + \sum_{j=1}^{\infty} \tilde{R}_j^{(\pi)} \xi_j c_\pi - \tilde{\xi}_1 c_\alpha - \sum_{j=1}^{\infty} \tilde{R}_j^{(\alpha)} \xi_j c_\alpha, \quad (8) \]

\[ \dot{\xi}_1 = \dot{w}_1 + \tilde{k}_\alpha c_\alpha - \tilde{R}_1^{(\alpha)} \xi_1 c_\alpha - \sum_{j=1}^{\infty} [K_{1j} \xi_1 F_{j1} + F_{1j} \xi_{1+j}], \quad (9) \]

\[ \dot{\xi}_k = \dot{w}_k + \left( \tilde{R}_{k-1}^{(\alpha)} \xi_{k-1} - \tilde{R}_k^{(\alpha)} \xi_k \right) c_\alpha + \frac{1}{2} \sum_{ij} [K_{ij} \xi_j \xi_j - F_{ij} \xi_k] - \sum_{j} [K_{kj} \xi_k \xi_j - F_{kj} \xi_{k+j}] \quad (10) \]

The first sum in Eq. (10) is restricted to \( i + j = k \).

1. Reaction rate constants

\[ \tilde{R}_\pi = \tilde{k}_\pi (c_\rho), \quad \tilde{R}_k^{(\pi)} = \tilde{R}_k^{(\pi)} (c_\rho), \quad \tilde{k}_\alpha = \tilde{k}_\alpha (c_\rho), \]

and \( \tilde{R}_k^{(\alpha)} = \tilde{R}_k^{(\alpha)} (c_\rho) \) functions appearing in Eqs. (9)-(10) describe the reducing agent concentration dependence of the reaction rates. If constant \( c_\rho(t) = c_\rho(0) \) is assumed, these functions become effective (observable) reaction rate constants for reactions (11), (12), and (13), respectively [40]. For \( k \geq 0 \), each \( \tilde{R}_k^{(\alpha)} (c_\rho) \) may be written as

\[ \tilde{R}_k^{(\alpha)} (c_\rho) = R_k^{(\alpha)} f_k^{(\alpha)} (c_\rho), \quad (11) \]

where \( R_0^{(\alpha)} \equiv \tilde{k}_\alpha, R_k^{(\pi)} \equiv \tilde{R}_k^{(\pi)}, \) and similarly for \( \tilde{R}_k^{(\alpha)} \) and \( R_k^{(\alpha)} \). We assume at this point that each \( f_k^{(\alpha)} (c_\rho) \) function (\( \sigma = \alpha, \pi; k \geq 0 \)) can be expanded in power series in \( c_\rho \)

\[ f_k^{(\sigma)} (c_\rho) = a_{1,1}^{(\sigma)} c_\rho + a_{1,2}^{(\sigma)} c_\rho^2 + \ldots \quad (12) \]

Applying, for colloidal systems we must have \( a_{0,k}^{(\sigma)} = 0 \), as there is no reduction reaction in the absence of the reducing agent. However, we should keep in mind that Eqs. (9)-(11) are valid only if reducing agent appears in excess, i.e., \( \max(c_\pi, c_\alpha) \ll c_\rho \). Consequently, behavior of \( f_k^{(\sigma)} (c_\rho) \) functions in the vicinity of \( c_\rho = 0 \) is not essential. Still, we assume that \( a_{1,1}^{(\sigma)} = 1 \), which can always be achieved by rescaling \( R_k^{(\sigma)} \). In such situation the simplest form of \( f_k^{(\sigma)} (c_\rho) \) is a linear function, \( R_k^{(\sigma)} = c_\rho R_k^{(\sigma)} \), i.e., \( a_{m,k}^{(\sigma)} = 0 \) for \( m \neq 1 \). For \( k > 0 \), i.e., for catalytic (\( \sigma = \pi \)) or autocatalytic (\( \sigma = \alpha \)) reaction, this particular form of \( R_k^{(\sigma)} \) corresponds to elementary reaction involving three molecules (trimolecular). However, autocatalytic or catalytic processes in solution are rarely elementary reactions, and it may be expected that the real reaction mechanism is more complex. In such situation, within the effective, approximate description, neglecting some elementary steps, terms nonlinear in \( c_\rho \) are present in Eq. (12) [41]. Higher-order terms are also important when the presence of reducing agent influences the rate of chemical reactions indirectly, by changing pH of the solution - again, we usually have to go beyond linear approximation to model such effect.

If the present model is to be used to describe a polymerization process with no reducing agent, in Eq. (12) we have to put \( a_{0,1}^{(\alpha)} = 1 \), and \( a_{m,k}^{(\alpha)} = 0 \) for \( m \geq 1 \).

From now on, for \( k \geq 0 \) we assume \( k \)-independent form of the \( f_k^{(\alpha)} \) functions appearing in Eqs. (11) and (12),

\[ f_k^{(\alpha)} (c_\rho) = f^{(\alpha)} (c_\rho). \quad (13) \]

The above assumption is crucial here, as it allows to get rid of \( c_\rho \)-dependence of the reaction rates, see below.

We also assume that clusters above the critical size \( (k = n) \) do not take part in an autocatalytic process

\[ R_k^{(\alpha)} = 0 \quad \text{for} \quad n = k, \]

\[ R_k^{(\alpha)} \neq 0 \quad \text{for} \quad 1 \leq k < n. \quad (14) \]

Still, \( n \) may be arbitrarily large. Introduction of \( n < \infty \) allows us to work with finite system of equations (6)-(10).

Finally, let us note that the temperature dependence of all the rate constants may be taken into account by invoking the standard Arrhenius, Eyring, or more general phenomenological equation [33], if necessary.

2. Coagulation and fragmentation kernels

\[ K_{ij} = K_{ji} \] and \( F_{ij} = F_{ji} \) in Eqs. (9) and (10) denote coagulation and fragmentation kernels, respectively.

What is important, in systems of interest the rate of coagulation process may depend on the concentration of chemical species, and therefore, within the present model, the \( c_\rho, c_\pi, \) or \( c_\alpha \)-dependence of \( K_{ij} \) cannot be ruled out. The reason for this may be analogical as in the case of reaction rate constants, namely, variations in pH of the solution caused by variable \( c_\rho, c_\pi, \) and \( c_\alpha \). pH value, in turn, may influence the surface charge of the clusters and consequently the strength of their mutual electrostatic interactions, hence the tendency towards coagulation.

The temperature dependence of \( K_{ij} \) and \( F_{ij} \) can also be taken into account, although the realistic functional form of this dependence is unclear and may be more complicated. The one for \( \tilde{k}_\pi, \tilde{R}_k^{(\pi)} \) and \( \tilde{R}_k^{(\alpha)} \) .

3. Source terms

\[ \dot{w}_\pi, \dot{w}_\alpha, \dot{w}_1 \] and \( \dot{w}_k \) appearing in Eqs. (9), (11), (12), (13) and (14) denote the source terms for \( R, P, \) and \( A \) molecules, monomers \( B_1 \), and the \( k \)-atom clusters \( B_k \).
Regarding, namely, corresponds to WF mechanism, \cite{20}) as defined by (1) and (2), which also expresses the reducing agent excess condition. Solutions we should have to be initially specified. In order to obtain nontrivial reactions and physical processes taking place in reverse micelles \cite{31}. In such situation, \( \dot{w}_\sigma(t) \) terms may be used to model the kinetics of intermicellar exchange process.

4. Initial conditions

Equations \cite{10}-\cite{12} have to be supplemented with appropriate initial conditions. First, from now on we assume

\[ \xi_i(0) = 0, \quad i > 1. \]  \( \text{(19)} \)

Consequently, values of only four parameters

\[ c_\rho(0) \equiv b_0, \quad c_\pi(0) \equiv c_0, \]
\[ c_\alpha(0) \equiv d_0, \quad \xi_1(0) \equiv e_0, \]  \( \text{(20)} \)

have to be initially specified. In order to obtain nontrivial solutions we should have

\[ 0 < c_0 + d_0 \equiv q_0 \ll b_0, \]  \( \text{(21)} \)

which also expresses the reducing agent excess condition.

The basic approach of Watzky and Finke ('two-step WF mechanism', \cite{22}) as defined by \cite{11} and \cite{22} corresponds to \( c_0 = e_0 = 0, \) \( d_0 \neq 0. \) When additional preliminary steps \cite{11} and \cite{5} are taken into account, \( c_0 \neq 0. \) Regarding \( c_0, \) in the present paper two cases are considered, namely

\[ e_0 = 0 \quad \text{for} \quad \tilde{k}_\alpha \neq 0, \]  \( \text{(22)} \)
\[ e_0 \neq 0 \quad \text{for} \quad \tilde{k}_\alpha = 0. \]  \( \text{(23)} \)

5. Conserved quantities

State variables \( c_\rho, c_\pi, c_\alpha \) and \( \xi_i \) are not independent. Namely, from Eqs. \cite{7}-\cite{10}, we obtain

\[ \dot{Q}_m(t) = e_\rho(t) - e_\pi(t) + \sum_{j=1}^{\infty} j\dot{\xi}_j(t) \]  \( \text{(24)} \)
\[ - \dot{w}_\pi(t) - \dot{w}_\alpha(t) - \sum_{j=1}^{\infty} j\dot{w}_j(t) = 0. \]

Integrating Eq. \cite{24}, one gets

\[ Q_m(t) = c_\pi(t) + c_\alpha(t) + \sum_{j=1}^{\infty} j\xi_j(t) \]  \( \text{(25)} \)
\[ - w_\pi(t) - w_\alpha(t) - \sum_{j=1}^{\infty} jw_j(t) = q_0 + e_0, \]

where \cite{21} and the initial conditions \cite{16} and \cite{20} have been invoked. Eq. \cite{27} is nothing but the mass conservation constraint. For colloidal systems ‘mass’ refers to a total number of transition metal atoms, regardless of its distribution amongst P, A, and B.

From Eqs. \cite{19}-\cite{21} yet another relation follows. Namely, we have

\[ Q_r(t) = e_\rho(t) - 2e_\pi(t) - e_\alpha(t) \]
\[ - w_\rho(t) + 2w_\pi(t) + w_\alpha(t) = 0. \]  \( \text{(26)} \)

From Eqs. \cite{16}, \cite{20}, and \cite{26} we obtain

\[ Q_r(t) = e_\rho(t) - 2e_\pi(t) - e_\alpha(t) \]
\[ - w_\rho(t) + 2w_\pi(t) + w_\alpha(t) = b_0 - 2c_0 - d_0. \]  \( \text{(27)} \)

6. Stationary solution

Stationary solution \cite{12} of Eqs. \cite{3}-\cite{10} is defined by the following condition

\[ e_\rho = e_\pi = e_\alpha = \xi_1 = \xi_2 = \ldots = \xi_n. \]  \( \text{(28)} \)

Stationary values of the state variables will be denoted by a bar, e.g. \( \bar{c}_\alpha. \) Due to \cite{18} and irreversible character of reactions \cite{11}, \cite{22}, \cite{14}, and \cite{5}, we have \( \bar{c}_\pi = \bar{c}_\alpha = \bar{c}_\rho = 0 \) if only

\[ \bar{c}_\pi = \lim_{t \to \infty} c_\pi(t) = 0, \]
\[ \bar{c}_\alpha = \lim_{t \to \infty} c_\alpha(t) = 0. \]  \( \text{(29)} \)

As a consequence of Eqs. \cite{29}, from Eq. \cite{25} we obtain

\[ \sum_{j=1}^{\infty} j\dot{\xi}_j = w_\pi + \dot{w}_\alpha + \sum_{j=1}^{\infty} j\dot{w}_j + c_0 + d_0 + e_0. \]  \( \text{(30)} \)

Note, that \cite{30} follows from the existence of the constant of motion, and therefore value of the sum \( \sum_{j=1}^{\infty} j\dot{\xi}_j \) does
not depend on the choice of $\tilde{k}_x$, $\tilde{R}_k^{(\sigma)}$, $\bar{k}_\alpha$, $\tilde{R}_k^{(\alpha)}$ functions or $K_{ij}$, $F_{ij}$ parameters. This is not the case for individual $\bar{\xi}_j$, however. In general situation, stationary value of each $\bar{\xi}_j$ depends on the choice of $K_{ij}$ and $F_{ij}$ \[33\]. Still, as will be shown below, in absence of both cluster source terms ($\tilde{w}_z = 0$) and physical processes of coagulation and fragmentation ($K_{ij} = F_{ij} = 0$), the sequence $\bar{\xi}_1, \bar{\xi}_2, \ldots, \bar{\xi}_n$ is uniquely determined by $n, q_0, c_0, \bar{k}_\alpha$ and $\tilde{R}_k^{(\alpha)}$ only. Its form depends neither on $\bar{K}_x$, $\tilde{R}_k^{(\pi)}$, nor on $\bar{w}_p, \tilde{w}_k$ or $\tilde{w}_\alpha$.

Finally, $\bar{c}_p$ can be found from \[27\] and \[29\], we get
\[
\bar{c}_p = \bar{w}_p - 2\bar{w}_x - \bar{w}_\alpha + b_0 - 2c_0 - d_0.
\] (31)

A. Method of moments

In some situations, in order to analyze properties of Eqs. \[10\]-\[11\], it is useful to rewrite these equations in terms of new variables. The $\mu$-th moment of the cluster mass distribution is defined as
\[
M_\mu(t) = \sum_{j=1}^{\infty} j^n \xi_j(t).
\] (32)

Presence of variable $c_\rho(t)$, source terms $\tilde{w}_\alpha$ or chemical reaction not involving B clusters \[14\] does not affect the form of time evolution equations for $M_\mu(t)$ as given by Eq. (6) of Ref. \[19\]. The only new contribution comes from the cluster source terms $\tilde{w}_k$. If the latter are present, instead of Eq. (6) of Ref. \[19\] we have then \[45\]
\[
M_\mu = \sum_{j=1}^{\infty} j^n \tilde{w}_j + \bar{k}_\alpha c_\alpha + \sum_{j=1}^{\infty} \tilde{G}_j^{(\mu)} \xi_j c_\alpha + \sum_{p=2}^{\infty} \tilde{S}_p^{(\mu)} \xi_p \tilde{S}_q + \sum_{p=2}^{\infty} \tilde{T}_p^{(\alpha)} \xi_p.
\] (33)

In Eq. \[34\], $\tilde{S}_p^{(\mu)} \equiv \tilde{S}_p^{(\mu)} \equiv \frac{1}{2}((p + q)^n - p^n - q^n)K_{pq}$,
\[
\tilde{T}_p^{(\alpha)} \equiv \sum_{i=0}^{\infty-1} ((i + 1)^n - i^n)\tilde{R}_k^{(\alpha)}.
\]

The analysis of general qualitative properties of Eq. \[33\], provided in Section III of Ref. \[19\], remains valid here with only minor modifications. Namely, first, the initial conditions for Eq. \[35\] read now $M_\mu(0) = c_\alpha$. Also, stationary value of $M_1$, i.e., $M_1 \equiv \lim_{t \to \infty} M_1(t)$ is now given by \[30\].

The remaining part of Section III of Ref. \[19\] can be also generalized in an obvious manner. Eqs. \[33\] for various $\mu$ supplemented by time-evolution equations for $c_\alpha$, $c_\sigma$ and $c_\rho$ can be given closed, tractable form, analogous to Eqs. \(\text{(8)}\)-(11) of Ref. \[19\], if a restriction is imposed on the parameter $n$ appearing in \[11\], $\mu$, as well as the values of the model parameters, namely, $n = \infty$, $\mu \in \mathbb{N} \cup 0$, $F_{ij} = 0$, and $\tilde{R}_k^{(\pi)}$, $\tilde{R}_k^{(\alpha)}$, $K_{ij}$ given by
\[
K_{ij} = \kappa_0 + \kappa_1(i + j) + \kappa_2 ij, \quad \tilde{R}_k^{(\sigma)} = \bar{a}_R^{(\sigma)} i + \bar{b}_R^{(\sigma)}.
\] (34)

In above equation, $\kappa_0, \kappa_1, \kappa_2$, and $\bar{a}_R^{(\sigma)}$, $\bar{b}_R^{(\sigma)}$ for $\sigma = \pi, \alpha$ are arbitrary non-negative coefficients. Note, that for finite $n$, and $\mu \neq 0$, the r.h.s. of Eq. \[33\] cannot be expressed as the function of only $M_\mu$ variables, even for $K_{ij} = F_{ij} = 0$.

IV. ABSENCE OF COAGULATION

A. General remarks

Important simplification of the present model is obtained if coagulation and fragmentation processes are neglected. For transition-metal nanocluster growth in solution such assumption is justified in some situations. First, if a stabilizing agent like polyvinyl alcohol (PVA) or polyvinylpyrrolidone (PVP) is present in a system, coagulation is severely limited or even entirely absent \[28\], \[31\]. Second, if nanocluster have no nonzero surface charge, the resulting repulsing electrostatic interactions between cluster may prevent coagulation. Third, lack of coagulation may be reasonable approximation for nanoparticle growth in reverse micelles, where the geometry or size of micelle water pool prohibits coagulation, at least to some extent. From now on we also assume that there is no injection of the nanoclusters. In consequence, for $K_{ij} = F_{ij} = 0$ and $\bar{w}_k = 0$, Eq. \[11\] takes the form
\[
\dot{\bar{\xi}}_1 = c_\alpha (\bar{k}_\alpha - \bar{R}_k^{(\alpha)} \bar{\xi}_1),
\] (35)

whereas for $1 < k < n$ from Eq. \[11\] we obtain
\[
\dot{\bar{\xi}}_k = c_\alpha (\bar{R}_k^{(\alpha)} \bar{\xi}_{k-1} - \bar{R}_k^{(\alpha)} \bar{\xi}_k).
\] (36)

It is convenient to consider the $k = n$ separately \[46\]. Invoking Eqs. \[21\] and \[50\] we get
\[
\dot{\bar{\xi}}_n = c_\alpha \bar{R}_n^{(\alpha)} \bar{\xi}_{n-1}.
\] (37)

We may expect, that in general $\bar{\xi}_n(t) \neq 0$ for $t > 0$. Yet, if only $\xi_{n+1}(0) = 0$, which is assumed to be the case here [cf. Eq. \[19\]], for $i > n$ we have $\xi_i(t) = 0$, regardless the values of the corresponding coefficients $\bar{R}_i^{(\alpha)}$. In other words, $n$-mers are the largest clusters appearing in a system and hence for $n \ll \infty$ we should expect some kind of ‘finite-size’ effects in the solutions of Eqs. \[33\]-\[34\].

Note, that the r.h.s. of Eq. \[33\], each of Eqs. \[36\] and Eq. \[37\] do not depend explicitly on time. Dividing \[36\] by \[37\] we obtain
\[
\frac{d\xi_k}{d\bar{\xi}_1} = \frac{\bar{R}_k^{(\alpha)} \bar{\xi}_{k-1} - \bar{R}_k^{(\alpha)} \bar{\xi}_k}{\bar{k}_\alpha - \bar{R}_k^{(\alpha)} \bar{\xi}_1} = \frac{\bar{R}_k^{(\alpha)} \bar{\xi}_{k-1} - \bar{R}_k^{(\alpha)} \bar{\xi}_k}{\bar{k}_\alpha - \bar{R}_k^{(\alpha)} \bar{\xi}_1},
\] (38)

whereas for $k = n$ from \[37\] and \[34\] we have
\[
\frac{d\xi_n}{d\bar{\xi}_1} = \frac{\bar{R}_n^{(\alpha)} \bar{\xi}_{n-1}}{\bar{k}_\alpha - \bar{R}_1^{(\alpha)} \bar{\xi}_1} = \frac{\bar{R}_n^{(\alpha)} \bar{\xi}_{n-1}}{\bar{k}_\alpha - \bar{R}_1^{(\alpha)} \bar{\xi}_1}.
\] (39)
Note also, that neither $c_\alpha$, nor $c_\rho$ appear in (38) and (39); for $c_s$ this follows from Eq. (13). Eqs. (38) and (39) form finite ($n < \infty$) or infinite ($n = \infty$) set of linear ordinary differential equation. Their solutions, denoted

$$
\xi_k \equiv s_k(\xi_1), \quad k < n
$$

$$
\xi_n \equiv u_n(\xi_1),
$$

$$
\xi_i = 0, \quad i > n,
$$

(40)

provide information about the structure of the cluster 'mass spectrum'. Please note, that in contrast to $u_n(\xi_1)$, the $s_k(\xi_1)$ functions do not depend on $n$. What is important, the form of Eqs. (38) and (39) and consequently, the functional form of $s_k(\xi_1)$ and $u_n(\xi_1)$ (40) is independent on presence of any reaction, which either do not involve $B_1$ clusters (e.g., Eq. (11)) or in which $B_1$ play a role of a passive catalyst (e.g., Eq. (3)). In fact, arbitrary number of such reactions may be present without affecting $s_k(\xi_1)$ and $u_n(\xi_1)$, which, in particular, depend neither on the source terms for R, P and A molecules, nor on the values of $\tilde{\kappa} \equiv \tau/\kappa$ and $R^{(\pi)}$. Moreover, for the latter parameters, no assumption like (13) is needed.

On the other hand, obviously, time evolution of $\xi_1$, $c_\alpha$, $c_\rho$ and $c_\sigma$ depends in general on the values of all model parameters, including those which do not change the 'structural' relations (40).

Note, that even if (the knowledge of) the explicit form of $s_k(\xi_1)$ and $u_n(\xi_1)$ functions alone does not give us hints about the system dynamics, it allows us to determine the asymptotic cluster size distribution (or, in case of polymerization, asymptotic molecular weight distribution). Namely, using (30) we obtain

$$
\tilde{M}_1 = \tilde{\xi}_1 + \sum_{k=1}^{n-1} is_k(\xi_1) + nu_n(\xi_1)
$$

$$
= \bar{w}_x + \bar{w}_a + c_0 + d_0 + e_0,
$$

(41)

where $\tilde{\xi}_1 \equiv \lim_{t \to \infty} \xi_1(t)$. Eq. (11) allows (in practice only numerically) to determine $\tilde{\xi}_1$, and therefore each $\xi_k$. In many applications (e.g., in modelling of the nanocluster fabrication or some polymerization processes) this may be much more interesting than any details of the system time evolution. Also for this reason, determination of an explicit form of $s_k(\xi_1)$ and $u_n(\xi_1)$ is the central result of the present paper.

At this point it is convenient to discuss in detail two distinct situations as defined by (22) and (23). Apart from the solution of Eqs. (38) and (39) for arbitrary injective sequence $R^{(\alpha)}_1, R^{(\alpha)}_2, \ldots, R^{(\alpha)}_n$, some relations between $\xi_1$ and other state variables $(M_0, M_1$ and $c_\alpha$) will be presented.

B. $\tilde{k}_\alpha \neq 0, c_\alpha = 0$ case

1. Relations between $M_0, \xi_1$ and $c_\alpha$

For $\mu = 0$ and $K_{ij} = F_{ij} = \dot{w}_j = 0$, Eq. (33) reads

$$
\dot{M}_0 = \tilde{k}_\alpha c_\alpha.
$$

(42)

In the present case, important relation is obtained by dividing Eq. (35) by Eq. (42). Due to assumption (13), $\dot{c}_s^{(\alpha)}(c_s)$ cancels out and we obtain

$$
\dot{\xi}_1 \over M_0 = \frac{d\xi_1}{dM_0} = 1 - \frac{\omega}{q_0} \xi_1.
$$

(43)

Dimensionless parameter $\omega$ in Eq. (43) is defined by

$$
\omega = \frac{\tilde{R}^{(\alpha)}_1}{c_\alpha} = \frac{R^{(\alpha)}_1}{\bar{c}_\alpha}.
$$

(44)

Eq. (43) can be easily solved, to get

$$
\xi_1 = h_0(M_0) = \frac{q_0}{\omega} \left[ 1 - \exp \left( -\frac{\omega}{q_0} M_0 \right) \right],
$$

(45)

cf. Eqs. (34) and (35) of Ref. [19]. We emphasize that Eq. (45) is universally valid for any $n > 1$, and for arbitrary choice of the $R^{(\alpha)}$, if only $R^{(\alpha)}_1 \neq 0$.

Next, for $c_\rho(t) = c_\rho(0)$, from Eqs. (38) and (42) we obtain

$$
\frac{\int_0^{\tilde{\xi}_1} \frac{d\xi}{\tilde{k}_\alpha - \tilde{R}^{(\alpha)}_1 \xi}}{M_0 / \tilde{k}_\alpha} = \int_0^t c_\alpha(t') dt' \geq 0.
$$

(46)

Eq. (46) establishes an universal relation between $c_\alpha(t)$ and $\xi_1(t)$, and allows to determine explicit form of the latter, once the former is known, or vice versa. From (44) and (46) it follows that

$$
\xi_1(t) < \frac{q_0}{\omega}, \quad t \geq 0.
$$

(47)

For $\tilde{k}_\alpha \neq 0$, $c_\alpha = 0$ and $c_\alpha(0) = d_0 \neq 0$, inequality (47) follows also from the fact that $\xi_1(0) > 0$, and therefore Eq. (35) implies that $\xi_1(t) > 0$. This in turn implies that $\xi_1(t) > 0$ for $t \in (0, \infty)$.

2. $\xi_k$ as a function of $\xi_1$

In the present case, Eq. (38) can be rewritten as

$$
\frac{d\xi_k}{d\xi_1} = \frac{r_{k-1} \xi_1 - r_k \xi_k}{\lambda - r_k \xi_1},
$$

(48)

where

$$
\lambda \equiv \frac{k_\alpha}{R} = r_0 q_0, \quad r_i \equiv \frac{R^{(\alpha)}_i}{R},
$$

(49)
and $R$ is a constant of the same dimension as $R_k^{(o)}$, e.g.
one may take $R = R_1^{(o)}$. Introducing new variables
\[
x = y_1 = \frac{r_1}{\lambda} \xi_1 - 1 = \frac{\omega}{q_0} \xi_1 - 1 = -e^{-\frac{\omega}{q_0} M_0},
\]
\[
y_k = \frac{r_k}{\lambda} \xi_k - 1 = \frac{r_k}{r_1} \frac{\omega}{q_0} \xi_k - 1,
\]  
(50)

$-1 \leq x < 0$, we may rewrite (51) as
\[
\frac{dy_k}{dx} = \frac{r_k}{r_1} \left( \frac{y_k - y_{k-1}}{x} \right). 
\]  
(51)

In terms of new variables, initial conditions (19) read
\[
y_k(-1) = -1, \quad k \geq 2. 
\]  
(52)

For $k = 2, 3, \ldots$ Eqs. (51) form a closed hierarchy of linear ordinary differential equations, which can be solved iteratively. We assume at this point that $r_i \neq r_j$ for $i \neq j$ and $k < n$ [cf. Eq. (13)], therefore $r_i \neq 0$, $r_j \neq 0$. The $k = n$ case will be discussed separately.

Solution of Eqs. (51) for arbitrary $k < n$ can be inferred by analyzing the form of $y_k(x)$ for $k \leq 4$. We find
\[
y_k(x) = (-1)^k \sum_{j=1}^{k} \left( \frac{\prod_{i=1}^{k} r_i}{r_j \prod_{m \neq j} (r_j - r_m)} \right) (-x)^{r_j^{-1}} \].
\]  
\[
= \frac{1}{V_k} \sum_{j=1}^{k} (-1)^j \left( \frac{\prod_{i=1}^{k} r_i}{r_j} \right) V^{(j)}_{k-1} (-x)^{r_j^{-1}} 
\]  
(53)

where
\[
\begin{align*}
V_k(x) &= (-x)^{r_1} r_1 \cdots r_1^{-2} r_1^{-k-1}
\end{align*}
\]  
\[
V^{(j)}_{k-1} = (-x)^{r_j} r_j \cdots r_j^{-2} r_j^{-k-1}
\]  
(54)

whereas $V^{(i)}_{k-1}$ and $V_k = V_k(-1)$ are Vandermonde determinants with $k - 1$ and $k$ rows, respectively,
\[
V^{(i)}_{k-1} = \begin{bmatrix} 1 & r_1 & \cdots & r_1^{-2} & r_1^{-k-2} \\
1 & r_2 & \cdots & r_2^{-2} & r_2^{-k-2} \\
\vdots & \vdots & \ddots & \vdots & \vdots \\
1 & r_{i-1} & \cdots & r_{i-1}^{-2} & r_{i-1}^{-k-2} \\
1 & r_{i+1} & \cdots & r_{i+1}^{-2} & r_{i+1}^{-k-2} \\
\vdots & \vdots & \ddots & \vdots & \vdots \\
1 & r_k & \cdots & r_k^{-2} & r_k^{-k-2} \end{bmatrix},
\]  
(55)

\[
V_k = \begin{bmatrix} 1 & r_1 & \cdots & r_1^{-2} & r_1^{-k-1} \\
1 & r_2 & \cdots & r_2^{-2} & r_2^{-k-1} \\
1 & r_3 & \cdots & r_3^{-2} & r_3^{-k-1} \\
\vdots & \vdots & \ddots & \vdots & \vdots \\
1 & r_k & \cdots & r_k^{-2} & r_k^{-k-1} \end{bmatrix}. 
\]  
(56)

From the last line of Eq. (53) it should be obvious that the initial condition (52) is indeed satisfied for each $k$. Correctness of this compact form of $y_k(x)$ may be in turn verified by simple algebraic manipulations, involving Laplace expansion of $V_k(x)$ (34). Eventually, returning to the original variables, from (50) and (53) we obtain
\[
\xi_k = s_k(\xi_1) = \frac{r_1}{r_k} \frac{q_0}{\omega} \left( 1 - \frac{\omega}{q_0} \xi_1 - 1 \right) / \frac{V_k(-1)}{V_k(1)}. \]  
(57)

So far we have assumed that $k < n$. Now we discuss the case of the largest cluster size, $k = n$. Although $R_n = 0$ implies $r_n = 0$, in order to be able to use transformation (50) in the present case, we assume that $r_n \neq 0$, but disregard the term proportional to $R_n$ on the r.h.s. of Eq. (53). This may formally be achieved by rewriting Eq. (53) for $k = n$ as
\[
\frac{d\xi_n}{d\xi_1} = \frac{r_n-1\xi_{n-1} - cr_n\xi_n}{\lambda - r_1 \xi_1}, \]  
(58)

and putting $c = 0$. Making use of (50), we obtain
\[
\frac{dy_n}{dx} = -\frac{r_n}{r_1} \left( \frac{1}{x} + \frac{y_{n-1}}{y_k(-1)} \right). \]  
(59)

where $y_{n-1}(x)$ is given by Eq. (53) and the initial conditions (52) reads $y_n(-1) = -1$. Eq. (59) can be integrated in a straightforward manner to get
\[
y_n(x) = \sum_{j=1}^{n-1} \frac{\prod_{i=1}^{n-1} r_i}{r_j} (-1)^j \frac{V^{(j)}_{n-2}}{V_{n-1}} \left[ 1 - (-x)^{r_j^{-1}} \right] 
\]  
\[= -\frac{r_n}{r_1} \ln(-x) - 1. \]  
(60)

In terms of $\xi_n$ and either $\xi_1$ or $M_0$, we get
\[
\xi_n = u_n(\xi_1) = -\frac{q_0}{\omega} \ln \left( 1 - \frac{\omega}{q_0} \xi_1 \right) \]  
(61)

\[
+ \frac{q_0}{\omega} \frac{r_1}{r_1} \sum_{j=1}^{n-1} \frac{\prod_{i=1}^{n-1} r_i}{r_j} \frac{V^{(j)}_{n-2}}{V_{n-1}} \left[ 1 - \left( 1 - \frac{\omega}{q_0} \xi_1 \right)^{r_j^{-1}} \right] \]  
\[= M_0 + \frac{q_0}{\omega} \frac{r_1}{r_1} \sum_{j=1}^{n-1} \frac{\prod_{i=1}^{n-1} r_i}{r_j} \frac{V^{(j)}_{n-2}}{V_{n-1}} \left[ 1 - e^{-\frac{\omega}{q_0} M_0} \right]. \]  
Please note that $r_n$ does not appear in Eq. (61).
3. Special case: \( r_j = j \)

For the linear reaction kernel \((r_j = j)\) analyzed in detail in Ref. [19], from Eq. (53) we obtain

\[
y_k(x) = (-1)^k \sum_{j=1}^{k} \frac{k!}{j! (j-m)!} (-x)^j
\]

\[
= (-1)^k \sum_{j=1}^{k} \frac{(-1)^{k-j} j!}{j!(j-1)!} (-x)^j
\]

\[
= -1 + \sum_{j=0}^{k} \binom{k}{j} x^j = (x + 1)^k - 1.
\]

(62)

Taking into account Eq. (60), for \( k < n \) we find

\[
\xi_k(1) = \frac{\lambda}{r_k} \left( \frac{r_1}{\lambda} \xi_1 \right)^k = \frac{1}{k} \frac{q_0}{\omega} \left( \frac{\omega}{q_0} \xi_1 \right)^k,
\]

(63)
in agreement with Eq. (21) of Ref. [19]. For \( k = n \), from Eq. (60) we get

\[
y_n(x) = n \sum_{j=1}^{n-1} \frac{1}{j} \left( \frac{n-1}{j} \right) \left[ (-1)^j - x^j \right] - n \ln(-x) - 1,
\]

(64)

and therefore

\[
\xi_n = u_n(1) = \frac{q_0}{\omega} \ln \left( 1 - \frac{\omega}{q_0} \xi_1 \right)
\]

\[
= \frac{q_0}{\omega} \sum_{j=1}^{n-1} \frac{1}{j} \left( \frac{n-1}{j} \right) \left[ (-1)^j - \left( 1 - \frac{\omega}{q_0} \xi_1 \right)^j \right].
\]

(65)

\[C. \quad \tilde{k}_\alpha = 0, \quad c_0 \neq 0 \text{ case}\]

In this Subsection we analyze a situation when \( P \rightarrow \)

A reaction [11] is absent, i.e., \( \tilde{k}_\alpha = 0 \). This case may be relevant to the modelling of certain polymerization processes, as well as for the description of growth of the core-shell type nanoparticles [32].

In order to obtain nontrivial solutions, we have to assume now that some clusters are initially present in a system. In accordance with Eqs. [19] and [20], we take \( c_0 = \xi(0) \neq 0 \).

1. Time dependence of \( M_0 \). Relations between \( \xi_1 \) and \( c_0 \)

For \( \tilde{k}_\alpha = 0 \), Eq. (63) has a simple form

\[
\dot{M}_0 = 0.
\]

Integrating (66), and taking Eqs. [19] and [20] into account, we get

\[
M_0(t) = M_0(0) = c_0.
\]

(67)

For constant \( c_\rho(t) = c_\rho(0) \) from Eq. (65), we obtain

\[
- \frac{1}{R_1^{(\alpha)}} \int_{c_0}^{\xi_1} \frac{d\xi}{\xi} = - \frac{1}{R_1^{(\alpha)}} \ln \left( \frac{\xi_1}{c_0} \right) = \int_0^t c_\alpha(t')dt' \geq 0.
\]

(68)

Analogously to Eq. (46), Eq. (65) expresses an universal relation between \( c_\alpha(t) \) and \( \xi_1(t) \). In the present case, where there is no monomer production or injection, \( \xi_1(t) \) must a decreasing function of time; condition \( \xi_1(t) \leq 0 \) clearly follows from Eq. (65). Therefore, for \( t \geq 0 \) we have

\[
\xi_1(t) \leq c_0.
\]

(69)

Inequality (69) follows also from Eq. (68) in a straightforward manner.

2. \( \xi_k \) as a function of \( \xi_1 \)

As a next step we determine functional form of the \( k \)-mer concentration \( \xi_k \) as a function of \( \xi_1 \). However, in the present situation we cannot make use of the results derived for \( k_\alpha \neq 0 \), because now \( \lambda = 0 \) and transformation [60] becomes singular. Dividing (65) by (53) we obtain

\[
\frac{d\xi_k}{d\xi_1} = \frac{r_k \xi_k - r_k - 1 \xi_k - 1}{r_1 \xi_1}.
\]

(70)

where \( r_i \) are defined by Eq. (49). In the present case we define auxiliary variables \( y_k \) and \( y_1 = x \) as follows

\[
x = y_1 = \frac{\xi_1}{c_0}, \quad y_k = \frac{r_k \xi_k}{r_1 c_0}.
\]

(71)

\[0 < x \leq 1. \text{ Making use of (71), we rewrite (70) as}\]

\[
\frac{dy_k}{dx} = \frac{r_k}{r_1} \left( \frac{y_k - y_k - 1}{x} \right).
\]

(72)

Note, that although Eq. (72) has exactly the same form as Eq. (51), now not only \( x \) and \( y_k \) are defined differently, but also instead of (52) we have

\[
y_k(1) = 0, \quad k \geq 2.
\]

(73)

Again, (72) corresponds to initial conditions (49) for the \( \xi_k \) variables.

As in the \( \tilde{k}_\alpha \neq 0, c_0 = 0 \) case, we first consider \( k < n \) [cf. Eq. (13)]; the \( k = n \) case will be discussed separately.

Also in the present situation, solutions of Eqs. (72) for arbitrary \( k < n \) can be simply inferred by solving the \( k = 2, 3, 4 \) cases. We find

\[
y_k(x) = (-1)^{k+1} \prod_{l=2}^{k} \frac{r_l}{r_1} \sum_{j=1}^{k} \frac{\left( \prod_{m \neq j} (r_m - r_m) \right)}{\prod_{m \neq j} (r_m - r_m)} \left( \prod_{m \neq j} r_j \right) \left( \prod_{m \neq j} r_m \right)
\]

\[
= - \left( \prod_{l=2}^{k} r_l \right) \sum_{j=1}^{k} (-1)^j \frac{V^{(j)}_{k-1}}{V_k} x^{r_1},
\]

(74)
where $V_{k-1}^{(j)}$ and $V_k$ are defined by Eqs. (55) and (56). The initial condition (53) follows easily from basic properties of the determinants (orthogonality of the Laplace expansion). Eventually, from (71) and (74) we obtain

$$
\xi_k = s_k(\xi_1) = -e_0 \left( \prod_{i=1}^{r} r_i \right) \left( \sum_{j=1}^{k} (-1)^j V_{k-1}^{(j)} \frac{\xi_j}{e_0} \right)^{r_1}. \tag{75}
$$

In order to analyze the $k = n$ case, we again assume $r_n \neq 0$, however, we disregard the appropriate terms on the r.h.s. of (70). In consequence, from Eqs. (70) and (71) we obtain

$$
dy_n \over dx = -\frac{r_n y_{n-1}}{r_1} x, \tag{76}
$$

where now $y_{n-1}(x)$ is given by Eq. (74) and the initial condition (52) is $y_n(1) = 0$. Solution of Eq. (76) reads

$$
y_n(x) = \left( \prod_{i=1}^{n} r_i \right) \left( \sum_{j=1}^{n} (-1)^j \frac{V_{n-2}^{(j)}}{V_{n-1}} \left( \frac{\xi_j}{e_0} \right)^{r_1} x \right) - 1. \tag{77}
$$

Using Eqs. (74) and (71) we finally get

$$
\xi_n = u_n(\xi_1) = e_0 \left( \sum_{j=1}^{n} (-1)^j \frac{\xi_j}{e_0} \right)^{r_1} - 1. \tag{78}
$$

Note, that $e_0$ plays here the role analogous to that of $\eta_0/\omega$ the parameter in the $k_n \neq 0$, $e_0 = 0$ case.

3. Special case: $r_j = j$

For $r_j = j$, $y_j(x)$ as given by Eq. (74) reads

$$
y_j(x) = -\sum_{j=1}^{k} (-1)^j k! \frac{(k-j)!}{(j-1)!} x^j = -x^j \frac{d}{dx} \left[ (1-x)^k - 1 \right] = k x (1-x)^{k-1}. \tag{79}
$$

Making use of Eq. (71), for $k < n$ we find

$$
\xi_k = s_k(\xi_1) = \xi_1 \left( 1 - \frac{\xi_1}{e_0} \right)^{k-1}. \tag{80}
$$

Obviously, $s_k(0) = 0$ for $k \geq 2$, as it should be. Next, for $k = n$, Eq. (71) reads now

$$
y_n(x) = n \sum_{j=1}^{n} (-1)^j \binom{n-1}{j} (x^j - 1) = n(1-x)^{n-1}. \tag{81}
$$

From Eqs. (71) and (81) we obtain

$$
\xi_n = u_n(\xi_1) = e_0 \left( 1 - \frac{\xi_1}{e_0} \right)^{n-1}. \tag{82}
$$

It could be easily verified, that Eq. (57) is indeed satisfied, both for $n = \infty$ and for $n < \infty$. In the former case, from (80) we also obtain

$$
M_1 = g_1(\xi_1) = \sum_{k=1}^{\infty} k \xi_1 \left( 1 - \frac{\xi_1}{e_0} \right)^{k-1} = e_0^2 \xi_1. \tag{83}
$$

whereas in the latter we have

$$
M_1 = g_1^{(n)}(\xi_1) = n \xi_n + \sum_{k=1}^{n-1} k \xi_k
$$

$$
= n e_0 \left( 1 - \frac{\xi_1}{e_0} \right)^{n-1} + \xi_1 \sum_{k=1}^{n-1} k \left( 1 - \frac{\xi_1}{e_0} \right)^{k-1}
$$

$$
= e_0^2 \xi_1 \left[ 1 - \left( 1 - \frac{\xi_1}{e_0} \right)^{n} \right]. \tag{84}
$$

In above, $g_1(\xi_1)$ is an inverse of the $h_1(M_1)$ function introduced in Ref. [19]; $g_1(\xi_1) = \lim_{n \to \infty} g_1^{(n)}(\xi_1)$, as could be expected. Correctness of Eq. (84) can be also verified by invoking Eq. (33) for $\mu = 1$. Namely, in the present case $\tilde{q}_j^{(1)} = j \tilde{R}_1^{(n)}$, $\tilde{G}_n^{(1)} = 0$, therefore we have

$$
\tilde{M}_1 = \tilde{R}_1^{(n)} \sum_{j=1}^{n} j \xi_j c_n = \left( -n \xi_n + \sum_{j=1}^{n} j \xi_j \right) \tilde{R}_1^{(n)} c_n. \tag{85}
$$

Eq. (85) divided by Eq. (33) yields

$$
\frac{dM_1}{d\xi_1} = \frac{n \xi_n - M_1}{\xi_1}, \tag{86}
$$

which is indeed obeyed for $M_1 = g_1^{(n)}(\xi_1)$ given by (84) and $\xi_n = u_n(\xi_1)$ given by (82).

Finally, let us note, that for $n = \infty$, the asymptotic cluster-size distribution $\tilde{\xi}_1, \tilde{\xi}_2, \ldots$ can be easily obtained by combining Eqs. (33), (81) and (84). In the simplest case, for $e_0 = 0$ and when no source terms are present, we obtain

$$
\tilde{\xi}_k = e_0^2 \left( \frac{d_0}{d_0 + e_0} \right)^k. \tag{87}
$$

D. Choice of $r_i$ parameters

So far, the only assumption about the $r_i$ coefficients we have made is that of single-valuedness of the sequence $r_1, r_2, \ldots, r_{n-1}$. Linear reaction kernel ($r_j = j$) analyzed in detail both in the present paper and in Ref. [19] has been chosen mainly because it leads to the considerable simplifications of the mathematical structure of the
model. This particular form of $r_j$ appears in a natural manner, when one describes colloidal system by referring only to the total mass (or concentration) of the zerovalent transition-metal atoms, $M_1$, and not by making use of the k-mer concentrations, $\xi_k$, cf. Refs. [20, 22]. In such situation, naive application of the mass-action law (rate of the autocatalytic reaction proportional to $c_\alpha M_1$) is equivalent to the choice $r_j = j$. Nevertheless, linear dependence of $r_j$ on $j$ has no real physical justification. More general, but still very simple form of $r_j$ is the power-law dependence

$$ r_j \propto j^{\zeta}, \quad (88) $$

$0 \leq \zeta \leq 1$. There are two simple cases of $r_j$ [88], which are nonetheless quite realistic, namely diffusion-limited growth ($\zeta = \frac{1}{4}$) and reaction-limited growth ($\zeta = \frac{1}{3}$) [38]. Another special case of [88], the size-independent reaction kernel ($\zeta = 0$) seems to be reasonable approximation for modelling of growth of some linear polymers but not for colloidal particles. The $\zeta = 0$ case of [88] is not analyzed in the present paper (cf. Refs. [18] and [19]).

Finally, let us note that for $0 < \zeta < 1$, in contrast to the $\zeta = 1$ or $\zeta = 0$ case, tractable equations for the time evolution of the moments [33] cannot be obtained. Also, all the above remarks are also relevant for the $R^{(\pi)}_i$ parameters.

V. TIME EVOLUTION EQUATIONS IN TERMS OF $s_k(\xi_1)$ AND $u_n(\xi_1)$ FUNCTIONS

The explicit form of $s_k(\xi_1)$ and $u_n(\xi_1)$ as given by Eqs. [57] and [61] or (75) and (78) makes the solution of the original time-evolution equations Eqs. [49-49] feasible even for quite arbitrary choice of the model parameters. Namely, with $s_k(\xi_1)$ and $u_n(\xi_1)$ at hand, it is sufficient to solve Eqs. (8) and (71) (if present), Eqs. (8) together with either Eq. (6) or any of Eq. (10) for $k \geq 2$, including the $k = n$ case.

Note, that two state variables and therefore two corresponding evolution equations can be eliminated by invoking Eqs. (23) and (27). Consequently, in some situations, e.g. for $R^{(\pi)}_i = \bar{w}_i = 0$, when Eq. (7) has an obvious solution $c_\rho(t) = c_\rho(0) \exp(-k_\pi t)$, we are left with only one equation for a single unknown function, say, $\xi_1(t)$ [if more convenient, in the $k_\alpha \neq 0$, $c_0 = 0$ case one may use $M_0(t)$ instead of $\xi_1(t)$, cf. Eqs. [45] and [60]]

$$ \dot{\xi}_1 = \left( \bar{k}_\alpha - \bar{R}^{(\alpha)}_1 \right) \left( d_0 - \sum_{j=1}^{\infty} j \bar{R}^{(\alpha)}_j s_j \right). \quad (89) $$

In the above equation, both $s_j$ and $\bar{k}_\alpha$, $\bar{R}^{(\alpha)}_j$ are now functions of $\xi_1$; the latter functions may also depend explicitly on time.

In the simplest situation ($c_\rho(t) = c_\rho(0)$, $c_0 = 0$) we obtain

$$ \int_{\xi_0}^{\xi_1} \frac{d\xi}{\left( \bar{k}_\alpha - \bar{R}^{(\alpha)}_1 \xi \right) \left( d_0 - \sum_{j=1}^{\infty} j \bar{R}^{(\alpha)}_j s_j(\xi) \right)} = t. \quad (90) $$

However, in a general case the solution of [90] cannot be expressed in terms of elementary functions or standard special functions. When $c_0 \neq 0$ or variable $c_\rho(t)$ is considered, situation becomes even worse. Therefore, we must depend on the numerical analysis [48]. Yet in such case it is generally not advised to eliminate any variables by using the constraints [20] or [21]. In consequence, we have to solve numerically the following equations

$$ \dot{c}_\rho = \bar{w}_\rho - \bar{k}_\pi c_\pi - \sum_{j=1}^{n-1} \bar{R}^{(\pi)}_j s_j(\xi_1) c_n - \bar{R}^{(\pi)}_n u_n(\xi_1) c_\pi $$

$$ - \bar{k}_\alpha c_\alpha - \sum_{j=1}^{n-1} \bar{R}^{(\alpha)}_j s_j(\xi_1) c_\alpha, \quad (91) $$

$$ \dot{\bar{c}}_\pi = \bar{w}_\pi - \bar{k}_\pi c_\pi - \sum_{j=1}^{n-1} \bar{R}^{(\pi)}_j s_j(\xi_1) c_\pi - \bar{R}^{(\pi)}_n u_n(\xi_1) c_\pi $$

$$ - \bar{k}_\alpha c_\alpha - \sum_{j=1}^{n-1} \bar{R}^{(\alpha)}_j s_j(\xi_1) c_\alpha, \quad (93) $$

$$ \dot{\xi}_1 = \bar{k}_\alpha c_\alpha - \bar{R}^{(\alpha)}_1 \xi_1 c_\alpha, \quad (94) $$

with the initial conditions [20]. For $c_0 = 0$ we disregard Eq. [92], whereas for $c_\rho(t) = c_\rho(0)$ Eq. [21] is absent. Also, let us point out again, Eq. [92] can be replaced by Eq. [10] for any $2 \leq k \leq n$ [49].

Some remarks are in place here. First, when solving Eqs. [91]-[94] numerically, care is needed whenever $r_i \approx r_j$, due to the $r_i - r_j$ terms appearing in denominators in Eqs. [57], [61], [75], and [78]. Second, the elegant and compact form of $s_k(\xi_1)$ and $u_n(\xi_1)$ involving Vandermonde determinants is useless from the point of view of numerical analysis, and all formulas have to be rewritten in an appropriate manner [cf. the first line of Eqs. [57] and [70]]. Third, the effect of finite $n$ on the numerical solutions of Eqs. [91]-[94] should be always carefully checked in order to avoid ‘finite-size effects’. Finally, for realistic choice of the parameter $n$, sums appearing on the l.h.s. of Eqs. [91]-[94] have large number of terms of alternating sign. This is likely to make the problem of numerical computation of such sums nontrivial.
VI. SELECTED EXACTLY SOLUBLE CASES OF TIME-EVOLUTION EQUATIONS

A. Simple model of autocatalytic reaction

In Ref. [19], the explicit form of the $\xi_1(t)$ function has been found in two special cases, in particular for the two-step WF scheme defined by Eqs. (1) and (2), with $r_j = j$, $n = \infty$, and $c_\rho(t) = c_\rho(0)$. Time-evolution equations for this case may be easily solved by employing the method of moments, cf. [19] and References therein.

For completeness, below we present the corresponding solution for the $\tilde{k}_\alpha = 0$, $e_0 \neq 0$ case. Time evolution equations for $M_1$ and $c_\alpha$ read now

$$M_1 = \tilde{a}_R M_1 c_\alpha = -\dot{c}_\alpha. \tag{95}$$

From Eqs. (94) mass conservation follows, i.e.,

$$M_1(t) + c_\alpha(t) = M_1(0) + c_\alpha(0) = e_0 + d_0. \tag{96}$$

Making use of Eqs. (96) and (95), we obtain the following time-evolution equation for $M_1$

$$\dot{M}_1 = \tilde{a}_R M_1 (e_0 + d_0 - M_1). \tag{97}$$

Equation (97) is the standard logistic equation. Integrating, we get

$$M_1(t) = \frac{e_0 + d_0}{1 + \frac{\tilde{a}_R}{e_0} \exp[-\tilde{a}_R(e_0 + d_0)t]}. \tag{98}$$

In order to obtain $\xi_1(t)$, we invoke Eq. (83), which yields

$$\xi_1(t) = \frac{e_0^2}{\bar{M}_1(t)} = \frac{e_0 + d_0 \exp[-\tilde{a}_R(e_0 + d_0)t]}{1 + \frac{d_0}{e_0}}. \tag{99}$$

Finally, combining (83) with (96) we obtain

$$\xi_k(t) = \frac{e_0^2}{d_0} \left(\frac{d_0}{d_0 + e_0}\right)^k \left(1 + \frac{d_0}{e_0} e^{-\tilde{k}t}\right) \left(1 - e^{-\tilde{k}t}\right). \tag{100}$$

where $\tilde{k} = -\tilde{a}_R(e_0 + d_0)$. Please note, that for $\xi_k(t)$ we have $\lim_{t \to \infty} \xi_k(t) = \xi_k$ as given by Eq. (87).

B. Two simple cases of injection mechanism

In some situations, exact analytical solution can be obtained also when the injection mechanism for precursor A is present. Here we assume that i) $c_0 = 0$ (reactions [4] and [5] are absent), ii) reducing agent concentration is constant, $c_\rho(t) = c_\rho(0)$, iii) $n = \infty$ in Eq. (14), iv) $\bar{R}_j(a) = \tilde{a}_R j$, i.e., $r_j = j$. We make no restrictions on values of $c_0 = M_1(0)$ and $\tilde{k}_\alpha$, therefore results presented below are valid for both cases analyzed in Subsections IV.B and IV.C.

In the present situation, it is again convenient to use the method of moments. Equations (8) and (53) for $\mu = 1$ read now

$$\dot{c}_\alpha = \tilde{w}_\alpha - \tilde{k}_\alpha c_\alpha - \tilde{a}_R M_1 c_\alpha, \tag{101}$$

$$\dot{M}_1 = \tilde{k}_\alpha c_\alpha + \tilde{a}_R M_1 c_\alpha. \tag{102}$$

From Eq. (25) we obtain

$$c_\alpha(t) = h_0 + w_\alpha(t) - M_1(t), \tag{103}$$

where $h_0 \equiv d_0 + e_0$. Using Eq. (103), we get

$$\dot{M}_1 = \left(\tilde{k}_\alpha + \tilde{a}_R M_1\right) \left(f(t) - M_1\right). \tag{104}$$

where we define $f(t) = h_0 + w_\alpha(t)$. The above equation has exactly the form of Eq. (14) of Ref. [19], however, the concrete form of $w_\alpha(t)$ and $f(t)$ is not specified as yet. Eq. (104) can be given the form of the Bernoulli equation and therefore it can be reduced to linear equation. We obtain (cf. Eq. (15) of Ref. [19])

$$M_1(t) = \frac{e^{\Phi(t)}}{\tilde{a}_R} \left(\frac{1}{\tilde{k}_\alpha + e_0 \tilde{a}_R} + \Xi(t)\right)^{-1} - \tilde{k}_\alpha \tilde{a}_R, \tag{105}$$

where

$$\Phi(t) = \int_0^t \left(\tilde{k}_\alpha + \tilde{a}_R h_0 + \tilde{a}_R w_\alpha(\eta)\right) d\eta,$$

$$\Xi(t) = \int_0^t e^{\Phi(\eta)} d\eta. \tag{106}$$

Below we analyze two simple cases of $w_\alpha(t)$ function [50].

First, consider the situation when the precursor A is added into the system at constant rate $U$ during the time interval $T$. We have then

$$w_\alpha(t) = \begin{cases} U, & t < T, \\ 0, & t \geq T. \end{cases} \tag{107}$$

and consequently

$$w_\alpha(t) = \begin{cases} U t, & t < T, \\ U T, & t \geq T. \end{cases} \tag{108}$$

Making use of (106) and (108), we get

$$\Phi(t) = \left(\tilde{k}_\alpha + \tilde{a}_R h_0\right) t + \Phi_a(t), \tag{109}$$

where we define

$$\Phi_a(t) = \begin{cases} \frac{1}{2} \tilde{a}_R U t^2, & t < T, \\ \frac{1}{2} \tilde{a}_R U T^2, & t \geq T. \end{cases} \tag{110}$$

From (106), (109), and (110) it follows that

$$\Xi(t) = \begin{cases} \Xi_1(t), & t < T, \\ \Xi_1(T) + \Xi_2(t), & t \geq T. \end{cases} \tag{111}$$
\[ \Xi_1(t) = \frac{\exp\left(-\frac{\alpha^2}{2}t^2\right)}{\sqrt{\alpha}} \left[ \Psi\left(t\sqrt{\alpha} + \frac{B}{2}\right) - \Psi\left(\frac{B}{2}\right) \right], \]
\[ \Xi_2(t) = e^{-AT^2} \left( e^{(2AT+B)t} - e^{(2AT+B)T} \right), \]
where \( \Psi(x) \equiv \int_0^x e^{-z^2} \, dz = e^{-x^2} D_+(x), D_+(x) \) is a Dawson function, \( A = \frac{1}{2} \tilde{\alpha}_R U \) and \( B = \tilde{\kappa}_0 + \tilde{\alpha}_R h_0 \).

\[ \tilde{w}_{\alpha}(t) = W \delta(t - t_i), \quad w_{\alpha}(t) = W \theta(t - t_i), \] (113)

where \( W \) is a constant, and \( \theta(x) \) denotes Heaviside step function. In the present case we have

\[ \Phi(t) = \begin{cases} (\tilde{\kappa}_0 + \tilde{\alpha}_R h_0) t, & t < t_i, \\ (\tilde{\kappa}_0 + \tilde{\alpha}_R h_0) t + \tilde{\alpha}_R W(t - t_i), & t \geq t_i, \end{cases} \] (114)

\[ \Xi(t) = \begin{cases} \Xi_1(t), & t < t_i, \\ \Xi_1(t_i) + \Xi_2(t), & t \geq t_i, \end{cases} \] (115)

where

\[ \Xi_1(t) = e^{Bt} - 1, \]
\[ \Xi_2(t) = e^{-Bt} \left( e^{(B+C)t} - e^{(B+C)t_i} \right) \left( B + C \right). \] (116)

In above formula, \( C = \tilde{\alpha}_R W; B \) is defined as in (112).

In both cases analyzed above, \( M_1(t) \) given by Eq. (105) reduces to \( x_{\alpha\beta}(t) \) given by Eq. (16) of Ref. 19 in an appropriate limit (i.e., \( U = 0 \) and \( W = 0 \), respectively). Also, making use of (115) we obtain

\[ \bar{M}_1 \equiv \lim_{t \to \infty} M_1(t) = d_0 + e_0 + \bar{w}_{\alpha}; \] (117)

both for \( \bar{w}_{\alpha} = UT \) \( \bar{M}_1 \) as well as for \( \bar{w}_{\alpha} = W \) \( \Xi_2(t) \), in agreement with the general formula (105).

Moreover, we emphasize again, that all relations, which are independent, in particular, on the form of \( \bar{w}_{\alpha}(t) \) function, may be used here. For example, for \( \tilde{\kappa}_0 \neq 0, e_0 = 0 \) we may invoke Eq. (63) as well as Eqs. (19) and (23) of Ref. 19

\[ M_0(M_1) = \frac{\bar{M}_0}{\bar{\omega}} \ln \left( 1 + \frac{\omega}{\bar{\omega}} M_1 \right), \] (118)

\[ \xi_1 = h^{(\omega)}(\bar{M}_1) = \frac{\bar{M}_1}{1 + \frac{\omega}{\bar{\omega}} M_1}, \] (119)

whereas for \( \tilde{\kappa}_0 = 0, e_0 \neq 0 \) Eqs. (67), (75), and (80). All those results are valid provided assumptions ii) and iv) of the present subsection are fulfilled, i.e., we have \( n = \infty \) and \( r_j = j \), respectively.

### VII. SUMMARY AND DISCUSSION

In this paper, we have presented a generalization of the autocatalytic growth model, proposed recently [19]. Time evolution of the system is described within the mean-field type rate-equation approach. Kinetic equations of our model are generalization of both the Smoluchowski coagulation equation, and the rate equations, describing the kinetics of chemical reactions.

If coagulation processes are neglected, the model equations simplify considerably, and a number of analytical results become available. In particular, in two nontrivial cases and for arbitrary injective functional dependence of the autocatalytic reaction rate constant on the cluster size, we obtain analytical expressions of the \( \xi_i \) as a function of \( \xi_1; \xi_i = s_i(\xi_1) \). In consequence, we obtain complete information about the structure of the cluster-size distribution without solving kinetic equations. In particular, we are able to determine the cluster mass distribution in the \( t \to \infty \) limit without solving kinetic equations. The latter result may be of practical importance if the present model is used to describe or predict the experimental results.

Moreover, knowing the explicit form of \( s_i(\xi_1) \) functions, in order to find time dependence of all of the state variables, we have to solve (either analytically, or, in general case, numerically) only small subset of the original system of the time evolution equations.

The present model may be applied to describe both nanocluster formation in aqueous solution and some polymerization phenomena.

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### Appendix A: Possible extensions of the present model

In this Appendix we discuss some of the chemical reactions and reaction mechanisms, which can be taken into account within the extensions of the present model as defined by Eqs. (11-19).

Firstly, either \( P \), or \( A \) molecules may form dimers (\( P_2, A_2 \)), or more generally, clusters consisting of small number of molecules

\[ P + P \rightarrow P_2, \quad A + A \rightarrow A_2. \] (A1)

Such dimers may be inert, i.e., do not take part in any chemical reaction. However, \( A_2 \) may also disproportionate according to

\[ A_2 \rightarrow P + B_1. \] (A2)
and \( \text{A2} \) may be also treated as a single step
\[
A + A \rightleftharpoons P + B_1. \tag{A3}
\]
Next, consider a situation when reducing agent decomposes on the surface of metallic nanoclusters, and the latter act as catalyst for this process
\[
R + B_i \rightarrow B_i + X_5. \tag{A4}
\]
By \( X_5 \) we collectively denote all products of \( \text{A3} \). More generally, we may consider reaction of the type
\[
Y + Y' + B_i \rightarrow B_i + X_6, \tag{A5}
\]
where \( Y \) and \( Y' \) are those constituents of the system, which do not take part in reactions \( \text{A1} \text{---}\text{A4} \) and \( X_6 \) denotes all possible products of \( \text{A5} \). Again, in \( \text{A5} \) metallic nanocluster play only the passive role of a catalyst.

As an example of \( \text{A5} \) we may give hydrogenation reaction used to monitor the reaction progress in Ref. [20]. In this case, \( Y \) denotes cyclohexene, \( Y' \) is a molecular hydrogen, and \( X_6 \) is cyclohexane.

Finally, consider a more complex reaction mechanism of the autocatalytic reaction \( \text{[2]} \). We may expect that the real mechanism of this reaction involves formation of intermediate complex \((AB_i)\). In effect, \( \text{[2]} \) should be replaced with
\[
A + B_i \rightarrow (AB_i) \rightarrow B_{i+1} + X_2. \tag{A6}
\]
Let us now discuss briefly how the presence of reactions \( \text{[A1} \text{---} \text{A6]} \) in some extension of the present model would change its mathematical structure, in particular, the form of Eqs. \( \text{[B5]} \text{ and } \text{[B9]} \).

First, note that the latter equations are not affected by the presence of reactions \( \text{[A1]} \text{. The same is true for } \text{[A1]}. \) and \( \text{[A3]} \), provided that interactions between molecules of different species \( A, B, Y \) or \( Y' \) near the surface of \( B_i \) nanoclusters can be neglected.

However, if either \( \text{[A2]} \text{ or } \text{[A3]} \) reaction is present, \( c_a \) does not cancel out in Eqs. \( \text{[B5]} \text{ and } \text{[B9]} \). Consequently, these equations cannot be solved independently of the time evolution equations for \( c_p, c_x, c_a, \) and \( \xi_1 \). Still, Eqs. \( \text{[B5]} \text{ and } \text{[B9]} \) may provide reasonable effective description of the time-evolution in any system where the mechanism of autocatalytic reaction is assumed to have the form \( \text{[A6]} \). This is analyzed in detail in Appendix B.

**Appendix B: Kinetic equations for a more complex mechanism of \( A + B_i \rightarrow B_{i+1} \) reaction**

In this Appendix we show that simple, effective mechanism \( \text{[2]} \) of autocatalytic reaction, together with the corresponding kinetic equations may provide sound approximation of a more realistic description [cf. Eq. \( \text{[A6]} \) of Appendix A].

Namely, in many cases it seems reasonable to assume that either a break up of each of the \((AB_i)\) complexes into substrates or transformation of \((AB_i)\) into products of autocatalytic reaction \( \text{[2]} \),
\[
A + B_i \stackrel{k_i^-}{\rightleftharpoons} (AB_i) \stackrel{k_i^+}{\rightarrow} B_{i+1} + X_2, \tag{B1}
\]
is much faster than its production
\[
A + B_i \rightarrow (AB_i). \tag{B2}
\]
In consequence, concentration of the \((AB_i)\) complexes remains both small and essentially time-independent. In such situation, steady-state approximation is legitimate.

Rate equations corresponding to \( \text{[A6]} \) reaction read
\[
\dot{\xi}_i = \tilde{k}_i^- \eta_i + \tilde{k}_i^{*-1} \tilde{\eta}_{i-1} - \tilde{k}_i^+ \xi_i c_a, \quad i > 1, \tag{B3}
\]
\[
\tilde{\eta}_i = -\tilde{k}_i^- \eta_i - \tilde{k}_i^{*-1} \eta_{i-1} + \tilde{k}_i^+ \xi_i c_a, \quad i > 1, \tag{B4}
\]
where \( \eta_i \) denotes concentration of \((AB_i)\). For \( i = 1 \), instead of \( \text{[B3]} \), we have
\[
\dot{\xi}_1 = \tilde{k}_1 c_a \eta_1 - \tilde{k}_1^+ \xi_1 c_a. \tag{B5}
\]
Within the present treatment, Eqs. \( \text{[B3]} \text{---} \text{[B5]} \) replace Eqs. \( \text{[B5]} \text{ and } \text{[B9]} \). Similarly to the case of \( \tilde{R}_k^{(a)} \) functions [Eq. \( \text{[11]} \)], \( \tilde{k}_i^+ \) and \( \tilde{k}_i^- \) in general depend on \( c_p \).

Next, we add Eq. \( \text{[B3]} \text{ and } \text{[B4]} \). This step yields
\[
\dot{\xi}_i + \tilde{\eta}_i = \tilde{k}_i^- \eta_{i-1} - \tilde{k}_i^+ \xi_i. \tag{B6}
\]
From a steady state assumption,
\[
\tilde{\eta}_i = 0, \tag{B7}
\]
by using Eq. \( \text{[B4]} \), we obtain
\[
\eta_i^{(ss)} = \frac{\tilde{k}_i^- c_a}{\tilde{k}_i^+ + \tilde{k}_i^-} \tilde{\xi}_i \equiv \tilde{R}_i^{(c)} \xi_i c_a. \tag{B8}
\]
We assume here, that \( \text{[B8]} \) holds for all \( i \geq 1 \) and for \( t > 0 \). Nonetheless, we should keep in mind that the steady-state assumption and therefore Eq. \( \text{[B8]} \) cannot be valid during the initial stage of the time evolution.

Making use of Eqs. \( \text{[B6]}, \text{[B7]}, \text{ and } \text{[B8]} \), we may rewrite Eqs. \( \text{[B5]} \text{ and } \text{[B9]} \) as
\[
\dot{\xi}_1 = \tilde{k}_1 c_a \eta_1 - \tilde{R}_1^{(c)} \xi_1, \tag{B9}
\]
and
\[
\dot{\xi}_i = c_a \left( \tilde{R}_i^{(c)} - \tilde{R}_{i-1}^{(c)} \xi_{i-1} - \tilde{R}_i^{(c)} \xi_i \right), \tag{B10}
\]
where for \( i \geq 1 \) we have
\[
\tilde{R}_i^{(c)} = \frac{\tilde{k}_i^+ \tilde{k}_i^-}{\tilde{k}_i^+ + \tilde{k}_i^-} = \tilde{k}_i^* \tilde{k}_i^{(c)}. \tag{B11}
\]
Eq. \( \text{[B9]} \) has exactly the form of Eq. \( \text{[55]} \), whereas Eq. \( \text{[B10]} \) has the same form as Eq. \( \text{[56]} \). Moreover, for the
largest clusters \((i = n)\), assuming that \(\tilde{k}_s = 0, \tilde{k}_c \neq 0\) (i.e., \((A_{B_1})\) complexes are formed, but are not reduced to \(B_{n+1}\) clusters) and using condition \((B8)\) for \(i = n - 1\) and \(i = n\), we obtain Eq. \((B7)\), again with \(\tilde{F}_{n-1}^{(a)}\) given by \((B11)\).

This provides justification for the effective approach of the present model even if reaction mechanism \((A6)\) of autocatalytic reaction is more likely to be present in a system of interest.

It remains to check the internal consistency of the steady state assumption \((B7)\). For \(F_{ij} = 0\) and \(\dot{w}_k = 0\), using \((B8)\), we obtain

\[
\dot{\eta}_i = \frac{d}{dt} \left( \frac{\tilde{k}_c c_{\alpha}}{\tilde{k}_s + \tilde{k}_c} \right) = \frac{d}{dt} \left( \tilde{k}_c c_{\alpha} \xi_i \right) = \tilde{k}_c c_{\alpha} \xi_i + \tilde{k}_c c_{\alpha} \dot{\xi}_i + \tilde{k}_c c_{\alpha} \dot{\xi}_i .
\]

(B12)

It is reasonable to assume, that \(\tilde{k}_c\) has only weak time dependence, or is even time independent if the \(c_{\alpha}\) dependence of \(\tilde{k}_s\) and \(\tilde{k}_c\) cancel out. Therefore, the remaining two terms in the last line of Eq. \((B12)\) have to be small. Note, that obviously \(c_{\alpha} < q_0\) for any \(t \in (0, \infty)\), and also \(\xi_i(t) \leq M_0(t) \leq M_1(t) \leq q_0 + e_0\). Consequently, we may write down the following, rather crude upper bound for \(|\dot{\eta}_i|\)

\[
|\dot{\eta}_i| < (q_0 + e_0) \tilde{k}_c (|\dot{c}_{\alpha}| + |\dot{\xi}_i|) .
\]

(B13)

Because \(|\dot{c}_{\alpha}| + |\dot{\xi}_i|\) is bounded, the sufficient self-consistency condition for the steady state assumption \((B7)\) reads

\[
(q_0 + e_0) \tilde{k}_c \leq \varepsilon \ll 1 ,
\]

(B14)

where \(\varepsilon\) is a sufficiently small positive constant. From Eq. \((B5)\) it follows, that if \((B14)\) is fulfilled for some \(i\) and \(\varepsilon\), then \(\eta_i\) is also small as compared to \(\xi_i\), i.e., we have \(\eta_i/\xi_i \ll 1\).

If two cases analyzed in Subsections \((IVB)\) and \((IVC)\) are considered separately, we can provide slightly more precise upper bound for \(|\dot{\eta}_i|\). For \(\tilde{k}_c \neq 0\) and \(e_0 = 0\), using Eq. \((B7)\) we obtain

\[
|\dot{\eta}_i| < q_0 \tilde{k}_c \left( \frac{1}{\omega} |\dot{c}_{\alpha}| + |\dot{\xi}_i| \right) ,
\]

(B15)

whereas for \(\tilde{k}_c = 0, e_0 \neq 0\) the upper bound for \(|\dot{\eta}_i|\) in general case reads

\[
|\dot{\eta}_i| < \tilde{k}_c \left( e_0 |\dot{c}_{\alpha}| + q_0 |\dot{\xi}_i| \right) .
\]

(B16)

However, for \(c_0 = 0\) we can give \((B15)\) a more concrete form. Namely, in such case, assuming that \(\forall_i : r_i \leq i\), we obtain [cf. Eqs. \((B5)\) and \((B8)\)]

\[
|\dot{\eta}_i| \leq \tilde{k}_c |\dot{\xi}_i| \tilde{k}_s \left[ d_0 e_0 (2d_0 + e_0) \right] .
\]

(B17)

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For simplicity, we do not analyze here time-evolution equations for the concentrations of X1, X2, X3, and X4 species.

Even for a variable $c_\sigma(t)$, the term ‘reaction rate constant’ will be used for $\tilde{k}_\sigma(c_\sigma)$, $\tilde{R}_k(\pi)$, $\tilde{k}_\alpha(c_\sigma)$, and $\tilde{R}_k(\alpha)(c_\sigma)$.

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[37] The motivation behind such more complete treatment is the following: in certain situations, spectroscopic techniques allow to measure the reductant concentration, but not a concentration of any other constituent of the system. Therefore, the information about change of the reducing agent concentration in time allows to monitor the reaction progress.
[38] Au(II) is very unstable, and therefore disregarded within such an effective reaction mechanism, cf. Ref. [28].
[39] For simplicity, we do not analyze here time-evolution equations for the concentrations of X1, X2, X3, and X4 species.
[40] In a more general situation, nonlinear dependence of $\tilde{R}_k^{(e)}$ on both $c_\rho$, $c_\sigma$, and $c_\alpha$ may be postulated.
[41] We assume here that such solution is unique.
[42] In the $t \to \infty$ limit, when chemical reactions can be neglected, time evolution equations of our model reduce to standard Smoluchowski coagulation equations.
[43] However, $B_1$ may play a role of a passive catalyst.
[44] Please note the change in notation: $\tilde{S}_j^{(\omega)} \to \tilde{G}_j^{(\mu)}$ and analogously for $\tilde{S}_p^{(\omega)}$ and $\tilde{T}_p^{(\alpha)}$ as compared to Ref. [19].
[45] Finite $n$ case is important for any numerical analysis of the present model. Therefore, in this paper $k < n$ and $k = n$ cases will be carefully distinguished.
[46] For $k = n + 1$ we obtain the following time-evolution equation: $\xi_{n+1} = -c_\sigma \tilde{R}_k^{(\sigma)} \xi_{n+1}$, which clearly has a $\xi_{n+1}(t) = 0$ function as its solution for $\xi_{n+1}(0) = 0$. In a similar manner, concentrations of all larger clusters are also equal to zero.
[47] Please note that it may be more convenient to solve numerically Eq. (49) then Eq. (50).
[48] Although with this respect different values of $k$, $1 \leq k \leq n$ are completely equivalent at the level of analytical solution, they may lead to slightly different results when the model time-evolution equations are solved numerically.
[49] $f(t) = d_0 + c_0 (1 - \exp(-k_\sigma t))$ function analyzed in Ref. [19] (for $c_0 \neq 0$ and $c_0 = 0$), results from the presence of reaction 4. However, in a model without the $P \to A$ reaction, identical form of $f(t)$ may be related to the presence of the following injection mechanism for A molecules: $w_\sigma = k_\sigma c_\sigma(t)$, $w_\alpha(t) = c_0 (1 - \exp(-k_\alpha t))$. In such case, however, even if $k_\sigma \neq 0$, $c_0 \neq 0$, P is not treated as an independent constituent of the system.