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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 [J. Jędrak, Phys. Rev. E **87**, 022132 (2013)], by introducing a more complete description of chemical reactions. In order to model time evolution of the system, equations describing chemical reaction kinetics are combined with the Smoluchowski coagulation equation. In the absence of coagulation and fragmentation processes, the model equations are solved in two steps. First, we obtain the explicit analytical form of the i-mer concentration, ξ_i, as a function of ξ_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 a small system of time-evolution equations, which, although rarely analytically tractable, can be relatively easily solved numerically.

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I. INTRODUCTION

Colloid formation, as well as polymerization processes of various kinds, usually involve chemical reactions. Consequently, a 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 the 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 it to say that even the standard Smoluchowski coagulation equation can be solved analytically only in a few cases; cf. [4].

In a recent paper [19], we proposed a reaction-aggregation model, which reduces to the model of autocatalytic reaction in the absence of coagulation. In such a situation, we were able to find an analytical solution of the model equations in two nontrivial cases. In the present work, we consider generalization of this model, for which a detailed analysis is provided and analytical results are presented. In particular, in the absence of coagulation, the analytical form of the k-mer (cluster consisting of k atoms or monomers) concentration (ξ_k) as a function of the monomer concentration (ξ_1), i.e., $\xi_k = s_k(\xi_1)$, has been found for essentially arbitrary values of the model parameters.

This result has two important consequences. First, it greatly reduces a number of independent time-evolution equations. The remaining ones are to be solved either analytically (in the simplest situation, only one time-evolution equation remains, which can be solved in quadratures) or, in general, numerically. Typically, we are left with a system consisting of 2–4 first order ordinary differential equations, which makes the numerical analysis of the model feasible.

Second, an explicit form of each of the $s_k(\xi_1)$ functions 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 only one algebraic equation (mass conservation constraint), but without solving any of the kinetic equations. It should be noted here that in many applications, the long-time 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 the mechanism proposed by Watzky and Finke [20–24]. Mathematical modeling 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 oxide or sulfide (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 introduce time-evolution rate equations of the model, being a generalization of those introduced and analyzed in Ref. [19]. In Sec. IV, we analyze in detail the situation when coagulation and fragmentation processes are absent. This section contains the central results of the present paper, i.e., the relationship between k-mer and monomer concentrations.

In Sec. V, we show how the results of Sec. IV can be applied in order to solve the time-evolution equations. In Sec. VI, 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. Limitations of the present model are discussed in Sec. VII. Section VIII contains a summary and

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discussion. Some possible generalizations of the present model are briefly discussed in the Appendices.

II. MODEL

The basic form of a 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., a zero-valent transition-metal atom (B_1) due to the reaction of a metal precursor (A), which is usually a transition-metal coordination compound, with the reducing agent (R),

$$A + R \rightarrow B_1 + X_1. \tag{1}$$

The second is a parallel autocatalytic reduction reaction taking place on the surface of an i-mer (B_i), i.e., the zero-valent metal cluster consisting of i atoms,

$$A + R + B_i \rightarrow B_{i+1} + X_2. \tag{2}$$

The remaining (apart from B_i) products of reactions (1) 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 (1) and (2) [26]. Usually, as an excess of the reducing agent is used, we may assume that its concentration is time independent. Consequently, both (1) and (2) are frequently treated as pseudo-first and pseudo-second order reactions, respectively [20–23,27–31]. However, in the present paper, this assumption is abandoned [32].

Two basic steps (1) and (2) may be supplemented with the coagulation process,

$$B_i + B_j \rightleftharpoons B_{i+j}; \tag{3}$$

cf. Ref. [21]. In addition, although chemical reactions (1) and (2) are assumed to be irreversible due to the presence of a large amount of the reducing agent, this does not need to be the case for the physical processes, and (3) is generalized to include fragmentation [19].

Various extensions of the original WF scheme (1)–(3) are possible, and frequently required, depending on the experimental situation at hand. First, in many cases of practical importance, a transition metal (e.g., Au) has more than one possible oxidation state. In such situation, at least one additional preliminary step,

$$P + R \rightarrow A + X_3, \tag{4}$$

should be introduced [27–31]; see also [19]. For example, P may be an Au(III) chloride complex ion $[\mathrm{AuCl_4}]^-$, resulting from dissociation of tetrachloroauric acid ($\mathrm{HAuCl_4}$). According to (4), Au(III) is reduced first to Au(I) [33], appearing in a form of $[\mathrm{AuCl_2}]^- \equiv A$ complex ion, and subsequently reduced to zero-valent gold forming nanoclusters of various size, $(\mathrm{Au}^0)_i \equiv B_i$ [30].

Next, analogously to the case of the $A \rightarrow B$ reduction reaction, (4) can also have its catalytic counterpart [28],

$$P + R + B_i \rightarrow A + B_i + X_4. \tag{5}$$

Again, X_3 and X_4 denote additional products of reactions (4) and (5), respectively. Also, in open systems, the supply of R, P, or A molecules or B_i clusters ($i \geqslant 1$) by an external source (injection mechanism) may be present.

Many other generalizations of the above-defined model are obtained if Eqs. (1)–(5) are augmented by additional chemical reactions, or if more complex mechanisms of (1), (2), (4), or (5) reactions are considered, i.e., by taking into account more elementary reactions steps (cf. e.g., Ref. [34]). Some such extensions are discussed in Appendices A and B.

III. TIME-EVOLUTION EQUATIONS

We assume here that our system can be treated as spatially homogeneous ("perfect mixing" assumption). The validity of this assumption and its limitations are discussed in Sec. VII. Also, we assume that temperature is time independent (isothermic process). Under such conditions, a 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_ρ, c_π, c_α, and ξ_i, respectively, are the state variables of the present model [35].

The kinetics of chemical reactions (1), (2), (4), and (5) is modeled here in a way that is usual for the rate-equation approach, whereas in order to describe the kinetics of reversible aggregation (3), an approach based on the Smoluchowski coagulation equation [3–18] is employed. In effect, we obtain the following set of time-evolution equations for c_ρ, c_π, c_α, ξ_1, and ξ_k, $k > 1$:

$$\dot{c}_\rho = \dot{w}_\rho - \tilde{k}_\pi c_\pi - \sum_{j=1}^{\infty} \tilde{R}_j^{(\pi)} \xi_j c_\pi - \tilde{k}_\alpha c_\alpha - \sum_{j=1}^{\infty} \tilde{R}_j^{(\alpha)} \xi_j c_\alpha, \tag{6}$$

$$\dot{c}_\pi = \dot{w}_\pi - \tilde{k}_\pi c_\pi - \sum_{j=1}^{\infty} \tilde{R}_j^{(\pi)} \xi_j c_\pi, \tag{7}$$

$$\dot{c}_\alpha = \dot{w}_\alpha + \tilde{k}_\pi c_\pi + \sum_{j=1}^{\infty} \tilde{R}_j^{(\pi)} \xi_j c_\pi - \tilde{k}_\alpha c_\alpha - \sum_{j=1}^{\infty} \tilde{R}_j^{(\alpha)} \xi_j c_\alpha, \tag{8}$$

$$\begin{aligned} \dot{\xi}_1 = {} & \dot{w}_1 + \tilde{k}_\alpha c_\alpha - \tilde{R}_1^{(\alpha)} \xi_1 c_\alpha \\ & - \sum_{j=1}^{\infty} [K_{1j}\xi_1\xi_j - F_{1j}\xi_{1+j}], \end{aligned} \tag{9}$$

$$\begin{aligned} \dot{\xi}_k = {} & \dot{w}_k + \big(\tilde{R}_{k-1}^{(\alpha)}\xi_{k-1} - \tilde{R}_k^{(\alpha)}\xi_k\big)c_\alpha \\ & + \frac{1}{2}\sum_{ij}[K_{ij}\xi_i\xi_j - F_{ij}\xi_k] - \sum_{j}[K_{kj}\xi_k\xi_j - F_{kj}\xi_{k+j}]. \end{aligned} \tag{10}$$

The first sum in Eq. (10) is restricted to $i + j = k$. As usual, the dot denotes a time derivative, e.g., $\dot{\xi}_k \equiv d\xi_k/dt$, etc.

A. Reaction rate constants

The $\tilde{k}_\pi = \tilde{k}_\pi(c_\rho)$, $\tilde{R}_k^{(\pi)} = \tilde{R}_k^{(\pi)}(c_\rho)$, $\tilde{k}_\alpha = \tilde{k}_\alpha(c_\rho)$, and $\tilde{R}_k^{(\alpha)} = \tilde{R}_k^{(\alpha)}(c_\rho)$ functions appearing in Eqs. (6)–(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 (4), (5), (1), and (2), respectively [36]. For $k \geqslant 0$, each $\tilde{R}_k^{(\alpha)}(c_\rho)$ may be written as

$$\tilde{R}_k^{(\alpha)}(c_\rho) = R_k^{(\alpha)} f_k^{(\alpha)}(c_\rho), \tag{11}$$

where $\tilde{R}_0^{(\alpha)} \equiv \tilde{k}_\alpha$, $R_0^{(\alpha)} \equiv k_\alpha$, and similarly for $\tilde{R}_k^{(\pi)}$ and $R_k^{(\pi)}$. We assume at this point that each $f_k^{(\sigma)}(c_\rho)$ function ($\sigma = \alpha,\pi$; $k \geqslant 0$) can be expanded in power series in c_ρ,

$$f_k^{(\sigma)}(c_\rho) = a_{0,k}^{(\sigma)} + a_{1,k}^{(\sigma)} c_\rho + a_{2,k}^{(\sigma)} c_\rho^2 + \cdots . \tag{12}$$

Apparently, 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. (6)–(10) are valid only if the reducing agent appears in excess, i.e., $\max(c_\pi, c_\alpha) \ll c_\rho$. Consequently, the behavior of $f_k^{(\sigma)}(c_\rho)$ functions in the vicinity of $c_\rho = 0$ is not that essential. Still, we assume that $a_{1,k}^{(\sigma)} = 1$, which can always be achieved by rescaling $R_k^{(\sigma)}$. We emphasize that the presence of an excess of the reducing agent allows us to model all chemical reactions as irreversible processes. However, in some situations, nontrivial time dependence of c_ρ should be taken into account for the reasons explained in Sec. II.

The simplest form of $f_k^{(\sigma)}(c_\rho)$ is a linear function, $\tilde{R}_k^{(\sigma)} \equiv c_\rho R_k^{(\sigma)}$, i.e., $a_{m,k}^{(\sigma)} = 0$ for $m \neq 1$. For $k > 0$, i.e., for a catalytic ($\sigma = \pi$) or autocatalytic ($\sigma = \alpha$) reaction, this particular form of $\tilde{R}_k^{(\sigma)}$ corresponds to an 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; cf. e.g., [34]. In such situation, within an effective, approximate description, neglecting some elementary steps, or treating them within the steady-state approximation, terms nonlinear in c_ρ are present in (12) [37]. Higher-order terms are also important when the presence of the reducing agent influences the rate of chemical reactions indirectly, by changing the pH or ionic strength 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 $a_{0,k}^{(\sigma)} = 1$, and $a_{m,k}^{(\sigma)} = 0$ for $m \geqslant 1$.

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

$$f_k^{(\alpha)}(c_\rho) = f^{(\alpha)}(c_\rho). \tag{13}$$

The above assumption is crucial here, as it allows one to get rid of c_ρ dependence of the reaction rates; see below.

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

$$\begin{aligned} R_k^{(\alpha)} &= 0 \quad \text{for} \quad n = k, \\ R_k^{(\alpha)} &\neq 0 \quad \text{for} \quad 1 \leqslant k < n. \end{aligned} \tag{14}$$

Still, n may be arbitrarily large. The introduction of $n < \infty$ allows us to work with a finite system of equations (6)–(10). This is essential if we want to solve these equations numerically. Also, in any real system, we always deal with a finite number of particles, but this rather trivial observation can provide us only with a crude upper bound for n. However, there may be yet another reason for introducing finite n, if a sedimentation process takes place, effectively removing larger particles from the system. However, for most of the colloidal systems of interest, the time scale of sedimentation in a gravitational field is expected to be much larger than the characteristic time scale of chemical reactions.

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 [38], if necessary.

B. Coagulation and fragmentation kernels

$K_{ij} = K_{ji}$ and $F_{ij} = F_{ji}$ in Eqs. (9) and (10) denote the coagulation and fragmentation kernel, respectively.

What is important is that in systems of interest, the rate of the coagulation process may depend on the concentration of chemical species, and, therefore, within the present model, the c_ρ, c_π, or c_α 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 the pH or ionic strength of the solution caused by variable c_ρ, c_π, and c_α. The pH or ionic strength 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 than the one for $\tilde{k}_\pi$, $\tilde{R}_k^{(\pi)}$, $\tilde{k}_\alpha$, and $\tilde{R}_k^{(\alpha)}$.

C. Source terms

$\dot{w}_\rho$, $\dot{w}_\pi$, $\dot{w}_\alpha$, $\dot{w}_1$, and $\dot{w}_k$ appearing in Eqs. (6)–(10) are the source terms for R, P, and A molecules, monomers B_1, and the k-atom clusters B_k, respectively. The total amount of a given substance injected into the system in the time interval $(0,t)$ is given by

$$w_\sigma(t) = \int_0^t \dot{w}_\sigma(t')dt', \tag{15}$$

where $\sigma = \alpha,\pi,\rho$, or k. Clearly,

$$w_\sigma(0) = 0. \tag{16}$$

For reactions taking place in the homogeneous aqueous phase, it is natural to assume

$$\forall t : \dot{w}_\sigma(t) \geqslant 0, \tag{17}$$

and

$$\lim_{t\to\infty} w_\sigma(t) \equiv \bar{w}_\sigma < \infty. \tag{18}$$

However, condition (17) may be abandoned when the present model is used for the description of chemical reactions and physical processes taking place in reverse micelles [39]. In such situation, $\dot{w}_\sigma(t)$ terms may be used to model the kinetics of the intermicellar exchange process.

D. Initial conditions

Equations (6)–(10) have to be supplemented with appropriate initial conditions. First, from now on we assume

$$\xi_i(0) = 0, \;\; i > 1. \tag{19}$$

Consequently, values of only four parameters,

$$\begin{aligned} c_\rho(0) &\equiv b_0, \quad c_\pi(0) \equiv c_0, \\ c_\alpha(0) &\equiv d_0, \quad \xi_1(0) \equiv e_0, \end{aligned} \tag{20}$$

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

$$0 < c_0 + d_0 \equiv q_0 \ll b_0, \tag{21}$$

which also expresses the reducing agent excess condition.

The basic approach of Watzky and Finke ("two-step WF mechanism" [20]) as defined by (1) and (2) corresponds to $c_0 = e_0 = 0$, $d_0 \neq 0$. When additional preliminary steps (4) and (5) are taken into account, $c_0 \neq 0$. Regarding e_0, in the present paper two cases are considered, namely,

$$e_0 = 0 \quad \text{for} \quad \tilde{k}_\alpha \neq 0, \tag{22}$$

$$e_0 \neq 0 \quad \text{for} \quad \tilde{k}_\alpha = 0. \tag{23}$$

E. Conserved quantities

State variables c_ρ, c_π, c_α, and ξ_i are not independent. Namely, from Eqs. (7)–(10), we obtain

$$\begin{aligned} \dot{Q}_m(t) &\equiv \dot{c}_\pi(t) + \dot{c}_\alpha(t) + \sum_{j=1}^{\infty} j\dot{\xi}_j(t) \\ &\quad - \dot{w}_\pi(t) - \dot{w}_\alpha(t) - \sum_{j=1}^{\infty} j\dot{w}_j(t) = 0. \end{aligned} \tag{24}$$

Integrating Eq. (24), one gets

$$\begin{aligned} Q_m(t) &\equiv c_\pi(t) + c_\alpha(t) + \sum_{j=1}^{\infty} j\xi_j(t) \\ &\quad - w_\pi(t) - w_\alpha(t) - \sum_{j=1}^{\infty} jw_j(t) = q_0 + e_0, \end{aligned} \tag{25}$$

where (21) and the initial conditions (16) and (20) have been invoked. Equation (25) 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_i.

From Eqs. (6)–(8), yet another relation follows. Namely, we have

$$\begin{aligned} \dot{Q}_r(t) &\equiv \dot{c}_\rho(t) - 2\dot{c}_\pi(t) - \dot{c}_\alpha(t) \\ &\quad - \dot{w}_\rho(t) + 2\dot{w}_\pi(t) + \dot{w}_\alpha(t) = 0. \end{aligned} \tag{26}$$

Making use of Eqs. (16), (20), and (26), we obtain

$$\begin{aligned} Q_r(t) &\equiv c_\rho(t) - 2c_\pi(t) - c_\alpha(t) \\ &\quad - w_\rho(t) + 2w_\pi(t) + w_\alpha(t) = b_0 - 2c_0 - d_0. \end{aligned} \tag{27}$$

F. Stationary solution

The stationary solution [40] of Eqs. (6)–(10) is defined by the following condition:

$$\dot{c}_\rho = \dot{c}_\pi = \dot{c}_\alpha = \dot{\xi}_1 = \dot{\xi}_2 = \cdots = \dot{\xi}_n = 0. \tag{28}$$

Stationary values of the state variables will be denoted by a bar, e.g., $\bar{c}_\alpha$. Due to (18) and the irreversible character of reactions (1), (2), (4), and (5), we have $\dot{c}_\pi = \dot{c}_\alpha = \dot{c}_\rho = 0$ only if

$$\bar{c}_\pi = \lim_{t\to\infty} c_\pi(t) = 0, \quad \bar{c}_\alpha = \lim_{t\to\infty} c_\alpha(t) = 0. \tag{29}$$

As a consequence of Eqs. (29), from Eq. (25) we obtain

$$\sum_{j=1}^{\infty} j\bar{\xi}_j = \bar{w}_\pi + \bar{w}_\alpha + \sum_{j=1}^{\infty} j\bar{w}_j + c_0 + d_0 + e_0. \tag{30}$$

Note that Eq. (30) follows from the existence of the constant of motion, and therefore the value of the sum $\sum_{j=1}^{\infty} j\bar{\xi}_j$ does not depend on the choice of $\tilde{k}_\pi$, $\tilde{R}_k^{(\pi)}$, $\tilde{k}_\alpha$, $\tilde{R}_k^{(\alpha)}$, or K_{ij} and F_{ij} functions.

This is not the case for individual $\bar{\xi}_j$, however. In the general situation, the stationary value of each $\bar{\xi}_j$ depends on the choice of K_{ij} and F_{ij} [41]. Still, as will be shown below, in the absence of both cluster source terms ($\dot{w}_j = 0$) 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 the following model parameters: n, q_0, e_0, $\tilde{k}_\alpha$, and $\tilde{R}_k^{(\alpha)}$ for $k = 1, \ldots, n-1$. Its form depends neither on $\tilde{k}_\pi$, $\tilde{R}_k^{(\pi)}$, nor on $\dot{w}_\rho$, $\dot{w}_\pi$, and $\dot{w}_\alpha$.

Finally, $\bar{c}_\rho$ can be found from (27) and (29); we get

$$\bar{c}_\rho = \bar{w}_\rho - 2\bar{w}_\pi - \bar{w}_\alpha + b_0 - 2c_0 - d_0. \tag{31}$$

G. Method of moments

In some situations, in order to analyze the properties of Eqs. (6)–(10), it is useful to rewrite these equations in terms of new variables. The μth moment of the cluster mass distribution is defined as

$$M_\mu(t) = \sum_{j=1}^{\infty} j^\mu \xi_j(t). \tag{32}$$

The presence of variable $c_\rho(t)$, source terms $\dot{w}_\sigma$, or a chemical reaction not involving B_i clusters [42] does not affect the form of the 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 $\dot{w}_k$. If the latter are present, instead of Eq. (6) of Ref. [19], we then have [43]

$$\begin{aligned} \dot{M}_\mu &= \sum_{j=1} j^\mu \dot{w}_j + \tilde{k}_\alpha c_\alpha + \sum_{j=1} \tilde{\mathcal{G}}_j^{(\mu)} \xi_j c_\alpha \\ &\quad + \sum_{p,q} \tilde{\mathcal{S}}_{pq}^{(\mu)} \xi_p \xi_q + \sum_{p=2} \tilde{\mathcal{T}}_p^{(\mu)} \xi_p. \end{aligned} \tag{33}$$

In Eq. (33), $\tilde{\mathcal{S}}_{pq}^{(\mu)} = \tilde{\mathcal{S}}_{qp}^{(\mu)} \equiv \frac{1}{2}[(p+q)^\mu - p^\mu - q^\mu]K_{pq}$, $\tilde{\mathcal{T}}_p^{(\mu)} \equiv \sum_{i=1}^{p-1}(i^\mu - \frac{1}{2}p^\mu)F_{i,p-i}$, and $\tilde{\mathcal{G}}_j^{(\mu)} \equiv [(j+1)^\mu - j^\mu]\tilde{R}_j^{(\alpha)}$. The analysis of the general qualitative properties of Eq. (33), provided in Sec. III of Ref. [19], remains valid here with only minor modifications. Namely, first, the initial conditions for Eq. (33) now read $M_\mu(0) = e_0$. Also, the stationary value of M_1, i.e., $\bar{M}_1 \equiv \lim_{t\to\infty} M_1(t)$, is now given by (30).

The remaining part of Sec. III of Ref. [19] can also be generalized in an obvious manner. Equations (33) for various μ, supplemented by time-evolution equations for c_ρ, c_π, and c_α, can be given a closed, tractable form, analogous to Eqs. (8)–(11) of Ref. [19], if a restriction is imposed on the parameter n appearing in (14), μ, as well as the values of the model parameters, namely, $n = \infty$, $\mu \in \mathbb{N} \cup 0$, $F_{ij} \equiv 0$, and $\tilde{R}_i^{(\pi)}$, $\tilde{R}_i^{(\alpha)}$, K_{ij} given by

$$K_{ij} = \kappa_0 + \kappa_1(i+j) + \kappa_2 ij, \quad \tilde{R}_i^{(\sigma)} = \tilde{a}_R^{(\sigma)} i + \tilde{b}_R^{(\sigma)}. \tag{34}$$

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

IV. ABSENCE OF COAGULATION

A. General remarks

An important simplification of the present model is obtained if coagulation and fragmentation processes are neglected. For transition-metal nanocluster growth in solution, such an assumption is justified in some situations. First, if a stabilizing agent such as polyvinyl alcohol (PVA) or polyvinylopyrrolidone (PVP) is present in a system, coagulation is severely limited or even entirely absent [29,31]. Second, if the nanocluster have a nonzero surface charge, then the resulting repulsing electrostatic interactions between clusters may prevent coagulation. Third, lack of coagulation may be a reasonable approximation for nanoparticle growth in reverse micelles, where the geometry or size of the micelle water pool prohibits coagulation, at least to some extent. From now on, we also assume that there is no injection of the nanoclusters. As a consequence, for $K_{ij} = F_{ij} = 0$ and $\dot{w}_k = 0$, Eq. (9) takes the form

$$\dot{\xi}_1 = c_\alpha\big(\tilde{k}_\alpha - \tilde{R}_1^{(\alpha)}\xi_1\big), \tag{35}$$

whereas for $1 < k < n$ from Eq. (10), we obtain

$$\dot{\xi}_k = c_\alpha\big(\tilde{R}_{k-1}^{(\alpha)}\xi_{k-1} - \tilde{R}_k^{(\alpha)}\xi_k\big). \tag{36}$$

Note that the presence of $c_\alpha(t)$ in Eqs. (35) and (36) makes this system of time-evolution equations nontrivial. Only for $c_\alpha(t) = \text{const}$ do we obtain a system of *linear* equations that are investigated, e.g., in Ref. [44]; cf. [45].

It is convenient to consider the $k = n$ separately [46]. Invoking Eqs. (14) and (36), we get

$$\dot{\xi}_n = c_\alpha \tilde{R}_{n-1}^{(\alpha)}\xi_{n-1}. \tag{37}$$

We may expect that, in general, $\xi_n(t) \neq 0$ 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 should have $\xi_i(t) = 0$, regardless of the values of the corresponding coefficients $\tilde{R}_i^{(\alpha)}$ [47]. In other words, n-mers are the largest clusters appearing in a system and, hence, for $n < \infty$, we should expect some kind of "finite-size" effects in the solutions of Eqs. (35)–(37).

Note that the rhs of Eq. (35), each of Eqs. (36), and Eq. (37) do not depend explicitly on time. Dividing (36) by (35), we obtain

$$\frac{d\xi_k}{d\xi_1} = \frac{\tilde{R}_{k-1}^{(\alpha)}\xi_{k-1} - \tilde{R}_k^{(\alpha)}\xi_k}{\tilde{k}_\alpha - \tilde{R}_1^{(\alpha)}\xi_1} = \frac{R_{k-1}^{(\alpha)}\xi_{k-1} - R_k^{(\alpha)}\xi_k}{k_\alpha - R_1^{(\alpha)}\xi_1}, \tag{38}$$

whereas for $k = n$, from (37) and (35) we find

$$\frac{d\xi_n}{d\xi_1} = \frac{\tilde{R}_{n-1}^{(\alpha)}\xi_{n-1}}{\tilde{k}_\alpha - \tilde{R}_1^{(\alpha)}\xi_1} = \frac{R_{n-1}^{(\alpha)}\xi_{n-1}}{k_\alpha - R_1^{(\alpha)}\xi_1}. \tag{39}$$

Note also that neither c_α nor c_ρ appear in (38) and (39); for c_ρ, this follows from Eq. (13). Equations (38) and (39) form a finite ($n < \infty$) or infinite ($n = \infty$) set of linear ordinary differential equations. Their solutions, denoted

$$\begin{aligned} \xi_k &\equiv s_k(\xi_1), \quad k < n, \\ \xi_n &\equiv u_n(\xi_1), \\ \xi_i &= 0, \quad i > n, \end{aligned} \tag{40}$$

provide information about the structure of the cluster "mass spectrum". Importantly, the $s_k(\xi_1)$ functions do not depend on n. What is also important is that the form of Eqs. (38) and (39) and, consequently, the functional form of $s_k(\xi_1)$ and $u_n(\xi_1)$ (40) do not depend on the presence of any chemical reaction, which either does not involve B_i clusters [e.g., Eq. (4)] or in which B_i play a role of a passive catalyst [e.g., Eq. (5)]. In fact, an 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 $\tilde{k}_\pi$ and $\tilde{R}_j^{(\pi)}$. Moreover, for the latter parameters, no assumption such as (13) is needed.

On the other hand, obviously, the time evolution of ξ_1, c_α, c_ρ, and c_π depends, in general, on the values of all model parameters, including those which do not change the "structural" relations (40).

Even if the knowledge of the explicit form of the $s_k(\xi_1)$ 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 the case of polymer systems, the asymptotic molecular weight distribution). Namely, using (30), we obtain

$$\begin{aligned} \bar{M}_1 &= \bar{\xi}_1 + \sum_{i=2}^{n-1} i s_i(\bar{\xi}_1) + n u_n(\bar{\xi}_1) \\ &= \bar{w}_\pi + \bar{w}_\alpha + c_0 + d_0 + e_0, \end{aligned} \tag{41}$$

where $\bar{\xi}_1 \equiv \lim_{t\to\infty} \xi_1(t)$. Equation (41) allows (in practice only numerically) one to determine $\bar{\xi}_1$ and, therefore, each $\bar{\xi}_k$. In many applications (e.g., in modeling of the nanocluster fabrication or some polymerization processes), this may be much more interesting than any details of the time evolution of the system. Also for this reason, the 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 $R_1^{(\alpha)}, R_2^{(\alpha)}, \ldots, R_{n-1}^{(\alpha)}$, some relations between ξ_1 and other state variables (M_0, M_1, and c_α) will be presented.

B. The $\tilde{k}_\alpha \neq 0$, $e_0 = 0$ case

1. Relations between M_0, ξ_1, and c_α

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

$$\dot{M}_0 = \tilde{k}_\alpha c_\alpha. \tag{42}$$

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

$$\frac{\dot{\xi}_1}{\dot{M}_0} = \frac{d\xi_1}{dM_0} = 1 - \frac{\omega}{q_0}\xi_1. \tag{43}$$

Dimensionless parameter ω in Eq. (43) is defined by

$$\frac{\omega}{q_0} = \frac{\tilde{R}_1^{(\alpha)}}{\tilde{k}_\alpha} = \frac{R_1^{(\alpha)}}{k_\alpha}. \tag{44}$$

Equation (43) can be easily solved, to get

$$\xi_1 = h_0(M_0) = \frac{q_0}{\omega}\left[1 - \exp\left(-\frac{\omega}{q_0}M_0\right)\right]; \tag{45}$$

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 $R_k^{(\alpha)}$ parameters, if only $R_1^{(\alpha)} \neq 0$.

Next, for $c_\rho(t) = c_\rho(0)$, from Eqs. (35) and (42) we obtain

$$\begin{aligned}\int_0^{\xi_1} \frac{d\xi}{\tilde{k}_\alpha - \tilde{R}_1^{(\alpha)}\xi} &= -\frac{1}{\tilde{R}_1^{(\alpha)}} \ln\left(1 - \frac{R_1^{(\alpha)}\xi_1}{k_\alpha}\right)\\ &= \frac{M_0}{\tilde{k}_\alpha} = \int_0^t c_\alpha(t')dt' \geqslant 0.\end{aligned} \tag{46}$$

In a more general case of time-dependent c_ρ, instead of Eq. (46) we have

$$\begin{aligned}\int_0^{\xi_1} \frac{d\xi}{k_\alpha - R_1^{(\alpha)}\xi} &= -\frac{1}{R_1^{(\alpha)}} \ln\left(1 - \frac{R_1^{(\alpha)}\xi_1}{k_\alpha}\right)\\ &= \int_0^t f^{(\alpha)}(c_\rho(t'))c_\alpha(t')dt'.\end{aligned} \tag{47}$$

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

$$\xi_1(t) < \frac{q_0}{\omega}, \quad t \geqslant 0. \tag{48}$$

For $\tilde{k}_\alpha \neq 0$, $e_0 = 0$, and $c_\alpha(0) = d_0 \neq 0$, inequality (48) follows also from the fact that $\xi_1(0) = 0$, and therefore Eq. (35) implies that $\dot{\xi}_1(0) > 0$. This, in turn, implies that $\dot{\xi}_1(t) > 0$ for $t \in (0,\infty)$.

2. ξ_k as a function of ξ_1

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

$$\frac{d\xi_k}{d\xi_1} = \frac{r_{k-1}\xi_{k-1} - r_k\xi_k}{\lambda - r_1\xi_1}, \tag{49}$$

where

$$\lambda \equiv \frac{k_\alpha}{\mathcal{R}} = r_1\frac{q_0}{\omega}, \quad r_i \equiv \frac{R_i^{(\alpha)}}{\mathcal{R}}, \tag{50}$$

and $\mathcal{R}$ is a constant of the same dimension as $R_k^{(\alpha)}$, e.g., one may take $\mathcal{R} = R_1^{(\alpha)}$. Introducing new variables

$$\begin{aligned} x = y_1 &= \frac{r_1}{\lambda}\xi_1 - 1 = \frac{\omega}{q_0}\xi_1 - 1 = -e^{-\frac{\omega}{q_0}M_0},\\ y_k &= \frac{r_k}{\lambda}\xi_k - 1 = \frac{r_k}{r_1}\frac{\omega}{q_0}\xi_k - 1,\end{aligned} \tag{51}$$

$-1 \leqslant x < 0$, we may rewrite (49) as

$$\frac{dy_k}{dx} = \frac{r_k}{r_1}\left(\frac{y_k - y_{k-1}}{x}\right). \tag{52}$$

In terms of y_i variables, initial conditions (19) read

$$y_k(-1) = -1, \quad k \geqslant 2. \tag{53}$$

For $k = 2,3,\ldots$, Eqs. (52) 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. (14)], therefore $r_{k-1} \neq 0$, $r_k \neq 0$. The $k = n$ case will be discussed separately.

Solution of Eqs. (52) for arbitrary $k < n$ can be inferred by analyzing the form of $y_k(x)$ for $k \leqslant 4$. We find

$$\begin{aligned} y_k(x) &= (-1)^k \sum_{j=1}^{k}\left[\frac{\prod_{l=1}^k r_l}{r_j\prod_{m\neq j}(r_j - r_m)}(-x)^{\frac{r_j}{r_1}}\right]\\ &= \frac{1}{V_k}\sum_{j=1}^{k}(-1)^j\left(\frac{\prod_{l=1}^k r_l}{r_j}\right)V_{k-1}^{(j)}(-x)^{\frac{r_j}{r_1}}\\ &= -\frac{\mathcal{V}_k(x)}{\mathcal{V}_k(-1)},\end{aligned} \tag{54}$$

where

$$\mathcal{V}_k(x) = \begin{vmatrix} (-x)^{\frac{r_1}{r_1}} & r_1 & r_1^2 & \cdots & r_1^{k-2} & r_1^{k-1}\\ (-x)^{\frac{r_2}{r_1}} & r_2 & r_2^2 & \cdots & r_2^{k-2} & r_2^{k-1}\\ (-x)^{\frac{r_3}{r_1}} & r_3 & r_3^2 & \cdots & r_3^{k-2} & r_3^{k-1}\\ \vdots & \vdots & \vdots & \ddots & \vdots & \vdots\\ (-x)^{\frac{r_k}{r_1}} & r_k & r_k^2 & \cdots & r_k^{k-2} & r_k^{k-1} \end{vmatrix}, \tag{55}$$

whereas $V_{k-1}^{(i)}$ and $V_k = \mathcal{V}_k(-1)$ are Vandermonde determinants with $k - 1$ and k rows, respectively,

$$V_{k-1}^{(i)} = \begin{vmatrix} 1 & r_1 & r_1^2 & \cdots & r_1^{k-3} & r_1^{k-2}\\ 1 & r_2 & r_2^2 & \cdots & r_2^{k-3} & r_2^{k-2}\\ \vdots & \vdots & \vdots & \ddots & \vdots & \vdots\\ 1 & r_{i-1} & r_{i-1}^2 & \cdots & r_{i-1}^{k-3} & r_{i-1}^{k-2}\\ 1 & r_{i+1} & r_{i+1}^2 & \cdots & r_{i+1}^{k-3} & r_{i+1}^{k-2}\\ \vdots & \vdots & \vdots & \ddots & \vdots & \vdots\\ 1 & r_k & r_k^2 & \cdots & r_k^{k-3} & r_k^{k-2} \end{vmatrix}, \tag{56}$$

$$V_k = \begin{vmatrix} 1 & r_1 & r_1^2 & \cdots & r_1^{k-2} & r_1^{k-1}\\ 1 & r_2 & r_2^2 & \cdots & r_2^{k-2} & r_2^{k-1}\\ 1 & r_3 & r_3^2 & \cdots & r_3^{k-2} & r_3^{k-1}\\ \vdots & \vdots & \vdots & \ddots & \vdots & \vdots\\ 1 & r_k & r_k^2 & \cdots & r_k^{k-2} & r_k^{k-1} \end{vmatrix}. \tag{57}$$

From the last line of Eq. (54), it should be obvious that the initial condition (53) is indeed satisfied for each k. The correctness of this compact form of $y_k(x)$ may be in turn verified by simple algebraic manipulations, involving Laplace expansion of $\mathcal{V}_k(x)$ [48]. Eventually, returning to the original variables, from (51) and (54) we obtain

$$\xi_k = s_k(\xi_1) = \frac{r_1}{r_k}\frac{q_0}{\omega}\left[1 - \frac{\mathcal{V}_k(\frac{\omega}{q_0}\xi_1 - 1)}{\mathcal{V}_k(-1)}\right]. \tag{58}$$

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 (51) in the present case, we assume that $r_n \neq 0$, but disregard the term proportional to R_n on the rhs of Eq. (38). This may be formally achieved by rewriting Eq. (49) for $k = n$ as

$$\frac{d\xi_n}{d\xi_1} = \frac{r_{n-1}\xi_{n-1} - c r_n \xi_n}{\lambda - r_1\xi_1}, \tag{59}$$

and putting $c = 0$. Making use of (51) again, we get

$$\frac{dy_n}{dx} = -\frac{r_n}{r_1}\left(\frac{1}{x} + \frac{y_{n-1}}{x}\right), \tag{60}$$

where $y_{n-1}(x)$ is given by Eq. (54) and the initial conditions (53) read $y_n(-1) = -1$. Equation (60) can be integrated in a straightforward manner to get

$$\begin{aligned} y_n(x) = \sum_{j=1}^{n-1} \frac{\prod_{l=1}^{n} r_l}{r_j^2}(-1)^j \frac{V_{n-2}^{(j)}}{V_{n-1}}\left[1 - (-x)^{\frac{r_j}{r_1}}\right] \\ - \frac{r_n}{r_1}\ln(-x) - 1. \end{aligned} \tag{61}$$

In terms of ξ_n and either ξ_1 or M_0, we obtain

$$\begin{aligned} \xi_n = u_n(\xi_1) &= -\frac{q_0}{\omega}\ln\left(1 - \frac{\omega}{q_0}\xi_1\right) \\ &\quad + \frac{q_0}{\omega}r_1 \sum_{j=1}^{n-1} \frac{(-1)^j \prod_{l=1}^{n-1} r_l}{r_j^2}\frac{V_{n-2}^{(j)}}{V_{n-1}}\left[1 - \left(1 - \frac{\omega}{q_0}\xi_1\right)^{\frac{r_j}{r_1}}\right] \\ &= M_0 + \frac{q_0}{\omega}r_1 \sum_{j=1}^{n-1} \frac{(-1)^j \prod_{l=1}^{n-1} r_l}{r_j^2}\frac{V_{n-2}^{(j)}}{V_{n-1}}\left[1 - e^{-\frac{\omega}{q_0}\frac{r_j}{r_1}M_0}\right]. \end{aligned} \tag{62}$$

Please note that r_n does not appear in Eq. (62).

3. *Special case: $r_j = j$*

For the linear reaction kernel ($r_j = j$) analyzed in detail in Ref. [19], from Eq. (54) we obtain

$$\begin{aligned} y_k(x) &= (-1)^k \sum_{j=1}^{k} \frac{k!}{j\prod_{m\neq j}(j-m)}(-x)^j \\ &= (-1)^k \sum_{j=1}^{k} \frac{(-1)^{k-j}k!}{j(k-j)!(j-1)!}(-x)^j \\ &= -1 + \sum_{j=0}^{k}\binom{k}{j}x^j = (x+1)^k - 1. \end{aligned} \tag{63}$$

Taking into account Eq. (51), for $k < n$ we find

$$\xi_k(\xi_1) = \frac{\lambda}{r_k}\left(\frac{r_1}{\lambda}\xi_1\right)^k = \frac{1}{k}\frac{q_0}{\omega}\left(\frac{\omega}{q_0}\xi_1\right)^k, \tag{64}$$

in agreement with Eq. (21) of Ref. [19]. For $k = n$, from Eq. (61) we get

$$y_n(x) = n\sum_{j=1}^{n-1}\frac{1}{j}\binom{n-1}{j}[(-1)^j - x^j] - n\ln(-x) - 1, \tag{65}$$

and therefore

$$\begin{aligned} \xi_n = u_n(\xi_1) &= -\frac{q_0}{\omega}\ln\left(1 - \frac{\omega}{q_0}\xi_1\right) \\ &\quad + \frac{q_0}{\omega}\sum_{j=1}^{n-1}\frac{1}{j}\binom{n-1}{j}\left[(-1)^j - \left(\frac{\omega}{q_0}\xi_1 - 1\right)^j\right]. \end{aligned} \tag{66}$$

C. The $\tilde{k}_\alpha = 0$, $e_0 \neq 0$ case

In this section, we analyze a situation when the $A \rightarrow B_1$ reaction (1) is absent, i.e., $\tilde{k}_\alpha = 0$. This case may be relevant to the problem of modeling certain polymerization processes, as well as for the description of growth of the core-shell-type nanoparticles.

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 $e_0 \equiv \xi_1(0) \neq 0$.

1. *Time dependence of M_0, and relations between ξ_1 and c_α*

For $\tilde{k}_\alpha = 0$, Eq. (33) has a simple form,

$$\dot{M}_0 = 0. \tag{67}$$

Integrating (67), and taking Eqs. (19) and (20) into account, we get

$$M_0(t) = M_0(0) = e_0. \tag{68}$$

For constant $c_\rho(t) = c_\rho(0)$ from Eq. (35), we obtain

$$\begin{aligned} -\frac{1}{\tilde{R}_1^{(\alpha)}}\int_{e_0}^{\xi_1}\frac{d\xi}{\xi} &= -\frac{1}{\tilde{R}_1^{(\alpha)}}\ln\left(\frac{\xi_1}{e_0}\right) \\ &= \int_0^t c_\alpha(t')dt' \geqslant 0. \end{aligned} \tag{69}$$

Analogously to Eq. (46), Eq. (69) expresses a 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 be a decreasing function of time; condition $\dot{\xi}_1(t) \leqslant 0$ clearly follows from Eq. (35). Therefore, for $t \geqslant 0$, we have

$$\xi_1(t) \leqslant e_0. \tag{70}$$

Inequality (70) follows also from Eq. (69) in a straightforward manner.

2. *ξ_k as a function of ξ_1*

As a next step, we determine the functional form of the k-mer concentration ξ_k as a function of ξ_1. However, in the present situation, we cannot make use of the results derived for

$\tilde{k}_\alpha \neq 0$ because now $\lambda = 0$ and transformation (51) becomes singular.

Dividing (36) by (35), we obtain

$$\frac{d\xi_k}{d\xi_1} = \frac{r_k\xi_k - r_{k-1}\xi_{k-1}}{r_1\xi_1}, \tag{71}$$

where r_i are defined by Eq. (50). In the present case, we define auxiliary variables y_k and $y_1 \equiv x$ as follows:

$$x = y_1 = \frac{\xi_1}{e_0}, \quad y_k = \frac{r_k}{r_1}\frac{\xi_k}{e_0}, \tag{72}$$

$0 < x \leqslant 1$. Making use of (72), we rewrite (71) as

$$\frac{dy_k}{dx} = \frac{r_k}{r_1}\left(\frac{y_k - y_{k-1}}{x}\right). \tag{73}$$

Note that although Eq. (73) has exactly the same form as Eq. (52), now not only are x and y_k defined differently, but also instead of (53) we have

$$y_k(1) = 0, \quad k \geqslant 2. \tag{74}$$

Again, (74) corresponds to initial conditions (19) for the ξ_k variables.

As in the $\tilde{k}_\alpha \neq 0$, $e_0 = 0$ case, we first consider $k < n$ [cf. Eq. (14)]; the $k = n$ case will be discussed separately. Also in the present situation, the solution of Eq. (73) for arbitrary $k < n$ can be inferred simply by solving this equation for $k = 2,3$, and 4. We find

$$\begin{aligned} y_k(x) &= (-1)^{k+1}\left(\prod_{l=2}^{k} r_l\right)\sum_{j=1}^{k}\left[\frac{x^{\frac{r_j}{r_1}}}{\prod_{m\neq j}(r_j - r_m)}\right] \\ &= -\left(\prod_{l=2}^{k} r_l\right)\sum_{j=1}^{k}(-1)^j\frac{V_{k-1}^{(j)}}{V_k}x^{\frac{r_j}{r_1}}, \end{aligned} \tag{75}$$

where $V_{k-1}^{(j)}$ and V_k are defined by Eqs. (56) and (57). The initial condition (74) follows easily from the basic properties of determinants (orthogonality of the Laplace expansion). Eventually, from (72) and (75) we obtain

$$\xi_k = s_k(\xi_1) = -e_0\left(\prod_{l=1}^{k-1} r_l\right)\sum_{j=1}^{k}\frac{(-1)^j V_{k-1}^{(j)}}{V_k}\left(\frac{\xi_1}{e_0}\right)^{\frac{r_j}{r_1}}. \tag{76}$$

In order to analyze the $k = n$ case, we again assume $r_n \neq 0$; however, we disregard the appropriate terms on the rhs of (71). As a consequence, from Eqs. (71) and (72), we obtain

$$\frac{dy_n}{dx} = -\frac{r_n}{r_1}\frac{y_{n-1}}{x}, \tag{77}$$

where now $y_{n-1}(x)$ is given by Eq. (75) and the initial condition (74) is $y_n(1) = 0$. The solution of Eq. (77) reads

$$y_n(x) = \left(\prod_{l=2}^{n} r_l\right)\sum_{j=1}^{n-1}\frac{(-1)^j}{r_j}\frac{V_{n-2}^{(j)}}{V_{n-1}}\left[x^{\frac{r_j}{r_1}} - 1\right]. \tag{78}$$

Using Eqs. (78) and (72), we finally get

$$\begin{aligned} \xi_n &= u_n(\xi_1) \\ &= e_0\sum_{j=1}^{n-1}\frac{(-1)^j\prod_{l=1}^{n-1} r_l}{r_j}\frac{V_{n-2}^{(j)}}{V_{n-1}}\left[\left(\frac{\xi_1}{e_0}\right)^{\frac{r_j}{r_1}} - 1\right]. \end{aligned} \tag{79}$$

3. *Special case:* $r_j = j$

For $r_j = j$, $y_k(x)$ as given by Eq. (75) reads

$$\begin{aligned} y_k(x) &= -\sum_{j=1}^{k}\frac{(-1)^j k!}{(k-j)!(j-1)!}x^j \\ &= -x\frac{d}{dx}[(1-x)^k - 1] \\ &= kx(1-x)^{k-1}. \end{aligned} \tag{80}$$

Making use of Eq. (72), for $k < n$ we find

$$\xi_k \equiv s_k(\xi_1) = \xi_1\left(1 - \frac{\xi_1}{e_0}\right)^{k-1}. \tag{81}$$

Obviously, $s_k(e_0) = 0$ for $k \geqslant 2$, as it should be. Next, for $k = n$, Eq. (78) now reads

$$y_n(x) = n\sum_{j=1}^{n-1}(-1)^j\binom{n-1}{j}(x^j - 1) = n(1-x)^{n-1}. \tag{82}$$

From Eqs. (72) and (82), we obtain

$$\xi_n = u_n(\xi_1) = e_0\left(1 - \frac{\xi_1}{e_0}\right)^{n-1}. \tag{83}$$

It could be easily verified that Eq. (68) is indeed obeyed, both for $n = \infty$ and for $n < \infty$. In the former case, from (81) we also obtain

$$M_1 \equiv g_1(\xi_1) = \sum_{k=1}^{\infty} k\xi_1\left(1 - \frac{\xi_1}{e_0}\right)^{k-1} = \frac{e_0^2}{\xi_1}, \tag{84}$$

whereas in the latter we have

$$\begin{aligned} M_1 &\equiv g_1^{(n)}(\xi_1) = n\xi_n + \sum_{k=1}^{n-1} k\xi_k \\ &= ne_0\left(1 - \frac{\xi_1}{e_0}\right)^{n-1} + \xi_1\sum_{k=1}^{n-1} k\left(1 - \frac{\xi_1}{e_0}\right)^{k-1} \\ &= \frac{e_0^2}{\xi_1}\left[1 - \left(1 - \frac{\xi_1}{e_0}\right)^{n}\right]. \end{aligned} \tag{85}$$

In the 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. The correctness of Eq. (85) can also be verified by invoking Eq. (33) for $\mu = 1$. Namely, in the present case, $\tilde{\mathcal{G}}_j^{(1)} = j\tilde{R}_1^{(\alpha)}$, $\tilde{\mathcal{G}}_n^{(1)} = 0$, therefore we have

$$\dot{M}_1 = \tilde{R}_1^{(\alpha)}\sum_{j=1}^{n-1} j\xi_j c_\alpha = \left(-n\xi_n + \sum_{j=1}^{n} j\xi_j\right)\tilde{R}_1^{(\alpha)} c_\alpha. \tag{86}$$

Equation (86) divided by Eq. (35) yields

$$\frac{dM_1}{d\xi_1} = \frac{n\xi_n - M_1}{\xi_1}, \tag{87}$$

which is indeed obeyed for $M_1 = g_1^{(n)}(\xi_1)$ given by (85) and $\xi_n = u_n(\xi_1)$ given by (83).

Finally, for $n = \infty$, the asymptotic cluster-size distribution $\xi_1, \xi_2, \ldots$ can be easily obtained by combining Eqs. (30), (81), and (84). In the simplest case, for $c_0 = 0$ and when no source terms are present, we obtain

$$\bar{\xi}_k = \frac{e_0^2}{d_0}\left(\frac{d_0}{d_0 + e_0}\right)^k. \tag{88}$$

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 $r_1, r_2, \ldots, r_{n-1}$, i.e., $r_j \neq r_i$ for $j \neq i$. The 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_i appears in a natural manner, when one describes a colloidal system by referring only to the total mass (or concentration) of the zero-valent transition-metal atoms, M_1, and not by making use of the k-mer concentrations, ξ_k; cf. Refs. [20–23]. 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, the linear dependence of r_j on j has no real physical justification. The more general, but still very simple, form of r_j is the power-law dependence

$$r_j \propto j^\zeta, \tag{89}$$

$0 \leqslant \zeta \leqslant 1$. There are two simple cases of r_j (89), which are nonetheless more realistic than the $\zeta = 1$ case, namely, diffusion-limited growth ($\zeta = \frac{1}{3}$) and reaction-limited growth ($\zeta = \frac{2}{3}$) [49]. Another special case of (89), the size-independent reaction kernel ($\zeta = 0$), seems to be a reasonable approximation for the modeling of growth of some linear polymers, but not for colloidal particles. The $\zeta = 0$ case of (89) 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.

The above remarks apply also to the $R_i^{(\pi)}$ 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. (58) and (62), or (76) and (79), makes the solution of the original time-evolution equations (6)–(10) feasible even for a 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. (6) and (7) (if present), and Eq. (8) together with either Eq. (9) or any of Eqs. (10) for $k \geqslant 2$, including the $k = n$ case.

Note that two state variables and therefore two corresponding evolution equations can be eliminated by invoking Eqs. (25) and (27). Consequently, in some situations, e.g., for $R_i^{(\pi)} = \dot{w}_\pi = 0$, when Eq. (7) has an obvious solution $c_\pi(t) = c_\pi(0)\exp(-\tilde{k}_\pi t)$, we are left with only one equation for a single unknown function, say $\xi_1(t)$ [50],

$$\dot{\xi}_1 = \left(\tilde{k}_\alpha - \tilde{R}_1^{(\alpha)}\xi_1\right)\left(d_0 - \sum_{j=1}^{\infty} j\tilde{R}_j^{(\alpha)} s_j\right). \tag{90}$$

In the above equation, both s_j and $\tilde{k}_\alpha$, $\tilde{R}_j^{(\alpha)}$ depend, in the general case, on ξ_1, but may also depend explicitly on time. If $c_0 = 0$ and no source terms are present, neither $\tilde{k}_\alpha$ nor $\tilde{R}_j^{(\alpha)}$ depend explicitly on time, and from (90) we obtain

$$\int_{e_0}^{\xi_1} \frac{d\xi}{\left(\tilde{k}_\alpha - \tilde{R}_1^{(\alpha)}\xi\right)\left[d_0 - \sum_{j=1}^{\infty} j\tilde{R}_j^{(\alpha)} s_j(\xi)\right]} = t. \tag{91}$$

However, in a general case, the solution of (91) cannot be expressed in terms of elementary functions or standard special functions. When $c_0 \neq 0$ or variable $c_\rho(t)$ is considered, the situation becomes even worse. Therefore, usually we have to depend on the numerical analysis [51]. Yet, in such case, it is generally not advised to eliminate any variables by using constraints. As a consequence, we have to numerically solve the following equations:

$$\begin{aligned}\dot{c}_\rho = \dot{w}_\rho - \tilde{k}_\pi c_\pi - \sum_{j=1}^{n-1} \tilde{R}_j^{(\pi)} s_j(\xi_1) c_\pi - \tilde{R}_n^{(\pi)} u_n(\xi_1) c_\pi \\ - \tilde{k}_\alpha c_\alpha - \sum_{j=1}^{n-1} \tilde{R}_j^{(\alpha)} s_j(\xi_1) c_\alpha,\end{aligned} \tag{92}$$

$$\dot{c}_\pi = \dot{w}_\pi - \tilde{k}_\pi c_\pi - \sum_{j=1}^{n-1} \tilde{R}_j^{(\pi)} s_j(\xi_1) c_\pi - \tilde{R}_n^{(\pi)} u_n(\xi_1) c_\pi, \tag{93}$$

$$\begin{aligned}\dot{c}_\alpha = \dot{w}_\alpha + \tilde{k}_\pi c_\pi + \sum_{j=1}^{n-1} \tilde{R}_j^{(\pi)} s_j(\xi_1) c_\pi + \tilde{R}_n^{(\pi)} u_n(\xi_1) c_\pi \\ - \tilde{k}_\alpha c_\alpha - \sum_{j=1}^{n-1} \tilde{R}_j^{(\alpha)} s_j(\xi_1) c_\alpha,\end{aligned} \tag{94}$$

$$\dot{\xi}_1 = \tilde{k}_\alpha c_\alpha - \tilde{R}_1^{(\alpha)} \xi_1 c_\alpha, \tag{95}$$

with the initial conditions (20). For $c_0 = 0$, we disregard Eq. (93), whereas for $c_\rho(t) = c_\rho(0)$, Eq. (92) is absent. Also, let us point out again that Eq. (95) can be replaced by Eq. (10) for any $2 \leqslant k \leqslant n$ [52].

Some remarks are appropriate here. First, when solving Eqs. (92)–(95) numerically, care is needed whenever $r_i \approx r_j$, due to the $r_i - r_j$ terms appearing in the denominators in Eqs. (58), (62), (76), and (79). 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. (58) and (76)]. Third, the effect of finite n on the numerical solutions of Eqs. (92)–(95) should always be carefully checked in order to avoid “finite-size effects”. Finally, for the realistic value of the parameter n, sums appearing on the left-hand side (lhs) of Eqs. (92)–(94) have a 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_α now read

$$\dot{M}_1 = \tilde{a}_R M_1 c_\alpha = -\dot{c}_\alpha. \tag{96}$$

From Eqs. (96), mass conservation follows, i.e.,

$$M_1(t) + c_\alpha(t) = M_1(0) + c_\alpha(0) = e_0 + d_0. \tag{97}$$

Making use of Eqs. (97) and (96), we obtain the following time-evolution equation for M_1:

$$\dot{M}_1 = \tilde{a}_R M_1 (e_0 + d_0 - M_1). \tag{98}$$

Equation (98) is the logistic equation. By integrating, we get

$$M_1(t) = \frac{e_0 + d_0}{1 + \frac{d_0}{e_0}\exp[-\tilde{a}_R(e_0 + d_0)t]}. \tag{99}$$

In order to obtain $\xi_1(t)$, we invoke Eq. (84), which yields

$$\xi_1(t) = \frac{e_0^2}{M_1(t)} = \frac{e_0 + d_0 \exp\left[-\tilde{a}_R(e_0 + d_0)t\right]}{1 + \frac{d_0}{e_0}}. \tag{100}$$

Finally, combining (81) with (100), we obtain

$$\xi_k(t) = \frac{e_0^2}{d_0}\left(\frac{d_0}{d_0 + e_0}\right)^k \left(1 + \frac{d_0}{e_0} e^{-\tilde{\kappa} t}\right)(1 - e^{-\tilde{\kappa} t})^{k-1}, \tag{101}$$

where $\tilde{\kappa} = \tilde{a}_R(e_0 + d_0)$. Please note that for $\xi_k(t)$ given by (101), we obtain $\lim_{t\to\infty} \xi_k(t) = \bar{\xi}_k$ with $\bar{\xi}_k$ given by Eq. (88), as well as $\xi_k(0) = 0$ for $k \geqslant 2$.

B. Two simple cases of injection mechanism

In some situations, the exact analytical solution can also be obtained when the injection mechanism for precursor A is present, $\dot{w}_\alpha \neq 0$. Here we assume that (i) $c_0 = 0$ [reactions (4) and (5) are absent], (ii) the reducing agent concentration is constant, $c_\rho(t) = c_\rho(0)$, (iii) $n = \infty$ in Eq. (14), and (iv) $\tilde{R}_j^{(\alpha)} = \tilde{a}_R j$, i.e., $r_j = j$. The results presented below are valid for both cases analyzed in Secs. IV B and IV C.

In the present situation, it is again convenient to use the method of moments. Equations (8) and (33) for $\mu = 1$ now read

$$\dot{c}_\alpha = \dot{w}_\alpha - \tilde{k}_\alpha c_\alpha - \tilde{a}_R M_1 c_\alpha, \tag{102}$$

$$\dot{M}_1 = \tilde{k}_\alpha c_\alpha + \tilde{a}_R M_1 c_\alpha. \tag{103}$$

From Eq. (25), we obtain

$$c_\alpha(t) = h_0 + w_\alpha(t) - M_1(t), \tag{104}$$

where $h_0 \equiv d_0 + e_0$. Using Eq. (104), we get

$$\dot{M}_1 = [\tilde{k}_\alpha + \tilde{a}_R M_1][f(t) - M_1], \tag{105}$$

where we define $f(t) = h_0 + w_\alpha(t)$. The above equation has the form of Eq. (14) of Ref. [19]; however, here the concrete form of $w_\alpha(t)$ and $f(t)$ is not yet specified. Equation (105) can be given the form of the Bernoulli equation and therefore it can be reduced to a linear equation. We obtain (cf. Eq. (15) of Ref. [19])

$$M_1(t) = \frac{e^{\Phi(t)}}{\tilde{a}_R}\left[\frac{1}{\tilde{k}_\alpha + e_0 \tilde{a}_R} + \Xi(t)\right]^{-1} - \frac{\tilde{k}_\alpha}{\tilde{a}_R}, \tag{106}$$

where

$$\begin{aligned} \Phi(t) &\equiv \int_0^t [\tilde{k}_\alpha + \tilde{a}_R h_0 + \tilde{a}_R w_\alpha(\eta)]d\eta, \\ \Xi(t) &\equiv \int_0^t e^{\Phi(\eta)} d\eta. \end{aligned} \tag{107}$$

Below we analyze two simple cases of the $w_\alpha(t)$ function [53].

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

$$\dot{w}_\alpha(t) = \begin{cases} U, & t < T \\ 0, & t \geqslant T, \end{cases} \tag{108}$$

and, consequently,

$$w_\alpha(t) = \begin{cases} Ut, & t < T \\ UT, & t \geqslant T. \end{cases} \tag{109}$$

Making use of (107) and (109), we get

$$\Phi(t) = (\tilde{k}_\alpha + \tilde{a}_R h_0)t + \Phi_a(t), \tag{110}$$

where we define

$$\Phi_a(t) = \begin{cases} \frac{1}{2}\tilde{a}_R U t^2, & t < T \\ \tilde{a}_R U T t - \frac{1}{2}\tilde{a}_R U T^2, & t \geqslant T. \end{cases} \tag{111}$$

From (107), (110), and (111), it follows that

$$\Xi(t) \equiv \begin{cases} \Xi_1(t), & t < T \\ \Xi_1(T) + \Xi_2(t), & t \geqslant T, \end{cases} \tag{112}$$

where $\Xi_1(t)$ and $\Xi_2(t)$ appearing in (112) are defined as

$$\begin{aligned} \Xi_1(t) &= \frac{\exp\left(-\frac{\mathcal{B}^2}{4\mathcal{A}}\right)}{\sqrt{\mathcal{A}}}\left[\Psi\left(t\sqrt{\mathcal{A}} + \frac{\mathcal{B}}{2\sqrt{\mathcal{A}}}\right) - \Psi\left(\frac{\mathcal{B}}{2\sqrt{\mathcal{A}}}\right)\right], \\ \Xi_2(t) &= e^{-\mathcal{A}T^2}\left[\frac{e^{(2\mathcal{A}T+\mathcal{B})t} - e^{(2\mathcal{A}T+\mathcal{B})T}}{(2\mathcal{A}T + \mathcal{B})}\right], \end{aligned} \tag{113}$$

$\Psi(x) \equiv \int_0^x e^{z^2} dz = e^{x^2} D_+(x)$, $D_+(x)$ is a Dawson function, $\mathcal{A} = \frac{1}{2}\tilde{a}_R U$ [54], and $\mathcal{B} = \tilde{k}_\alpha + \tilde{a}_R h_0$.

The second injection mechanism we consider is the following: at $t = t_i$, a portion of the precursor is rapidly introduced into the system. If the duration of injection is sufficiently short, we may reasonably approximate any function describing the real time dependence of the injection process by the Dirac δ function. Therefore, we assume

$$\dot{w}_\alpha(t) = W\delta(t - t_i), \quad w_\alpha(t) = W\theta(t - t_i), \tag{114}$$

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

$$\Phi(t) = \begin{cases} (\tilde{k}_\alpha + \tilde{a}_R h_0)t, & t < t_i \\ (\tilde{k}_\alpha + \tilde{a}_R h_0)t + \tilde{a}_R W(t - t_i), & t \geqslant t_i, \end{cases} \tag{115}$$

$$\Xi(t) \equiv \begin{cases} \Xi_1(t), & t < t_i \\ \Xi_1(t_i) + \Xi_2(t), & t \geqslant t_i, \end{cases} \tag{116}$$

where

$$\Xi_1(t) = \frac{e^{\mathcal{B}t} - 1}{\mathcal{B}},$$
$$\Xi_2(t) = e^{-\mathcal{C}t_i}\left[\frac{e^{(\mathcal{B}+\mathcal{C})t} - e^{(\mathcal{B}+\mathcal{C})t_i}}{(\mathcal{B}+\mathcal{C})}\right]. \tag{117}$$

In the above formula, $\mathcal{C} = \tilde{a}_R W$, whereas $\mathcal{B}$ is defined as in (113).

For $\tilde{k}_\alpha \neq 0$, $e_0 = 0$, in both cases analyzed above, $M_1(t)$ given by Eq. (106) 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 (106), we obtain

$$\bar{M}_1 \equiv \lim_{t\to\infty} M_1(t) = d_0 + e_0 + \bar{w}_\alpha, \tag{118}$$

both for $\bar{w}_\alpha = UT$ (109) as well as for $\bar{w}_\alpha = W$ (114), in agreement with the general formula (30).

Moreover, we emphasize again that all relations, which are independent, in particular, of the form of the $\dot{w}_\alpha(t)$ function, may be invoked here. For example, for $\tilde{k}_\alpha \neq 0$, $e_0 = 0$, we may invoke Eq. (64) as well as Eqs. (19) and (23) of Ref. [19],

$$M_0(M_1) = \frac{q_0}{\omega} \ln\left(1 + \frac{\omega}{q_0} M_1\right), \tag{119}$$

$$\xi_1 = h_1^{(a)}(M_1) = \frac{M_1}{1 + \frac{\omega}{q_0} M_1}, \tag{120}$$

whereas for $\tilde{k}_\alpha = 0$, $e_0 \neq 0$, we may use Eqs. (68), (76), and (84). This is because those results are valid if only assumptions (iii) and (iv) of the present section are fulfilled, i.e., we have $n = \infty$ and $r_j = j$, respectively.

VII. LIMITATIONS OF THE PRESENT APPROACH

The approach proposed in the present paper has some intrinsic limitations.

First, we have assumed that the clusters are characterized solely by their mass (number of atoms or mers), and the cluster geometry is disregarded. Needless to say, there are many situations in which cluster shape should be taken into account. Within the present approach, this could be achieved by promoting single cluster-size index i to a double index $[i,\nu(i)]$, where $\nu(i) = 1,2,\ldots,\nu_m(i)$ labels different cluster geometries possible for a given cluster size i. However, although such an extension is conceptually simple, it yields a more complicated mathematical model (greater number of time-evolution equations), and therefore, in some cases, it may lead to considerable technical difficulties.

Second, if any molecules taking part in reactions (1)–(5) are present in low copy numbers, particle number fluctuations may be significant. In such situation, a description making use of the chemical master equation (CME) is more appropriate than any approach based on macroscopic kinetic rate equations (REs). However, for most of the colloidal or polymer systems of interest, a solution of the corresponding CME is out of the question, and we are forced to employ a RE description. Still, the latter approach is a reasonable choice, provided that the system in question is large enough.

Third, for each particular system of interest, characteristic time scales of the chemical reactions (τ_r) should be compared with characteristic time scales of the diffusive (τ_d) or convective (τ_c) transport. This allows us to check if the assumption of spatial homogeneity is justified, which is the case for sufficiently small values of the *Damköhler numbers* Da_I, Da_{II}, defined as

$$\text{Da}_I = \frac{\tau_c}{\tau_r}, \quad \text{Da}_{II} = \frac{\tau_d}{\tau_r}. \tag{121}$$

It should be noted here that values of Da_I and Da_{II} depend on many factors, such as temperature. Moreover, in the colloidal systems that we are most interested in (gold colloids), values of the Damköhler numbers strongly depend on the reducing agent which is used. This is because by changing the reducing agent, we may obtain rates of both (1), (2), (4), and (5) reactions differing by orders of magnitude [29–31]. At the same time, a change of the reducing agent affects diffusion or convection to a much lesser extent. Finally, let us note that stirring of the reagents also strongly influences the degree of homogeneity of the system. In consequence, we may expect that at least for some experimental situations, it is legitimate to treat the system at hand as spatially homogeneous.

If concentration gradients cannot be neglected, we should promote the state variables of the present approach to time-dependent scalar fields. In such case, time-evolution equations are no longer ordinary differential equations, but rather partial differential equations (PDEs) of the reaction-diffusion type. Although it is, in principle, rather straightforward to write down such a system of PDEs, its solution, either analytical or numerical, usually provides a formidable task.

However, concentration inhomogeneities, if initially present, may substantially affect the time evolution of the system. For example, it has been shown [55,56] that for reversible coagulation, density (or concentration) spatial fluctuations change the asymptotic ($t \to \infty$) time dependence of the concentrations from the exponential law predicted by the mean-field (MF) approach to the power law, with the exponent depending on the spatial dimensionality of the system.

VIII. SUMMARY AND DISCUSSION

In this paper, we have presented a generalization of the autocatalytic growth model, proposed recently [19]. The time evolution of the system is described within the mean-field-type rate-equation approach. The kinetic equations of our model are a 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, for arbitrary injective functional dependence of the autocatalytic reaction rate constant on the cluster size i, in two nontrivial cases we derive analytical expression of the i-mer concentration ξ_i as a function of ξ_1; $\xi_i = s_i(\xi_1)$. Consequently, 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 by solving a single algebraic equation describing the mass conservation condition.

Moreover, knowing the explicit form of the $s_i(\xi_1)$ functions, in order to find the time dependence of all the state variables, we have to solve (either analytically or, in the general case, numerically) only a 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: SELECTED 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. (1)–(5).

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

$$P + P \rightleftharpoons P_2, \quad A + A \rightleftharpoons A_2. \tag{A1}$$

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

$$A_2 \rightleftharpoons P + B_1. \tag{A2}$$

(A1) and (A2) may also be treated as a single step,

$$A + A \rightleftharpoons P + B_1. \tag{A3}$$

Next, consider a situation when the reducing agent decomposes on the surface of metallic nanoclusters, and the latter act as a catalyst for this process,

$$R + B_i \to B_i + X_5. \tag{A4}$$

By X_5, we collectively denote all products of (A4). More generally, we may consider a reaction of the type

$$Y + Y' + B_i \to B_i + X_6, \tag{A5}$$

where Y and Y' are some constituents of the system, which do not take part in reactions (1)–(5), and X_6 denotes all possible products of (A5). Again, in (A5), the metallic nanocluster plays only the passive role of a catalyst.

As an example of (A5), we may give the 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, let us return to the autocatalytic reaction (2). We may expect that the real mechanism of this reaction involves formation of an intermediate complex (AB_i). In effect, (2) should be replaced with

$$A + B_i \rightleftharpoons (AB_i) \to B_{i+1} + X_2. \tag{A6}$$

Let us now discuss briefly how the presence of reactions (A1)–(A6) in some extension of the present model would change its mathematical structure, in particular, the form of Eqs. (38) and (39).

First, note that the latter equations are not affected by the presence of reactions (A1). The same is true for (A4) and (A5), provided that interactions between molecules of different species (A, B_j, X_5, X_6, Y, or Y') near the surface of B_i nanoclusters can be neglected.

However, if either (A2) or (A3) reaction is present, c_α does not cancel out in Eqs. (38) and (39). Consequently, these equations cannot be solved independently of the time-evolution equations for c_ρ, c_π, c_α, and ξ_1. Still, Eqs. (38) and (39) may provide a reasonable effective description of the time evolution in any system where the mechanism of autocatalytic reaction is assumed to have the form (A6). This is analyzed in detail in Appendix B.

APPENDIX B: KINETIC EQUATIONS FOR A MORE COMPLEX MECHANISM OF $A + B_i \to B_{i+1}$ REACTION

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

Namely, in many cases, it seems reasonable to assume that either a breakup of each of the (AB_i) complexes into substrates or transformation of (AB_i) into products of autocatalytic reaction (2),

$$A + B_i \xleftarrow{\tilde{k}_i^-} (AB_i) \xrightarrow{\tilde{k}_i^*} B_{i+1} + X_2, \tag{B1}$$

is much faster than its production,

$$A + B_i \xrightarrow{\tilde{k}_i^+} (AB_i). \tag{B2}$$

As a consequence, the concentration of each (AB_i) remains both small and essentially time independent. In such situation, the steady-state approximation is legitimate.

Rate equations corresponding to the (A6) reaction read

$$\dot{\xi}_i = \tilde{k}_i^- \eta_i + \tilde{k}_{i-1}^* \eta_{i-1} - \tilde{k}_i^+ \xi_i c_\alpha, \quad i > 1, \tag{B3}$$

$$\dot{\eta}_i = -\tilde{k}_i^- \eta_i - \tilde{k}_i^* \eta_i + \tilde{k}_i^+ \xi_i c_\alpha, \quad i \geqslant 1, \tag{B4}$$

where η_i denotes concentration of (AB_i). For $i = 1$, instead of (B3), we have

$$\dot{\xi}_1 = \tilde{k}_\alpha c_\alpha + \tilde{k}_1^- \eta_1 - \tilde{k}_1^+ \xi_1 c_\alpha. \tag{B5}$$

Within the present treatment, Eqs. (B3)–(B5) replace Eqs. (35) and (36). Similarly to the case of $\tilde{R}_k^{(\alpha)}$ functions [Eq. (11)], $\tilde{k}_i^{\pm}$ and $\tilde{k}_i^{*}$, in general, depend on c_ρ. Next, we add Eqs. (B3) and (B4). This step yields

$$\dot{\xi}_i + \dot{\eta}_i = \tilde{k}_{i-1}^{*}\eta_{i-1} - \tilde{k}_i^{*}\eta_i. \tag{B6}$$

From a steady-state assumption,

$$\dot{\eta}_i = 0, \tag{B7}$$

by using Eq. (B4), we obtain

$$\eta_i^{(ss)} = \frac{\tilde{k}_i^{+}c_\alpha}{\tilde{k}_i^{*}+\tilde{k}_i^{-}}\xi_i \equiv \tilde{k}_i^{(e)}\xi_i c_\alpha. \tag{B8}$$

We assume here that (B8) holds for all $i \geqslant 1$ and for $t > 0$. Nonetheless, we should keep in mind that the steady-state assumption and, therefore, Eq. (B8) cannot be valid during the initial stage of the time evolution.

Making use of Eqs. (B6)–(B8), we may rewrite Eqs. (B5) and (B3) as

$$\dot{\xi}_1 = \tilde{k}_\alpha c_\alpha - \tilde{R}_1^{(\alpha)}\xi_1 c_\alpha \tag{B9}$$

and

$$\dot{\xi}_i = c_\alpha\big(\tilde{R}_{i-1}^{(\alpha)}\xi_{i-1} - \tilde{R}_i^{(\alpha)}\xi_i\big), \tag{B10}$$

where, for $i \geqslant 1$, we have

$$\tilde{R}_i^{(\alpha)} = \frac{\tilde{k}_i^{+}\tilde{k}_i^{*}}{\tilde{k}_i^{*}+\tilde{k}_i^{-}} = \tilde{k}_i^{*}\tilde{k}_i^{(e)}. \tag{B11}$$

Equation (B9) has exactly the form of Eq. (35), whereas Eq. (B10) has the same form as Eq. (36). Moreover, for the largest clusters ($i = n$), assuming that $\tilde{k}_n^{*} = 0$, $\tilde{k}_n^{\pm} \neq 0$ [i.e., (AB_n) 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. (37), again with $\tilde{R}_{n-1}^{(\alpha)}$ given by (B11).

This provides justification for the effective approach of the present model even if the reaction mechanism (A6) of the 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 $K_{ij} = F_{ij} = 0$ and $\dot{w}_k = 0$, using (B8), we obtain

$$\begin{aligned}\dot{\eta}_i &= \frac{d}{dt}\left(\frac{\tilde{k}_i^{+}c_\alpha}{\tilde{k}_i^{*}+\tilde{k}_i^{-}}\xi_i\right) = \frac{d}{dt}\big(\tilde{k}_i^{(e)}c_\alpha\xi_i\big)\\ &= \dot{\tilde{k}}_i^{(e)}c_\alpha\xi_i + \tilde{k}_i^{(e)}\dot{c}_\alpha\xi_i + \tilde{k}_i^{(e)}c_\alpha\dot{\xi}_i.\end{aligned} \tag{B12}$$

It is reasonable to assume that $\tilde{k}_i^{(e)}$ has only weak time dependence, or is even time independent if the c_ρ dependence of $\tilde{k}_i^{\pm}$ and $\tilde{k}_i^{*}$ cancels 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 $\xi_i(t) \leqslant M_0(t) \leqslant M_1(t) \leqslant q_0 + e_0$. Consequently, we may write down the following, rather crude upper bound for $|\dot{\eta}_i|$:

$$|\dot{\eta}_i| < (q_0 + e_0)\tilde{k}_i^{(e)}(|\dot{c}_\alpha| + |\dot{\xi}_i|). \tag{B13}$$

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

$$(q_0 + e_0)\tilde{k}_i^{(e)} \leqslant \varepsilon \ll 1, \tag{B14}$$

where ε is a sufficiently small positive constant. From Eq. (B8), it follows that if (B14) is fulfilled for some i and ε, then η_i is also small as compared to ξ_i, i.e., we have $\eta_i/\xi_i \ll 1$.

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[32] The motivation behind such more complete treatment is the following: In certain situations, spectroscopic techniques allow one 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 one to monitor the reaction progress.

[33] Au(II) is unstable, and therefore its presence is disregarded within the present effective reduction reaction mechanism defined by steps (1), (2), (4) and (5); cf. Ref. [27].

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[35] For simplicity, here we do not analyze the time-evolution equations for the concentrations of the X_1, X_2, X_3, and X_4 species.

[36] Even for a variable $c_\rho(t)$, the term "reaction rate constant" will be used for $\tilde{k}_\pi(c_\rho)$, $\tilde{R}_k^{(\pi)}(c_\rho)$, $\tilde{k}_\alpha(c_\rho)$, and $\tilde{R}_k^{(\alpha)}(c_\rho)$.

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[40] We assume here that such solution is unique and that the stationary point is a stable one. More detailed analysis required to investigate either the number or character of stationary points will not be presented here.

[41] In the $t \to \infty$ limit, when chemical reactions can be neglected, time-evolution equations of our model reduce to standard Smoluchowski coagulation equations.

[42] However, B_i may play a role of a passive catalyst.

[43] Please note the change in notation: $\mathcal{G}_j^{(\mu)} \to \tilde{\mathcal{G}}_j^{(\mu)}$ and analogously for $\tilde{\mathcal{S}}_{pq}^{(\mu)}$ and $\tilde{\mathcal{T}}_p^{(\mu)}$ as compared to Ref. [19].

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[46] The finite n case is important for a numerical analysis of the present model. Therefore, in this paper, the $k < n$ and $k = n$ cases will be carefully distinguished.

[47] For $k = n + 1$, we obtain the following time-evolution equation: $\dot{\xi}_{n+1} = -c_\alpha \tilde{R}_{n+1}^{(\alpha)} \xi_{n+1}$, with the solution $\xi_{n+1}(t) = 0$ for $\xi_{n+1}(0) = 0$. In a similar manner, concentrations of all larger clusters remain equal to zero.

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[50] If more convenient, in the $\tilde{k}_\alpha \neq 0$, $e_0 = 0$ case, one may use $M_0(t)$ instead of $\xi_1(t)$; cf. Eqs. (45) and (51).

[51] Please note that it may be more convenient to numerically solve Eq. (91) than Eq. (90).

[52] Although, in this respect, different values of k, $1 \leqslant k \leqslant n$, 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.

[53] The $f(t) = d_0 + c_0[1 - \exp(-\tilde{k}_\pi t)]$ function analyzed in Ref. [19] (for $c_0 \neq 0$ and $e_0 = 0$) results from the presence of reaction $P \to A$ (4). However, in a model without this reaction, an identical form of $f(t)$ may be related to the presence of the following injection mechanism for A molecules: $w_\alpha(t) = c_0[1 - \exp(-\tilde{k}_\pi t)]$.

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