Associations and dissociations with time-dependent reaction coefficients in finite polymer mixtures: The model and analytical-numerical method for solution by successive approximations

E. Mamontov [a,*], K. Hansen [b,c]

[a] *Versati AB, Askim SE-436 36, Sweden*
[b] *Tianjin International Center of Nanoparticles and Nanosystems (TICNN), Tianjin University, 92 Weijin Road, Nankai, Tianjin 300072, PR China*
[c] *Department of Physics, University of Gothenburg, Gothenburg SE-412 96, Sweden*

ARTICLE INFO

ABSTRACT

The work deals with the association and dissociation reactions with time-dependent coefficients in finite mixtures of polymers dispersed in fluid media with solid components. The polymers are regarded to be formed by identical units, polymer-forming units (PFUs) and, thus, present homopolymers. The model takes into account the porosity of the dispersion-medium/polymer-mixture system. The work derives the model for the reactions in the finite mixtures. The model presents a non-autonomous quadratic finite ODE system in a time-independent hyperplane and is based on the conservation law for the total number of PFUs. A variety of engineering applications of the derived finite-mixture model are discussed. The simplest case of the finite mixtures, i.e., the monomer-dimer mixtures with time-independent reaction coefficients is completely analyzed. An analytical-numerical (AN) method of the successive-approximations (SA) type is proposed for solving the derived model. The AN/SA method includes explicit analytical expressions for each of the approximations in terms of the preceding approximation. The method is exact in the dissociation-only case. The approximations are expected to converge if the association-reaction coefficients are not too large and the zeroth approximations are not very far from the solution. The AN/SA method comprises two sequences of the approximations. If the first one converges uniformly in the entire time axis, then the limit function is a steady-state (or "dynamic equilibrium") solution of the non-autonomous quadratic ODE system. The second sequence presumes that the first sequence is convergent in the above mentioned sense. The second sequence is intended for calculation of the solutions of initial-value problems for the above ODE system in a semi-infinite time interval. The main differences from common computational methods are formulated. The AN/SA method is quantitatively illustrated with a few examples of the settings in the aforementioned case of monomer-dimer mixtures, also in comparison with the explicit Euler method. The form of the AN/SA method allows especially efficient implementation on multi-processor/multi-

* Corresponding author at: Versati AB, SE-436 36 Askim, Sweden.
  E-mail address: eugmav@gmail.com (E. Mamontov).

core personal computers with graphic processing units even if the dimension of the state space is large. The developed model and method form a constructive framework for analysis or design of polymer mixtures dispersed in fluid-solid media. An application to prospective manufacturing of spatially heterogeneous polymer products is noted. A few directions for future research are proposed as well.

1. Introduction

Physics, Chemistry, and engineering deal with various complex systems. Along with this, there are systems, which are in a certain sense, much more complex. For instance [1, p. C49]:

Biological systems are very different from the physical or chemical systems analyzed by statistical mechanics or hydrodynamics. Statistical mechanics typically deals with systems containing many copies of a few interacting components, whereas cells contain from a million to a few copies of each of thousands of different components, each with very specific interactions.

One of the well-known examples of the systems with a large number of the components is a mixture of polymers. By polymers, we understand particles composed of specific numbers of identical elementary units, e.g., atoms or molecules. Strictly speaking, such polymers are called homopolymers.

The study of the association of such polymers was initiated by Smoluchowski who wrote down an equation for the association of particles [2]. The equation contains kernels that multiply the concentrations in quadratic forms to describe the time development of the concentrations. Smoluchowski solved the equations for the special case of constant kernels [3]. Apart from the constant kernels, the treatment was also approximate because the equations only included terms that describe association and no dissociation of the formed particles is possible, i.e., the reactions were considered irreversible. It was later realized, still within the description of the elementary processes as irreversible, that for other choices of the kernels, the equations can give rise to gelling, i.e., a process where monomers associate into an infinite size polymer in a finite time [4]. Kernels that can give rise to gelling transitions include those that resemble the chemically relevant polymerization processes that produce, for example, technologically important plastics. These result was later extended to reversible cases [5].

Other solutions in closed forms have been given for several types of kernels, beyond the solution given by Smoluchowski. They include kernels on the form $i + j$ and $i\,j$ where i and j are the sizes of the reacting polymers [6,7] (see also the review in [8] for a summary of the state of the art around the turn of the millennium).

Importantly, it was established that solutions of both the irreversible and reversible association equation will under some circumstances scale. This scaling also holds for the kernels that cause a gelling transition [9,10]. For irreversible association, in particular, the scaling means that the polymer size distribution will be given by a single parameter. This can be chosen as the average size.

Most of these results have been derived for explicitly defined kernels or kernels with certain properties, e.g., being harmonic functions. The limited number of kernels for which exact solutions are known shows that the solution of the more general problem with time and position dependent coefficients, in addition to size dependent values, is a rather complicated problem. The present work aims at extending procedures for solutions of the equations where the kernels are time dependent.

Polymers can also be composed by a few types of units (e.g., [11, Section 4.3]). In this case, polymers are known as copolymers. In particular, copolymers present most of the molecules typical in biological systems. Moreover, all biochemical transformations are fundamentally unimolecular or bimolecular (e.g., [12, the left column on p. 171/2]), similarly to reactions in homopolymer systems. One of the examples of copolymers in biological systems is illustrated with biochemical reactions of intracellular molecules (e.g., [13]).

The present work considers homopolymers only. They are for brevity referred as polymers. Physical aspects of various polymer mixtures are reviewed, e.g., in [14].

A mixture of polymers contains j-mers at values of j in set $\mathbb{N} = 1, 2, 3, \ldots$, i.e., monomers, dimers, trimers, tetramers, and so on. A j-mer consists of j units. For this reason, we call j the size of a j-mer. Let parameters υ and m such that

$$0 \leq \upsilon < \infty \tag{1.1}$$

and $0 < m < \infty$ be the volume and mass of the unit. The present work assumes that they are independent of the sizes of the polymers. Then the volume and mass of a j-mer are υj and $m j$, respectively.

In general, at any fixed j, j-mers may differ from each other in their shapes and structures. Following a number of other works on the topic, we assume that, at any j fixed, all j-mers are identical. Thus, a polymer mixture can be regarded as a population of the polymer-forming units (PFUs), which is subdivided into a number of components in such a way that, at any fixed j, the jth component consists of identical j-mers.

In practical problems (e.g., experiments or manufacturing processes) in physics, chemistry, biotechnology, or various areas of engineering, a polymer mixture usually comprises the *j*-mer components at many different values of *j* and, thus, presents a population of disparate particles with a large number of components. This feature significantly complicates the corresponding theoretical analysis. Advanced theoretical approaches to the problem are exemplified with work [15]. It focuses on the nonlinear kinetic equations for populations of disparate particles undergoing dissipative binary collisions and association/dissociation phenomena. The work studies collision dynamics and provides a derivation of the corresponding kinetic equations. Viscoelastic flows of polymeric liquids are analyzed in terms of an evolution equation in [16].

Approaches based on more particular, discrete models have also drawn a considerable attention (e.g., [17, Section 7.5] [11,18,19]). The discrete models describe the association and dissociation reactions of polymers by means of a system of quadratic ordinary differential equations (ODEs) for the concentrations (or volumetric number densities) of the polymers of different sizes.

The present work focuses on the three research questions formulated in Remarks 1.1–1.3 below.

Remark 1.1 (Research Question 1)**.** The association and dissociation reactions, by their definitions, do not alter the total number of PFUs (TNPFU). Consequently, any discrete model, which represents the reaction of this types only, i.e., does not include the terms for the formation or disintegration of the units, must assure the conservation law of this number.

As a rule, PFUs are not only massive but also voluminous rather than point particles. (The most well-known example of a massive point particle is an electron.) The terrestrial environment, due to its natural limitations, does not have resources to provide or store an infinite set of PFUs. Indeed, the total volume and the total mass of an infinite set of PFUs are infinite. Of a practical importance at the terrestrial scale are *finite* polymer mixtures, i.e., the ones with finite TNPFUs. For this reason, the main text of the present work, which is below Section 2, only considers the polymer mixtures that are finite.

Moreover, it is somewhat surprising that few works are devoted to the finite mixtures. To be specific, we note papers [19–21]. Even more surprising is the fact that the settings for the finite ODE system, which provide the TNPFU-conservation law, are unavailable in the literature.

This feature poses the **first research question**: What is the form of the reaction ODE system for finite polymer mixtures that provides the TNPFU-conservation law?

As is shown below (see Remark 2.1), the maximum polymer size (MPS) in a finite polymer mixture is finite and, generally, depends on time $t \in \mathbb{R} = (-\infty, \infty)$. Consequently, the present work analyzes the mixtures with the finite MPSs only.

If MPS in a polymer mixture depends on time, the aforementioned ODE system cannot be used as a model for the mixture because the settings for ODE systems in the state spaces with time-dependent dimensions are unknown. For this reason, the present work deals with the case where MPS in a polymer mixture does not depend on time. In this case, the ODE system can be used as a model for polymer mixtures and is finite, with the number of variables (or equations) equal to the dimension of the state space of the system.

Remark 1.2 (Research Question 2)**.** The coefficients of the polymer reactions are usually considered in the literature to be independent of time, thereby resulting in the reaction ODE systems that are autonomous. This limitation prevents application of the related results to many practical problems where the coefficients are time-dependent resulting in non-autonomous reaction ODE systems. For instance, the mentioned time-dependence can be due to time-varying electromagnetic field or time-varying temperature of a manufacturing process. One of the examples is the prospective production of spatially heterogeneous polymer products.

The spatial heterogeneity of polymer products will enhance their functional performance to the level that will potentially revolutionize the entire polymer-product technology [22]. The spatially heterogeneous products may be generated by combinations of UV-light and temperature curing within the 3D-printing/additive-manufacturing (3D/AM) technology. The term curing, in brief, denotes the settings where the time-dependences of the UV light and temperature are controlled in the course of a manufacturing process. The spatial heterogeneity can only be achieved by proper quantitative modeling and planning the process conditions, not only the initial state but also the time variations of the UV-light or temperature.

Nowadays, 3D/AM (e.g., [23]) presents one of the most rapidly developing technologies and markets. The global 3D-market – embracing 3D print machines, printing materials, and solution providers – is growing very fast. It was in 2014 about \$3 billion and is expected to reach \$8.3 billion by 2020, corresponding to an annual growth rate of 18–22%, between 2014 and 2020 [24]. The UV-cured 3D/AM version (e.g., [24,25]) is getting dominating because the well-known unparalleled advantages (described in detail in, e.g., [26]) that allow the technology to create 3D objects in plastic. This is the new focus for a wide range of industries, from medical devices to toys, custom jewelry, electronics, and automotive components.

Consequently, the main text of the present work, which is presented below Section 2, discusses the polymer mixtures with time-dependent reaction coefficients only. These time dependences are usually due to the time-dependence of the UV intensity. Presently, considerable research in both theoretical and applied physics is carried out towards the expressions for the UV-sensitive reaction coefficients that will be both physically consistent and practically feasible. This is a vast field of research, which is still in its infancy. A review of the field is therefore beyond the scope of the present work.

The time-dependences of the reaction coefficients pose the **second research question**: Is there any method suitable for practical analysis of the reaction ODE systems with the time-dependent coefficients?

The following remark logically continues the topic related to Research Question 2 formulated in Remark 1.2. The remark formulates the **third research question.**

Remark 1.3 (Research Question 3). If there is no method for the purpose indicated in Research Question 2, what method can be suggested and what are its main features?

Countably infinite representations, which are formal in the sense that they are not rigorously determined, are often used in polymer-mixture modeling. Taking that into account, we use them in order to briefly discuss and illustrate certain structural features of certain models. More specifically, we present an approach, which allows for the porosity of the dispersion-medium/polymer-mixture system, and illustrate the TNPFU-conservation law in the case of formal countably infinite ODE systems.

Formal countably infinite representations are only used in Section 2, which deals with preliminary considerations. The corresponding rigorous finite version is analyzed in the subsequent sections, Section 3–5, which give answers to Research Questions 1–3 formulated in Remarks 1.1–1.3, respectively.

Section 3 derives the reaction ODE system, which provides the conservation law of TNPFUs in finite polymer mixtures. Engineering application of this system is discussed in Section 4. It also presents the complete analysis of the simplest case of the finite mixtures, i.e., the monomer-dimer mixtures with time-independent reaction coefficients. The analysis indicates that the stability picture for the reaction system is not very simple. This explains why common computational methods may be unsuitable, even for this simple system, and less restrictive practical methods are needed. Section 5 proposes an analytical-numerical method of the successive-approximations type for solution of the system derived in Section 3. This method in particular enables an explicit analytical insight in the solutions, especially to show how the time-dependent reaction parameters influence the time evolution of the polymer concentrations. Section 5 also formulates the main differences of the proposed method from common computational techniques and illustrates the method with quantitative-simulation results in the aforementioned case of the monomer-dimer mixture. Section 6 concludes the work, specifies a constructive framework for analysis or design of polymer mixtures, and suggests a few directions for future research.

2. Preliminaries

The present work considers a polymer mixture dispersed in a fluid medium with solid components or, briefly, fluid-solid medium and describes the interactions of j-mers with the help of their concentrations, or volumetric number densities,

$$n_j \geq 0. \qquad j = 1, 2, \ldots. \tag{2.1}$$

Since the concentration of the units, which belong to j-mers, is $j\, n_j$, the total concentration of PFUs in the mixture is

$$n = \sum_{j=1}^{\infty} j n_j. \tag{2.2}$$

However, generally speaking, concentrations (2.1) cannot be used in the corresponding reaction equations. The reason is the following.

The first inequality in (1.1) means that a PFU and, thus, the polymers need not be point particles. Consequently, j-mers are generally voluminous particles. In contrast to that, the common statistical-mechanics models (such as the Bogolyubov–Born–Green–Kirkwood–Yvon equation chain, kinetic equations, hydrodynamics models, reaction-advection-diffusion equations, equations of chemical kinetics, and others) are only available for point particles, volumeless rather than voluminous (e.g., [27]). Thus, one needs to establish a one-to-one correspondence of concentrations (2.1), which are physically measurable, and the concentrations in the point-particle case. The latter are not physically measurable. They present the terms directly modeled by theoretical-physics models.

The above correspondence can be implemented by the volume-scaling method developed in [28]. It provides the above correspondence of n_j and the point-particle, or scaled, concentrations c_j of j-mers by means of the relations

$$c_j = n_j/(1 - \phi - \upsilon n), \ \ j = 1, 2, \ldots, \tag{2.3}$$

where υ is, as before (see Section 1), the volume of a PFU, υn is, in view of (2.2), the fraction of the volume occupied by the bodies of PFUs or, equivalently, by the bodies of the polymers in the mixture, and ϕ is the fraction of the volume that can be occupied by the bodies other than the ones of the above units, $0 \leq \phi < 1$. For example, in a filter, ϕ can be associated with the filtering solid component. In a living tissue, ϕ corresponds to the extracellular matrix, which is solid and immersed in the interstitial fluid. Volume υ and volume fraction ϕ indicate the volumes, which the polymers cannot penetrate into. Both υ and ϕ are assumed to be independent of n. The denominator in (2.3), $1 - \phi - \upsilon n > 0$, is the fraction of the free volume, i.e., the volume which is not occupied by the PFU bodies and is, thus, available for their motion. This fraction in fact presents the porosity of the system, which comprises the dispersion fluid-solid medium and the entire polymer mixture.

Relations (2.1), (2.3), and the mentioned inequality imply that

$$c_j \geq 0, \ \ j = 1, 2, \ldots. \tag{2.4}$$

It also follows from (2.3) that

$$c = n/(1 - \phi - \upsilon n) \tag{2.5}$$

where

$$c = \sum_{j=1}^{\infty} j c_j \tag{2.6}$$

is the total scaled concentration of PFUs in the polymer mixture. Expressing n from (2.5) in terms of c and substituting the result into (2.3), one obtains

$$n_j = [(1 - \phi)/(1 + \upsilon c)] c_j, \ \ j = 1, 2, \dots \tag{2.7}$$

Relations (2.3) and (2.7) indicate the one-to-one correspondence between concentrations n_j and scaled concentrations c_j. The mentioned one-to-one correspondence explicitly shows how the modeled concentrations, c_j, are coupled with the physically measurable, or experimentally available, concentrations, n_j. This coupling not only explains the difference between these concentrations but also indicates a specific quantitative correspondence between them. It should be emphasized that, as follows from (2.3) or (2.7), concentrations c_j and n_j coincide if and only if both υ and ϕ are zero or, equivalently, the porosity is unit.

Scaled concentrations c_j, $j = 1, 2, \dots$, describe j-mers as point particles and, due to this feature, are the concentrations used in the equations originated from common statistical mechanics. In view of the above one-to-one correspondence, we, in what follows, consider c_j rather than n_j, and for brevity omit the word "scaled" in the term "scaled concentration".

The corresponding models for polymer mixtures describe the association and dissociation of polymers by means of quadratic ODEs for concentrations c_j of j-mers at all values $j \in \mathbb{N}$ of the polymer size. These ODE systems are countably infinite. However, the work does not analyze solutions of the countably infinite ODE systems for the following reason.

Remark 2.1. As is noted in Section 1, in any polymer mixture in the terrestrial environment at any time point t, TNPFU $N(t) \in \mathbb{N}_0 = \mathbb{N} \cup 0$ is finite,

$$N(t) < \infty. \tag{2.8}$$

The polymer-number counterpart of concentration relation (2.2) is $N(t) = \sum_{j=1}^{\infty} j N_j(t)$ where $N_j(t) \in \mathbb{N}_0$ is the number of j-mers in the mixture. Combining this equality and (2.8), and taking into account the well-known mathematical results, one obtains

$$\lim_{j \to \infty} j N_j(t) = 0.$$

In view of the fact that numbers $N_j(t) \in \mathbb{N}_0$ in this limit relation are non-negative integers (see above), the relation implies that at every fixed t, there exists number $J(t) \in \mathbb{N}$ such that $N_{J(t)}(t) \neq 0$ and $N_j(t) = 0$ at all $j > J(t)$.

This property indicates that natural number $J(t)$ is MPS in the mixture at time point t.

Remark 2.1 shows that MPS in a finite (see (2.8)) mixture is, at any time point t, finite. As is specified in Remark 1.1, the present work focuses on this case and on the finite ODE system, which provides the conservation law for TNPFU.

However, this law can be illustrated even with an ODE system, which is countably infinite rather than finite. The outcome of the discussion below is noted in Proposition 2.1 in Section 2.3.

We consider the following two types of reactions in a polymer mixture.

The first one is the association of α- and β-mers, $\alpha, \beta = 1, 2, \dots$, into $(\alpha + \beta)$-mers. The corresponding contributions to the derivatives of the concentrations with respect to time t are additive and can be determined in terms of coefficients $a_{\alpha\beta}(t)$, which are such that

functions $a_{\alpha\beta}(t), \alpha, \beta = 1, 2, \dots,$ are piecewise continuous,

as well as non-negative and uniformly bounded at all t,

i.e., there are t-independent $A_{\alpha\beta} > 0$ such that $0 \leq a_{\alpha\beta}(t) \leq A_{\alpha\beta}$, (2.9)

and

equalities $a_{\alpha\beta}(t) = a_{\beta\alpha}(t)$ hold, $\alpha, \beta = 1, 2, \dots.$ (2.10)

The contribution to $dc_{\alpha+\beta}/dt$ is $a_{\alpha\beta}(t) c_\alpha c_\beta$, whereas the contributions to dc_α/dt and dc_β/dt are the same, $-a_{\alpha\beta}(t)c_\alpha c_\beta$. The latter is valid only if $\alpha \neq \beta$. If $\alpha = \beta$, then $c_\alpha \equiv c_\beta$ and, thus, the contribution to dc_α/dt is $-2a_{\alpha\alpha}(t)c_\alpha^2$. In fact, the contributions to dc_α/dt and dc_β/dt can be expressed with a single term, no matter if $\alpha \neq \beta$ or $\alpha = \beta$, namely with $-(1 + \delta_{\alpha\beta})a_{\alpha\beta}(t)c_\alpha c_\beta$ where $\delta_{\alpha\beta}$ is the Kronecker delta.

The physical dimension of every $a_{\alpha\beta}$ is volume divided by time. The model component for the above reactions in the polymer mixture is summarized in Section 2.1.

The second type of reactions in the mixture is the dissociation of $\alpha + \beta$-mers, $\alpha, \beta = 1, 2, \dots$, into α-mers and β-mers. The corresponding contributions to the time derivatives of the concentrations are additive and can be determined in terms of coefficients $b_{\alpha\beta}(t)$, which are of the properties similar to the ones of coefficients $a_{\alpha\beta}(t)$, namely are such that

functions $b_{\alpha\beta}(t), \alpha, \beta = 1, 2, \ldots,$ are piecewise continuous,

as well as non-negative and uniformly bounded at all t,

i.e., there are t-independent $B_{\alpha\beta} > 0$ such that $0 \le b_{\alpha\beta}(t) \le B_{\alpha\beta}$, $\qquad$ (2.11)

and

equalities $b_{\alpha\beta}(t) = b_{\beta\alpha}(t)$ hold, $\alpha, \beta = 1, 2, \ldots.$ $\qquad$ (2.12)

The contribution to $dc_{\alpha+\beta}/dt$ is $-b_{\alpha\beta}(t)c_{\alpha+\beta}$, whereas the contributions to dc_α/dt and dc_β/dt are the same, $b_{\alpha\beta}(t)c_{\alpha+\beta}$. The latter is valid only if $\alpha \ne \beta$. If $\alpha = \beta$, then $c_\alpha \equiv c_\beta$ and, thus, the contribution to dc_α/dt is $2\,b_{\alpha\alpha}(t)\,c_{2\alpha}$. In fact, the contributions to dc_α/dt and dc_β/dt can be expressed with a single term, no matter if $\alpha \ne \beta$ or $\alpha = \beta$, namely with $(1 + \delta_{\alpha\beta})b_{\alpha\beta}(t)c_{\alpha+\beta}$ where $\delta_{\alpha\beta}$ is the aforementioned Kronecker delta.

We note that the total contribution to dc_β/dt, $\beta = 1, 2, \ldots$, which corresponds to all $\alpha = 1, \ldots, \beta - 1$, is $-b_{+.\beta}(t)c_\beta$ where

$$b_{+.\beta}(t) = \sum_{\alpha=1}^{[\beta/2]} b_{\alpha.\beta-\alpha}(t), \beta = 2, 3, \ldots. \qquad (2.13)$$

The physical dimension of every $b_{\alpha\beta}(t)$ is unit divided by time. The model component for the above reactions in the polymer mixture is summarized in Section 2.2. Section 2.3 combines the models of Sections 2.1 and 2.2.

2.1. Formal countably infinite ODE system for association of polymers. Discrete Smoluchowski model

The beginning of Section 2 summarizes two types of reactions in the polymer mixture. The present subjection assumes that the reactions of the second type are not present. The reactions of the first type, i.e., association of j-mers, can be formulated with the help of (2.9) and (2.10) and the description of the contributions in the paragraph below (2.10). The result is the equations

$$dc_1/dt = -\left[\sum_{i=1}^{\infty}(1 + \delta_{i1})a_{i1}(t)c_i\right]c_1, \qquad (2.14)$$

$$dc_j/dt = -\left[\sum_{i=1}^{\infty}(1 + \delta_{ij})a_{ij}(t)c_i\right]c_j + \sum_{i=1}^{[j/2]} a_{i.j-i}(t)c_i c_{j-i}, j = 2, 3, \ldots. \qquad (2.15)$$

These equations present a formal countably infinite ODE system for concentrations (2.4).

In view of the non-negativeness in (2.4) and (2.9), the first terms on the right-hand sides of (2.14) and (2.15) present the rate of decrease of concentration c_j due to participation of j-mers in the association of more complex polymers, namely $(i + j)$-mers at $i = 1, 2, \ldots$. The second term on the right-hand side of (2.15) presents the rate of increase in concentration c_j due to the association of j-mers from smaller polymers, namely i-mers and $(j - i)$-mers, $i = 1, \ldots, j - 1$.

Systems (2.14) and (2.15) is the non-autonomous generalization of the well-known autonomous discrete Smoluchowski equations (e.g., [17, (7.63)], [11, (2.2) and (2.3)], [21, (1.1)]).

2.2. Formal countably infinite ODE system for dissociation of polymers

The beginning of Section 2 summarizes two types of reactions in the polymer mixture. The present subsection assumes that the reactions of the first type are not present. The reactions of the second type, i.e., dissociation of j-mers, can be formulated with the help of (2.11), (2.12), and the description of the contributions in the paragraph below (2.12). The result is equations

$$dc_1/dt = \sum_{i=1}^{\infty}(1 + \delta_{i1})b_{i1}(t)c_{i+1}, \qquad (2.16)$$

$$dc_j/dt = \sum_{i=1}^{\infty}(1 + \delta_{ij})b_{ij}(t)c_{j+i} - b_{+.j}(t)c_j, j = 2, 3, \ldots, \qquad (2.17)$$

where coefficients $b_{+.j}(t)$ are specified with (2.13). These equations present a formal countably infinite ODE system for concentrations (2.4).

In view of expression (2.13) and the non-negativeness in (2.4) and (2.11), the first terms on the right-hand sides of (2.16) and (2.17) present the rate of increase in concentration c_j due to participation of j-mers in the dissociation of bigger polymers, namely $(i + j)$-mers at $i = 1, 2, \ldots$ The second term on right-hand side of (2.17), in view of (2.13), presents the rate of decrease in concentration c_j due to dissociation of j-mers into more simple polymers, namely i-mers and $(j - i)$-mers, $i = 1, \ldots, j - 1$.

System (2.16), (2.17) and expression (2.13) are the non-autonomous generalization of the well-known autonomous equations (e.g., [17, (7.71)] or [11, (4.1)]).

2.3. Unified formal countably infinite ODE system for association and dissociation of polymers

The beginning of Section 2 summarizes two types of reactions in the polymer mixture. In order to describe the general case, i.e., the one when the reactions of both the first and second types are present, one combines the models of Subsections 2.1 and 2.2 in a single, unified model. This can be achieved by adding the right-hand sides of system (2.14), (2.15), on the one hand, and system (2.16), (2.17), on the other hand. The result is equations

$$dc_1/dt = -\left[\sum_{i=1}^{\infty}(1+\delta_{i1})a_{i1}(t)c_i\right]c_1 + \sum_{i=1}^{\infty}(1+\delta_{i1})b_{i1}(t)c_{i+1}, \tag{2.18}$$

$$dc_j/dt = -\left[\sum_{i=1}^{\infty}(1+\delta_{ij})a_{ij}(t)c_i\right]c_j + \sum_{i=1}^{[j/2]}a_{i.j-i}(t)c_ic_{j-i}$$
$$+ \sum_{i=1}^{\infty}(1+\delta_{ij})b_{ij}(t)c_{j+i} - b_{+.j}(t)c_j, \, j=2,3,\ldots \tag{2.19}$$

for concentrations (2.4). System (2.18), (2.19) and expression (2.13) is the non-autonomous generalization of the well-known autonomous equations (e.g., [17, (7.72)]).

Since in the polymer association/dissociation reactions there is no loss of PFUs, the total concentration of these units c (see (2.6)) is conserved. This is the topic of the following proposition.

Proposition 2.1. *We consider relation*

$$dc/dt = \sum_{j=1}^{\infty} j \, dc_j/dt \tag{2.20}$$

obtained by formal differentiation of (2.6) in t. If terms dc_j/dt in (2.20) are described with formal countably infinite ODE system (2.18), (2.19), then

$$dc/dt = 0, \tag{2.21}$$

i.e., volumetric density c of PFUs is independent of t.

Proof. Expressions (2.18) and (2.19) are obtained with the help of (2.10), (2.12), and (2.13) directly by means of the rules described in the text on (2.9)–(2.13). These rules, as well as expressions (2.18) and (2.19), show that the right-hand side of (2.20) consists of the association-related and dissociation-related terms.

The association-related terms comprise terms $(\alpha+\beta)a_{\alpha\beta}(t)c_\alpha c_\beta$, $-\alpha(1+\delta_{\alpha\beta})a_{\alpha\beta}(t)c_\alpha c_\beta$, and $-\beta(1+\delta_{\alpha\beta})a_{\alpha\beta}(t)c_\alpha c_\beta$ at all $\alpha, \beta = 1, 2, \ldots$. They are mutually compensating.

The dissociation-related terms comprise terms $-(\alpha+\beta)b_{\alpha\beta}(t)c_\beta$, $\alpha(1+\delta_{\alpha\beta})b_{\alpha\beta}(t)c_\beta$, and $\beta(1+\delta_{\alpha\beta})b_{\alpha\beta}(t)c_\beta$ at all $\alpha, \beta = 1, 2, \ldots$. These terms are also mutually compensating. The above means that the right-hand side of (2.20) is identically zero and, thus, (2.21) holds. □

We emphasize that the proof of Proposition 2.1 is based on the fact that ODE system (2.18), (2.19) is countably infinite and only comprises the terms, which are mutually compensating. Since this fact is independent of whether the settings for the system are rigorous or formal, the proof is valid in the case of the formal system.

Equality (2.21) expresses the law of conservation of TNPFU. Proposition 2.1 shows that this is a fundamental feature of countably infinite system (2.18), (2.19). The next section derives and discusses the finite version of this system.

3. Finite version of the formal countably infinite ODE system

The present section obtains an answer to Research Question 1 formulated in Remark 1.1. The section derives the finite version of the formal countably infinite ODE system (2.18), (2.19). As shown in Remark 2.1, the finite version is inherently associated with MPS, $J(t)$. It is thought to be the dimension of the state space of the corresponding model. However, since the settings for finite ODE systems in the spaces with the t-dependent dimensions are unknown, we regard the finite version of ODE system (2.18), (2.19) in the particular case where $J(t)$ is independent of t, i.e., $J(t) = J$. This is the case analyzed in the present work.

We assume that $J \geq 2$. The J-dimensional versions of (2.4) and (2.6) are

$$c_j \geq 0, \, j = 1, 2, \ldots, J, \tag{3.1}$$

$$c = \sum_{j=1}^{J} j c_j, \tag{3.2}$$

$$0 < c < \infty. \tag{3.3}$$

We note that the number J is of the same meaning as that of the term n_{max} in [21, p. 3683]. That work in particular reports the results for $J = 100$ (see [21, Section 5.2]).

Remark 3.1. As follows from (3.1) and (3.2), the term jc_j / c is the probability of that the polymer size is j. Discrete functions of $j = 1, 2, \ldots, J$ determine the probability density of the probability distribution of the polymer size.

As is emphasized below Proposition 2.1, equality (2.21) expresses the law of conservation of TNPFU. Certainly, any finite version of countably infinite ODE system (2.18), (2.19) should inherit this law. The derivation of the finite, J-dimensional version depends on an answer to the question of how one can close the countably infinite system. To our knowledge, until now there is no consistent answer to this question. It may seem that the J-dimensional version of ODE system (2.18), (2.19) can be obtained if one merely truncates it to the first J equations and the first J variables (cf., [21, p. 3683]). However, this does not provide the conservation law (2.21) in the resulting J-dimensional case. The matter is resolved in the proposition below.

Proposition 3.1. *The necessary and sufficient condition for every solution of the J-dimensional version of system (2.18), (2.19) to possess conservation law (2.21) of variable (3.2) is the property that this version consists of the first J equations of the system where terms $a_{\alpha \beta}(t) c_\alpha c_\beta$ and $b_{\alpha \beta}(t) c_\beta$ at all $\alpha + \beta > J$ are omitted.*

Proof. First, one can readily see that the property indicated in the assertion is sufficient for the J-dimensional version to possess conservation law (2.21). The proof is based on the consideration presented in the proof of Proposition 2.1 and applied to the case when c is determined with (3.2) rather than (2.6).

Let us prove the necessity of the above property, i.e., the fact that it follows from the conservation law (2.21) for every solution of the J-dimensional version of system (2.18), (2.19). Relations (3.2) and (2.18), (2.19) at $j \leq J$ imply that

$$dc/dt = R(t, c_1, \ldots, c_J) \tag{3.4}$$

where the remainder term $R(t, c_1, \ldots, c_J)$ is formed by the terms, which are not compensated by the other term in the sense of the aforementioned proof of the sufficiency based on the proof of Proposition 2.1. Equalities (2.21) and (3.4) result in

$$R(t, c_1, \ldots, c_J) = 0. \tag{3.5}$$

This relation determines a hyper-surface in the state space of the system (i.e., a $J - 1$ -dimensional surface in the J-dimensional space) and, thereby, restricts the solution to the ones which are in this surface only. Since every solution of the system cannot be in it, the left-hand side of (3.5), as a function of $c_1, \ldots, c_J$ at fixed t, must be identically zero, i.e., the J-dimensional version must only include the terms, which are mutually compensated, or, equivalently, the terms prescribed by the property indicated in the assertion of the proposition. This completes the proof of the proposition. $\square$

Proposition 3.1 shows that there exists a unique J-dimensional version of ODE system (2.18), (2.19), which possesses the conservation law (2.21) or, equivalently (see also (3.2)), the property that

$$\text{parameter } c \text{ (see (3.2), (3.3)) does not depend on } t, \tag{3.6}$$

and this version is of the following form

$$dc_1/dt = -\left[\sum_{i=1}^{J-1}(1 + \delta_{i1})a_{i1}(t)c_i\right]c_1 + \sum_{i=1}^{J-1}(1 + \delta_{i1})b_{i1}(t)c_{i+1}, \tag{3.7}$$

$$dc_j/dt = -\left[\sum_{i=1}^{J-j}(1 + \delta_{ij})a_{ij}(t)c_i\right]c_j + \sum_{i=1}^{[j/2]}a_{i,j-i}(t)c_i c_{j-i}$$
$$-b_{+,j}(t)c_j + \sum_{i=1}^{J-j}(1 + \delta_{ij})b_{ij}(t)c_{i+j}, J \geq 3, j = 2, \ldots, J-1. \tag{3.8}$$

$$dc_J/dt = \sum_{i=1}^{[J/2]}a_{i,J-i}(t)c_i c_{J-i} - b_{+J}(t)c_J, \tag{3.9}$$

We remind that version (3.7)–(3.9) is only regarded under conditions (3.1)–(3.3) and (3.6).

Remark 3.2. The finite, J-dimensional version (3.7)–(3.9) of countably infinite system (2.18), (2.19) is a closed description for concentrations c_j, $j = 1, \ldots, J$. Moreover, comparison of the form of ODE system (2.18), (2.19) with the form of ODE system (3.7)–(3.9) shows that the latter in the limit as $J \to \infty$ contains all of the terms which are contained in the former. This indicates how the countably infinite system can be studied by means of its finite version.

Remark 3.2 emphasizes a methodological consistency of finite version (3.7)–(3.9) for analysis of countably infinite system (2.18), (2.19). We also note that, as follows from Proposition 3.1, any solution of ODE system (3.7)–(3.9) should be not only in the first orthant $\mathbb{R}_+^J$ (see (3.1)) of the J-dimensional Euclidean space $\mathbb{R}^J$ but also in hyper-plane (3.2).

The equations in system (3.7)–(3.9) are linearly dependent because of (3.2) and the fact that they express the derivatives of concentrations $c_1, \ldots, c_J$ involved in (3.2). Equations in the system are generally quadratic in the concentrations. In contrast to that, Eq. (3.2) is linear in the concentrations and is, thus, simpler than any of the system equations. Consequently, one can replace any equation in the system with the expression of the corresponding variable obtained from (3.2). We apply this operation to the first equation in the system because it does not include the term analogous to terms $b_{+.j}(t)c_j$ that appear in all of the other equations. This results in the equation system that consists of equation

$$c_1 = c - \sum_{j=2}^{J} jc_j \tag{3.10}$$

and Eqs. (3.8), (3.9). Therefore, Eqs. (3.8), (3.9) present a system of non-autonomous quadratic ODEs in the t-independent hyperplane (3.10) in $\mathbb{R}_+^J$ under condition (3.3).

Remark 3.3. The finite, J-dimensional ODE model (3.8)–(3.10) differs from the countably infinite system (2.18), (2.19) in not only that the reaction coefficients depend on time and the number of the variables (or ODEs) is finite. The structure of the finite model is different as well because the form of the ODE system (3.8), (3.9) is peculiar.

Indeed, all of the quadratic terms in the system are the association-related terms. Neglecting them, one obtains the linear part of the system, which is

$$dc_j/dt = -b_{+.j}(t)c_j + \sum_{i=1}^{J-j}(1 + \delta_{ij})b_{ij}(t)c_{i+j}, J \geq 3, \ j = 2, \ldots, J - 1, \tag{3.11}$$

$$dc_J/dt = -b_{+.J}(t)c_J. \tag{3.12}$$

This is a homogeneous non-autonomous linear ODE system. It presents the dissociation-only case of system (3.8), (3.9). The matrix of system (3.11), (3.12) is upper triangular.

Accepting the vector notation

$$\bar{c} = \begin{pmatrix} c_2 \\ \vdots \\ c_J \end{pmatrix}, \tag{3.13}$$

one can rewrite system (3.8), (3.9) in the following vector form

$$d\bar{c}/dt = \bar{B}(t)\bar{c} + \bar{a}(t, c_1, \bar{c}) \tag{3.14}$$

where $\bar{B}(t)$ is the upper triangular matrix of system (3.11), (3.12) and the entries of vector $\bar{a}(t, c_1, \bar{c})$ result from the corresponding grouping of the association-related terms of the mentioned system. Thus, the vector form (3.14) of quadratic system (3.8), (3.9) shows that this system is formally quasi-linear. Moreover, as is well known from theory of non-autonomous linear ODE systems (e.g., [31]), the Cauchy matrix for the linear part of (3.14), $C(t, s)$, presents the solution of the initial-value problem

$$dC(t, s)/dt = \bar{B}(t)C(t, s), C(t, s)|_{t=s} = I, t > s, \tag{3.15}$$

where I is the identity matrix. Since matrix $\bar{B}(t)$ is triangular, the Cauchy matrix can be determined analytically.

The above features are remarkable because they hold in spite of the fact that model (3.8)–(3.10) is derived for a fairly general family of homopolymer mixtures.

We note that, in order to specify individual solutions of system (3.8)–(3.10) under conditions (3.1), it is sufficient to introduce the initial conditions

$$c_j|_{t=t_o} = c_{o.j}, j = 2, \ldots, J, \tag{3.16}$$

where t_o is the initial time point. In terms of vector notation (3.13), inequalities (3.1) are equivalent to

$$c_1 \geq 0, \tag{3.17}$$

$$\bar{c} \in \mathbb{R}_+^{J-1}, \tag{3.18}$$

and relations (3.10) and (3.16) are equivalent to

$$c_1 = c - (2 \ 3 \ \ldots \ J-1 \ J)\bar{c}, \tag{3.19}$$

$$\bar{c}|_{t=t_o} = \bar{c}_o, \tag{3.20}$$

respectively, where $(2\ 3\ \ldots\ J-1\ J)$ is a row-vector and

$$\bar{c}_{\mathrm{o}} = \begin{pmatrix} c_{\mathrm{o}.2} \\ \vdots \\ c_{\mathrm{o}.J} \end{pmatrix}.$$

Note that (3.17) and (3.18) are necessary for the settings to be physically meaningful.

Remark 3.4. The derived model for analysis of finite polymer mixtures dispersed in fluid-solid media comprises:

- Time-independent parameters n, ϕ, υ, and t_{o};
- Relation (2.5) and condition (3.3) for c;
- Relations (2.3) and (2.7) at all $j = 1, 2, \ldots, J$;
- Initial values for concentrations (2.1) at all $j = 2, \ldots, J$, which, in view of (2.3), provide initial values (3.20);
- Conditions (3.1);
- Expression (3.10) for c_1; this expression presents a time-independent hyperplane for the ODE system below;
- ODE system (3.8), (3.9) for c_j, $j = 2, \ldots, J$, and initial conditions (3.16) for this system.

The model takes into account the porosity of the dispersion-medium/polymer-mixture system (see the text in Section 2 above Remark 2.1). Solutions of the model grant the time evolution of concentrations (2.1) by means of relations (2.7) at all $j = 1, 2, \ldots, J$.

This remark formulates the main outcomes of the present section.

4. Engineering applications of the finite ODE system

The present section briefly discusses engineering applications of the finite ODE system derived in the previous section. It also obtains an answer to Research Question 2 formulated in Remark 1.2.

Both synthetic and natural polymers play an essential and ubiquitous role in everyday life. Book [29] provides an in-depth discussion and presents numerous examples in the natural/life sciences and engineering. Polymers range from synthetic plastics (e.g., polystyrene) to natural biological polymers such as DNA and proteins that are fundamental to biological structure and function. Polymers, both natural and synthetic, are created via polymerization of many PFUs. Due to their large molecular mass relative to the ones of small molecule compounds, polymers possess unique physical properties. The distribution of the polymer size (e.g., see Remark 3.1) is one of the crucial characteristics of polymerization processes. This characteristic is especially complex in the polymer mixtures with time-dependent reaction coefficients. One of the most important potential industrial application of these mixtures is discussed in Remark 1.2.

Polymerization-like processes produce large compounded particles from nano-particles, in particular, create large particles from vapors [17, Section 7]. The list of the systems inherently associated with the phenomena similar to polymerization can readily be extended. For instance, a good quantitative understanding of nucleation in the atmosphere is essential input in climate models. Likewise is the particle growth through all its size regimes in proto-stellar space mandatory knowledge for the understanding of planet formation in solar-system-like scenarios. Technologically, the application of nanotechnology has caused an increased use of, and demand for, nanoparticles in bulk quantities, in addition to single particle applications in, for example, electronics. Coating of large surfaces with nanoparticles for optical or maintenance purposes and using carbon nanotubes as additives to construction material are two examples. Also, the discoveries of several size effects in clusters, such as the fullerene structures, the electronic shell structure, and geometric shell structures, have been made by experimental observation of the structures with very non-uniform particle-size distributions.

Polymers of different types determine different families of the reaction coefficients $a_{\alpha\beta}(t)$ and $b_{\alpha\beta}(t)$ (see (2.9)–(2.13)). The corresponding examples in the case where these coefficients are independent of time can found in [17, pp. 162–164], [11, Section 2.4], and [21, (1.2)].

The finite ODE system developed in the present work and summarized in Remark 3.4 is applicable to any of the aforementioned engineering polymer systems provided that the polymers are homopolymers rather then copolymers. These applications can be implemented only if a suitable quantitative method is available. However, nowadays there are a number of unmet challenges on the way to such method.

Another challenge is that system (3.8)–(3.10) has a quadratic right-hand side. This feature implies a number of complications. They are exemplified below.

Example 4.1. In the particular case where ODE system (3.8), (3.9) is autonomous, i.e., its coefficients are independent of t, expressions (3.8) and (3.9) are reduced to

$$dc_j/dt = -\left[\sum_{i=1}^{J-j}(1+\delta_{ij})a_{ij}c_i\right]c_j + \sum_{i=1}^{[j/2]} a_{i,j-i}c_i c_{j-i}$$

$$-b_{+.j}c_j + \sum_{i=1}^{J-j}(1 + \delta_{ij})b_{ij}c_{i+j}, J \geq 3, j = 2, \ldots, J-1. \tag{4.1}$$

$$dc_J/dt = \sum_{i=1}^{[J/2]} a_{iJ-i}c_ic_{J-i} - b_{+.J}c_J. \tag{4.2}$$

As before, c_1 is determined with (3.10). System (3.10), (4.1), (4.2) does not have the zero vector as an equilibrium point due to positive c in (3.10) (see also the first inequality in (3.3)). However, it may have one or more non-zero equilibrium points. They may be of different types of stability. The picture is not very simple already in the case of monomer-dimer mixtures, i.e., where $J = 2$.

In this case, Eq. (4.1) are not applicable and Eqs. (3.10) and (4.2) are reduced to

$$c_1 = c - 2c_2, \tag{4.3}$$

$$dc_2/dt = a_{1.1}c_1^2 - b_{+.2}c_2, \tag{4.4}$$

respectively. In the corresponding analysis, we skip the trivial case $a_{1.1} = 0$ and, thus (see (2.9)), only consider the case where

$$a_{1.1} > 0, \tag{4.5}$$

If $b_{+.2} = 0$, then Eq. (4.4), in view of (4.3), becomes $-dc_1/dt = a_{1.1}c_1^2$ that results in solutions of the form $c_1 = c_{0.1}/[1 + 2c_{0.1}a_{1.1}(t - t_o)]$. The case where $b_{+.2} > 0$ is considered below.

Relations (3.1) at $j = 1, 2$ and (3.2) at $J = 2$, i.e., (4.3) are equivalent to the relation

$$0 \leq c_2 \leq c/2. \tag{4.6}$$

In view of (4.3), ODE (4.4) can be rewritten as follows

$$dc_2/dt = 4a_{1.1}c_2^2 - (4a_{1.1}c + b_{+.2})c_2 + a_{1.1}c^2. \tag{4.7}$$

Consequently, equation system (4.3), (4.4) for c_1 and c_2 is equivalently reduced to the integral manifold (4.3) for c_1 and the closed ODE (4.7) for c_2. This ODE is, thus, the main equation of the monomer-dimer model.

One can readily check that ODE (4.7) has exactly two equilibrium points,

$$c_{2.as} = c_{2.*} - \sqrt{8a_{1.1}b_{+.2}c + b_{+.2}^2}/(8a_{1.1}) \tag{4.8}$$

and

$$c_{2.u} = c_{2.*} + \sqrt{8a_{1.1}b_{+.2}c + b_{+.2}^2}/(8a_{1.1}) \tag{4.9}$$

where

$$c_{2.*} = c/2 + b_{+.2}/(8a_{1.1}). \tag{4.10}$$

Point (4.8) is asymptotically stable. Point (4.9) is unstable. These points indicate the following picture for the phase portrait of ODE (4.7):

$$c_2 < c_{2.u}, \text{ the domain of asymptotic stability}, \tag{4.11}$$

$$c_2 > c_{2.u}, \text{ the domain of instability}. \tag{4.12}$$

Finally, one can solve the initial-value problem for ODE (4.7) analytically due to well known results (e.g., [30, 160.01]). The solution is

$$\left| \frac{c_2 - c_{2.as}}{c_2 - c_{2.u}} \right| = \left| \frac{c_{0.2} - c_{2.as}}{c_{0.2} - c_{2.u}} \right| \exp\left[-\sqrt{8a_{1.1}b_{+.2}c + b_{+.2}^2}(t - t_o) \right]. \tag{4.13}$$

Resolving the absolute values in (4.13) and applying an extra part of the above results [30, 160.01, 702, 703], one obtains the following explicit expression for c_2

$$c_2 = \frac{c_{2.as}(c_{0.2} - c_{2.u}) - c_{2.u}(c_{0.2} - c_{2.as}) \exp\left[-\sqrt{8a_{1.1}b_{+.2}c + b_{+.2}^2}(t - t_o) \right]}{(c_{0.2} - c_{2.u}) - (c_{0.2} - c_{2.as}) \exp\left[-\sqrt{8a_{1.1}b_{+.2}c + b_{+.2}^2}(t - t_o) \right]}. \tag{4.14}$$

It presents the exact solution of ODE (4.7) with initial condition

$$c_2|_{t=t_o} = c_{0.2}. \tag{4.15}$$

The instability of equilibrium point (4.9) manifests itself in terms of (4.14) in the following way. If $c_{o.2} = c_{2.u}$, then $c_{o.2} \neq c_{2.as}$, the solution is identically equal to $c_{2.u}$. If $c_{o.2} \neq c_{2.u}$, then $\lim_{t \to -\infty} c_2 = c_{2.u}$, $\lim_{t \to \infty} c_2 = c_{2.as}$, and dependence (4.14) describes the $(t_o, c_{o.2})$ -specific transition of c_2 from unstable equilibrium point $c_{2.u}$ to asymptotically stable equilibrium point $c_{2.as}$. The above consideration presents the complete analytical analysis of monomer-dimer mixtures in the case where the reaction coefficients are time-independent.

As indicated in Example 4.1, the physically relevant settings for ODE (4.7) include relation (4.6), which results from (3.1) and (3.10) (or (3.2)). Note that, under condition (4.6) and in view of expressions (4.9), (4.10), ODE (4.7) has exactly one equilibrium point (see (4.8)), and this point is asymptotically stable. These features inspire the following hypothesis related to the general model.

Hypothesis 4.1. Quadratic ODE system (3.8), (3.9) under conditions (3.10) and (3.1) has exactly one equilibrium point, and this point is asymptotically stable.

It is unknown if this hypothesis is true or not. However, the analysis presented in Example 4.1 shows that the hypothesis is true in the particular case where the ODE system is autonomous and $J = 2$. This feature and the fact that conditions (3.10) and (3.1) are physically relevant indicate in favor of that the hypothesis can be true in the general case.

Until the validity of Hypothesis 4.1 is proven, quadratic ODE system (3.8), (3.9) under conditions (3.10) and (3.1) can, in general, have more than one equilibrium point, and they can be unstable or stable but not asymptotically. An example that does not seem too unrealistic is the following. If autonomous version (4.1), (4.2) of system (3.8), (3.9) has, under conditions (3.10) and (3.1), a non-constant periodic solution, this solution cannot be asymptotically stable (e.g., [31, Example 2 in Section 19 of Chapter 4]).

Generally speaking, stability analysis of models for the reactions in polymer mixtures remains severely under-represented in the literature. This fact prompts to survey the available numerical methods.

In the literature, there is a lack of numerical methods that can properly deal with the autonomous-ODE solutions, which are sufficiently close to non-asymptotically stable or unstable equilibrium points. The test equations are $dx/dt = \gamma x$ and $d^2x/dt^2 = -\gamma x$ where x is a real scalar and $\gamma > 0$ is independent of t. The first equation is unstable, whereas the second one is stable but not asymptotically stable. One can apply any of the commonly used finite-difference/finite-element (FD/FE) methods (one-step, multi-step, explicit, implicit, semi-implicit, etc.) to each of these equations and compare the errors between the obtained numerical solutions at arbitrary small fixed time step, on the one hand, and the corresponding exact solutions, on the other hand. As a result, one will see that these errors accumulate in the course of time. This problem is not resolved until now and is not properly acknowledged in the non-mathematical sciences.

The above means that an answer to Research Question 2 (see Remark 1.2) is negative. The next section proposes a method, which is intended to enable all of the aforementioned engineering applications and has a chance to be free from the indicated drawbacks. This method is combined analytical-numerical. It can be useful for various purposes. For instance, in applications to technologies, it will noticeably facilitate the design of production processes that aim to obtain particles of specific size distributions. Also, if additional particle-specific knowledge is available, it has the potential to select particles with special properties in addition to the size. It will also be useful in characterizing particle ensembles and provide a tool to design particles with special sizes and properties. This list can easily be continued.

5. Analytical-numerical method for solution of the finite ODE system

The present section develops an answer to Research Question 3 formulated in Remark 1.3. The method mentioned in the formulation of this question is supposed to solve the initial-value problems for non-autonomous quadratic ODE system (3.8)–(3.10) or, in the vector form (3.14), (3.19). In the latter case, the initial condition is (3.20) and the conditions that assure the physical meaningfulness of the solution are (3.17) and (3.18). However, as is shown in Example 4.1, the state space of system (3.8), (3.9) even in the simplest case, i.e., where $J = 2$ and the reaction coefficients are independent of time, is subdivided into the domain of asymptotic stability and the domain of instability. In contrast to that, in the general case, until Hypothesis 4.1 is proven, it is unknown whether the initial value in the above problem is located in the domain of asymptotic stability, the domain of non-asymptotic stability, or the domain of instability. For this reason, purely numerical methods are generally useless (see the discussion below Hypothesis 4.1). Methods of another nature can probably be more helpful. One of these alternatives is the analytical-numerical (AN) one.

The AN techniques are in many cases based on successive approximations (SA). Methods of this type presume solving mathematical problems by means of a sequence of approximations that converges to the solution and is constructed recursively, i.e., each new approximation is calculated on the basis of the preceding approximation. The choice of the initial approximation is, to some extent, arbitrary. The methods are used to approximate the roots of algebraic and transcendental equations. They are also used to prove the existence of a solution and to approximate the solutions of differential, integral, or integro-differential equations. Other uses include obtaining a qualitative characterization of a solution or an analytical insight in the structure of a solution. The latter is especially valuable in engineering problems.

In order to construct an SA method for the present problem, the special features of the model, which is summarized in Remark 3.4, are useful. According to Remark 3.3, ODE (3.14) is of the quasi-linear form and the linear part of this equation, which is the dissociation-only part, is analytical solvable. The time evolution of a polymer mixture is determined by the

competition of the association and dissociation terms. This competition presents a physically relevant basis for design of an SA technique. Specifically, we consider a technique that benefits from the above two features. It comprises the relations listed below.

The zeroth approximations, $\bar{c}^{(0)}(t)$ and $c_1^{(0)}(t)$, are determined as follows. Vector $\bar{c}^{(0)}(t)$ is set to zero,

$$\bar{c}^{(0)}(t) = 0, \text{ the entire } t\text{-axis}, \tag{5.1}$$

and $c_1^{(0)}(t)$ is determined from (3.19) and (5.1), i.e.,

$$c_1^{(0)}(t) = c, \text{ the entire } t\text{-axis}. \tag{5.2}$$

Why the zeroth approximations are chosen as shown in (5.1) and (5.2) is explained in the text below (5.21).

At every $k = 1, 2, \ldots$, the kth approximations, $\bar{c}^{(k)}(t)$ and $c_1^{(k)}(t)$, are determined in terms of the preceding, $(k-1)$th approximations. Vector $\bar{c}^{(k)}(t)$ is determined as the solution of non-autonomous linear ODE system

$$d\bar{c}^{(k)}(t)/dt = \bar{B}(t)\bar{c}^{(k)}(t) + \bar{a}(t, c_1^{(k-1)}(t), \bar{c}^{(k-1)}(t)), t > t_o, k = 1, 2, \ldots, \tag{5.3}$$

with initial condition (cp., (3.20))

$$\bar{c}^{(k)}(t)|_{t=t_o} = \bar{c}_o, k = 1, 2, \ldots. \tag{5.4}$$

It is possible to indicate an explicit expression for solution of initial-value problem (5.3), (5.4).

As is well known, ODE system (3.14) with initial condition (5.4) corresponds to integral equation

$$\bar{c}(t) = C(t, t_o)\bar{c}_o + \int_{t_o}^{t} C(t, s)\bar{a}(s, c_1(s), \bar{c}(s))ds, t \geq t_o, \tag{5.5}$$

where $C(t,s)$ is the Cauchy matrix discussed in Remark 3.3. The SA procedure (5.3), (5.4) corresponds to solving equation (5.5) in the following way:

$$\bar{c}^{(k)}(t) = C(t, t_o)\bar{c}_o + \int_{t_o}^{t} C(t, s)\bar{a}(s, c_1^{(k-1)}(s), \bar{c}^{(k-1)}(s))ds, t \geq t_o, k = 1, 2, \ldots. \tag{5.6}$$

The corresponding scalar $c_1^{(k)}(t)$ is determined as (cp., (3.19))

$$c_1^{(k)}(t) = c - (2 \ 3 \ \ldots \ J-1 \ J)\bar{c}^{(k)}(t), t \geq t_o, k = 1, 2, \ldots. \tag{5.7}$$

Thus, the proposed SA technique comprises relations (5.1), (5.2), (5.6), and (5.7).

This includes the explicit analytical expressions (5.6) for each of the approximations in terms of the preceding approximation. These expressions show how the time-dependent reaction parameters influence the time evolution of the approximations. This information in general facilitates analysis or design of polymer mixtures.

Remark 5.1. The AN/SA method is, by its origin, exact in the particular, dissociation-only case. This is the unique advantage compared to any other available computational method.

The noted feature means that the proposed method provides adequate results if the influence of the association terms is not too high.

As is noted in Remark 3.3, the Cauchy matrix used in (5.6) can be evaluated analytically. The second term on the right-hand side of (5.6) can also be evaluated analytically. In practice, all of these calculations can be implemented at a sequence of time points on computer even if J is large, i.e., in the case noted in Section 1. Common multi-processor/multi-core personal computers with graphic processing units enable one to carry out the corresponding computing efficiently. In other words, the above SA method admits AN implementation. Taking that into consideration, we term the proposed method (5.1), (5.2), (5.6), (5.7) the AN/SA method.

Remark 5.2. In addition to the feature in Remark 5.1, another striking difference of the proposed AN/SA method from common, purely numerical methods such as the FD/FE ones is outlined in the next to last paragraph of Section 4. The common methods concentrates on extrapolation of a trajectory for the time interval, which is between the subsequent and present time-discretization points, on the basis of knowledge of the trajectory in the time interval, which is between the present point and preceding point (or points). In this paradigm, the focus is on the time-local details in favor of attempts to see the trajectory in the whole, in the entire time interval where it is defined.

In contrast to the above local paradigm, the proposed AN/SA method suggests the vision, which is global in the sense that it deals with a sequence of approximations to the trajectory, each of which is defined in the entire time interval of the definition of the trajectory.

Lemma 5.1. *Let there exist scalars* $\Gamma > 0$ *and* $\gamma > 0$ *, which do not dependent on t and s, and are such that*

$$\|C(t, s)\| \leq \Gamma \exp[-\gamma(t - s)], t > s, \tag{5.8}$$

where $\| \cdot \|$ *is a norm of a matrix. (This means that ODE system (3.11), (3.12) is globally exponentially stable (and, thus, globally asymptotically stable).*

If $k = 1, 2, \ldots$ is arbitrary fixed, then the following properties are valid.

ODE system (5.3), as an equation system for vector $\bar{c}^{(k)}(t)$, is globally exponentially stable,

and function $\bar{c}^{(k)}(t)$ is a globally exponentially stable solution of Eq. (5.3), $\qquad$ (5.9)

functions $\bar{c}^{(k)}(t)$ and $c_1^{(k)}(t)$ are uniformly bounded in $t \geq t_o$, $\qquad$ (5.10)

$$\bar{c}^{(k)}(t) - \bar{c}(t) = \int_{t_o}^{t} C(t,s)[\bar{a}(s, c_1^{(k-1)}(s), \bar{c}^{(k-1)}(s)) - \bar{a}(s, c_1(s), \bar{c}(s))]ds, t \geq t_o, k = 1, 2, \ldots. \qquad (5.11)$$

function $\bar{a}(s, c_1(s) + \zeta_1, \bar{c}(s) + \overline{\zeta}) - \bar{a}(s, c_1(s), \bar{c}(s))$ where $\overline{\zeta}$ is a $(J-1)$-vector and $\zeta_1 = c - (2\ 3\ \ldots\ J-1\ J)\overline{\zeta}$,

as a function of $\Delta \overline{\zeta}$, is quadratic and homogeneous but has generally non-zero linear part. $\qquad$ (5.12)

Proof. Property (5.9) follows from Remark 3.3, the form of ODE system (5.3), and inequality (5.8).

Since functions $\bar{c}^{(k)}(t)$ and $c_1^{(k)}(t)$ and at $k = 0$ are uniformly bounded in $t \geq t_o$ because of (5.1) and (5.2), it is sufficient to prove property (5.10) under the condition that functions $\bar{c}^{(k-1)}(t)$ and $c_1^{(k-1)}(t)$ are uniformly bounded in $t \geq t_o$. Taking into account this condition, the form of function $\bar{a}$ (see Remark 3.3), the uniform boundedness in (2.9), and inequality (5.8), one obtains property (5.10).

Expression (5.11) results from (5.3) and (3.14). Property (5.12) follows from the aforementioned form of function $\bar{a}$, the role of c_1 (see (3.19)) in the association-related terms in (3.8) and (3.9), and the fact that c is finite and positive (see (3.3)). $\square$

The present work does not rigorously consider sufficient conditions for the convergence of AN/SA method (5.1), (5.2), (5.6), and (5.7) for two reasons. Firstly, development of the approximation error (5.11) is significantly complicated by property (5.12). Secondly, the form of expression (5.11) specifies the feature noted in Remark 5.1. This form shows that the convergence is expected if the association-related term $\bar{a}(s, c_1, \bar{c})$ is small, i.e., if the association-reaction coefficients in (3.8) and (3.9) are not too large, and the zeroth approximations are not very far from the solution.

We consider below certain implications of the convergence. In order to do that, we introduce the following notations:

$$\bar{c}_{ss}^{(0)}(t) = \bar{c}^{(0)}(t), t \in \mathbb{R}, \qquad (5.13)$$

$$c_{1.ss}^{(0)}(t) = c_1^{(0)}(t), t \in \mathbb{R}, \qquad (5.14)$$

$$\bar{c}_{ss}^{(k)}(t) = \int_{-\infty}^{t} C(t,s)\bar{a}(s, c_{1.ss}^{(k-1)}(s), \bar{c}_{ss}^{(k-1)}(s))ds, t \in \mathbb{R}, k = 1, 2, \ldots, \qquad (5.15)$$

$$c_{1.ss}^{(k)}(t) = c - (2\ 3\ \ldots\ J-1\ J)\bar{c}_{ss}^{(k)}(t), t \in \mathbb{R}, k = 1, 2, \ldots. \qquad (5.16)$$

These equalities are somewhat similar to equalities (5.1), (5.2), (5.6), and (5.7).

Lemma 5.2. *Let hypothesis of Lemma 5.1 holds. Let also $k = 1, 2, \ldots$ be arbitrary fixed.*
Then the following assertions are valid.

(i) *Functions $\bar{c}_{ss}^{(k)}(t)$ and $c_{1.ss}^{(k)}(t)$ are uniformly bounded in $t \in \mathbb{R}$.*
(ii) *Limit relation*

$$\bar{c}_{ss}^{(k)}(t) = \lim_{t_o \to -\infty} \bar{c}^{(k)}(t), uniformly\ in\ t \in \mathbb{R}, \qquad (5.17)$$

holds. Function $\bar{c}_{ss}^{(k)}(t)$ is a steady-state solution of non-autonomous linear system (5.3), i.e., a solution of (5.3), which is independent of initial value $\bar{c}_o$ (see initial condition (5.4)).
(iii) *Limit relation*

$$\lim_{t \to \infty} |\bar{c}^{(k)}(t) - \bar{c}_{ss}^{(k)}(t)| = 0, t \in \mathbb{R}, \qquad (5.18)$$

holds as well.

Proof. The proof of assertion (I) is based on relations (5.13)–(5.16), and is similar to the proof of property (5.10) in *Lemma 5.1*.

Passing to the limit as $t_o \to -\infty$ in (5.6) and allowing for inequality (5.8), one obtains (5.15) and, thus, (5.17). The last sentence in assertion (ii) results from comparison of (5.15) and (5.6) where the latter presents the solution of initial-value problem (5.3), (5.4). This proves assertion (ii).

Assertion (iii) follows from the global exponential stability of $\bar{c}^{(k)}(t)$ in property (5.9). This completes the proof of the proposition. □

The role of the steady-state, or "dynamic-equilibrium" solutions of non-autonomous ODEs in the real-life problems is discussed in more detail in [32]. Briefly, one can note that, in a domain of asymptotic stability of a non-autonomous ODE system, the steady-state solution of the system presents the core behavior of the system, i.e. the behavior, which is not specified with an initial condition.

In terms of finite polymer mixtures, these solutions can easily be illustrated with calculation (5.17) in the case of Example 4.1. In this case, passing in (4.14) to the limit, which is indicated in (5.17), one obtains

$$c_{2.ss}(t) = c_{2.as}, t \in \mathbb{R}. \tag{5.19}$$

Also, as is noted in Remark 5.1, the AN/SA method is exact in the dissociation-only case. The zeroth approximations are chosen in the way of (5.1) and (5.2) because these relations present the steady-state solutions of system (3.14), (3.19) in the mentioned case.

Theorem 5.1. *Let hypothesis of Lemma 5.2 holds. Let also the sequence of steady-state solutions of linear ODEs (5.3), i.e., functions $\bar{c}_{ss}^{(k)}(t)$, in the limit as $k \to \infty$ converges uniformly in $t \in \mathbb{R}$ to the limit function denoted with $\bar{c}_{ss}(t)$.*
Then the following assertions are valid.

(i) *Functions $\bar{c}_{ss}(t)$ and*

$$c_{1.ss}(t) = c - (2 \ 3 \ \ldots \ J-1 \ J)\bar{c}_{ss}(t) \tag{5.20}$$

are uniformly bounded in $t \in \mathbb{R}$.
(ii) *Function $\bar{c}_{ss}(t)$ is a steady-state solution of nonlinear ODE (3.14).*

Proof. Assertion (i) follows form assertion (i) of Lemma 5.2 and the convergence mentioned in the hypothesis.
Passing to the limit as $k \to \infty$ in (5.15) and allowing for both inequality (5.8) and equality (5.20), one obtains

$$\bar{c}_{ss}(t) = \int_{-\infty}^{t} C(t,s)\bar{a}(s, c_{1.ss}(s), \bar{c}_{ss}(s))ds, t \in \mathbb{R}. \tag{5.21}$$

Comparison of (5.21) and (5.5) where the latter presents the solution of initial-value problem (3.14), (5.4), results in assertion (ii). This completes the proof. □

Theorem 5.1 proposes a procedure for constructing a steady-state (or "dynamic-equilibrium") solution of a non-autonomous quadratic ODE system. Presently, results on steady-state solutions of non-autonomous nonlinear ODEs are still rare in the literature.

Theorem 5.2. *Let hypothesis of Theorem 5.1 holds. Then the following assertions are valid.*

(i) *The sequence of functions $\bar{c}^{(k)}(t)$ (see (5.6)) in the limit as $k \to \infty$ converges to $\bar{c}_{ss}(t)$ at point $t = \infty$.*
(ii) *If the sequence of functions $\bar{c}^{(k)}(t)$ in the limit as $k \to \infty$ converges uniformly in $t \in [t_o, \infty)$, then*

$$\lim_{k \to \infty} \bar{c}^{(k)}(t) = \bar{c}(t) uniformly \ in \ t \in [t_o, \infty) \tag{5.22}$$

where, as before, $\bar{c}(t)$ is the solution of initial value problem (3.14), (5.4), this solution is asymptotically stable, and initial value $\bar{c}_o$ (see (5.4)) is in a domain of asymptotic stability of non-autonomous quadratic ODE (3.14).
(iii) *If initial value $\bar{c}_o$ is not in the above domain, the convergence specified in the antecedent of assertion (ii) is not the case.*

Proof. Function $\bar{c}^{(k)}(t)$ can obviously be presented as follows

$$\bar{c}^{(k)}(t) = [\bar{c}^{(k)}(t) - \bar{c}_{ss}^{(k)}(t)] + \bar{c}_{ss}^{(k)}(t). \tag{5.23}$$

The passing to the limit as $t \to \infty$ in (5.23) and allowing for (5.18), one obtains

$$\lim_{t \to \infty} \bar{c}^{(k)}(t) = \lim_{t \to \infty} \bar{c}_{ss}^{(k)}(t). \tag{5.24}$$

The passing to the limit as $k \to \infty$ in (5.24) results in

$$\lim_{k \to \infty} [\lim_{t \to \infty} \bar{c}^{(k)}(t)] = \lim_{k \to \infty} [\lim_{t \to \infty} \bar{c}_{ss}^{(k)}(t)], \tag{5.25}$$

Interchanging the limits in (5.25) and taking into account the convergence in the hypothesis of Lemma 2, one gets limit relation

$$\lim_{t \to \infty} [\lim_{k \to \infty} \bar{c}^{(k)}(t)] = \lim_{t \to \infty} \bar{c}_{ss}(t)$$

that expresses the convergence at point $t = \infty$. This proves assertion (i).
Passing to the limit as $k \to \infty$ in (5.3) and allowing for the convergence in the antecedent of assertion (ii), one obtains that ODEs (5.3) are transformed into (3.14) and, thus, (5.22) holds. The asymptotic stability of $\bar{c}(t)$ follows from the facts that

$\bar{c}(t)$ and approximations $\bar{c}^{(k)}(t)$ at all $k = 1, 2, \ldots$ have the same initial value (see (5.5) and (5.6)), each of the approximation is an exponentially stable solution of the corresponding ODE in sequence of ODEs (5.3), and the convergence is uniformly in $t \in [t_o, \infty)$. Since $\bar{c}(t)$ is asymptotically stable, the corresponding initial value, i.e., $\bar{c}_o$ is in a domain of asymptotic stability of non-autonomous quadratic ODE (3.14). This proves assertion (ii).

Assertion (iii) directly follows from the formulation of assertion (ii). This completes the proof. □

Remark 5.3. The meaning of the assertions of Theorem 5.2 under the hypothesis of this theorem can be summarized in less formal terms.

If the AN/SA method is used for solution of an initial-value problem for the finite-mixture ODE system, then, according to assertion (i), the approximations converge to a steady-state solution of this system at infinite time. This, in particular, means that, at any sufficiently large k, there is time interval $[t_k, \infty)$ where the kth approximation sufficiently accurately describes the solution $\bar{c}_{ss}(t)$. The procedure converges, irrespective of whether or not the initial value is in a domain of asymptotic stability of the system.

If, besides, the above convergence is uniform in $t \in [t_k, \infty)$, then, according to assertion (ii) of Theorem 5.2, the approximations converge to the solution of the initial-value problem, this solution is asymptotically stable, and the initial value is in the above domain.

If the initial value is not in this domain, then, according to assertion (iii), assertion (ii) is inapplicable but assertion (i) can be used as before. In other words, the the AN/SA method always produce useful results. This is another striking difference from common computational methods, in addition to the difference noted in Remark 5.2.

Remark 5.4. Obviously, the results provided by the AN/SA method are physically meaningful only if they meet conditions (3.17) and (3.18). This meaningfulness can be assured in the following way.

If the results do not meet any of the conditions, one should increase c in (5.7) or decrease at least one entry of vector $\bar{c}_o$ in (5.4), and apply the method again. This recipe is, in particular, inspired by the second inequality in (4.6).

Example 5.1. In order to illustrate the AN/SA method, we consider the method in the case of monomer-dimer mixture with time-independent reaction coefficients, which is completely analyzed in Example 4.1. In this case, expressions (5.1), (5.2), (5.6), and (5.7) reduce to

$$c_2^{(0)}(t) = 0, t \geq t_o, \tag{5.26}$$

$$c_1^{(0)}(t) = c, t \geq t_o, \tag{5.27}$$

$$c_2^{(k)}(t) = \exp[-b_{+.2}(t - t_o)]c_{o.2} + a_{1.1} \int_{t_o}^{t} \exp[-b_{+.2}(t - s)][c_1^{(k-1)}(s)]^2 ds, t \geq t_o, k = 1, 2, \ldots, \tag{5.28}$$

$$c_1^{(k)}(t) = c - 2c_2^{(k)}(t), t \geq t_o, k = 1, 2, \ldots, \tag{5.29}$$

In particular,

$$c_2^{(1)}(t) = \exp[-b_{+.2}(t - t_o)]c_{o.2} + a_{1.1}c_{o.1}^2 \int_{t_o}^{t} \exp[-b_{+.2}(t - s)]ds, t \geq t_o,$$

where $\int_{t_o}^{t} \exp[-b_{+.2}(t - s)]ds = (1/b_{+.2})[1 - \exp[-b_{+.2}(t - t_o)]]$ and, thus,

$$c_2^{(1)}(t) = \frac{a_{1.1}c_{o.1}^2}{b_{+.2}} + \left(c_{o.2} - \frac{a_{1.1}c_{o.1}^2}{b_{+J}}\right)\exp[-b_{+.2}(t - t_o)], t \geq t_o.$$

The corresponding value of $c_1(t)$ is (see 5.31)

$$c_1^{(1)}(t) = \left(c - 2\frac{a_{1.1}c_{o.1}^2}{b_{+.2}}\right) - 2\left(c_{o.2} - \frac{a_{1.1}c_{o.1}^2}{b_{+.2}}\right)\exp[-b_{+.2}(t - t_o)], t \geq t_o.$$

A quantitative implementation of the proposed AN/SA method in the case of monomer-dimer mixtures is considered in Example 5.2.

Application of the proposed AN/SA method to a monomer-dimer mixture with time-independent reaction coefficients (see Example 5.1) is quantitatively illustrated below. This particular case of polymer mixtures is chosen for the only reason that the exact analytical solution of the main equation, ODE (4.7), is available. It is (4.14). This solution enables one to evaluate the quality of the AN/SA method in specific terms.

Example 5.2. The present example considers equation system (4.3), (4.7) at $a_{1.1} = b_{+.2} = 1$ and $c = 0.2$. The values of the first two parameters can be set to unity with a scaling of the time unit and the concentration unit, and no loss of generality is implied by the two values. The $c = 0.2$ value implies a choice of concentration which, together with the initial condition, defines the problem. The corresponding values of the square-root term in (4.14), as well as parameters $c_{2.*}$, $c_{2.as}$, and $c_{2.u}$ (see (4.10), (4.8), and (4.9), respectively) are $(8a_{1.1}b_{+.2}c + b_{+.2}^2)^{1/2} = \sqrt{2.6} \approx 1.6125$, $c_{2.*} = 0.225$, $c_{2.as} \approx 0.0234$, and $c_{2.u} \approx 0.4266$, respectively. Note that the first of these numbers presents the inverse value of the relaxation time. This parameter is (approximately) 0.62.
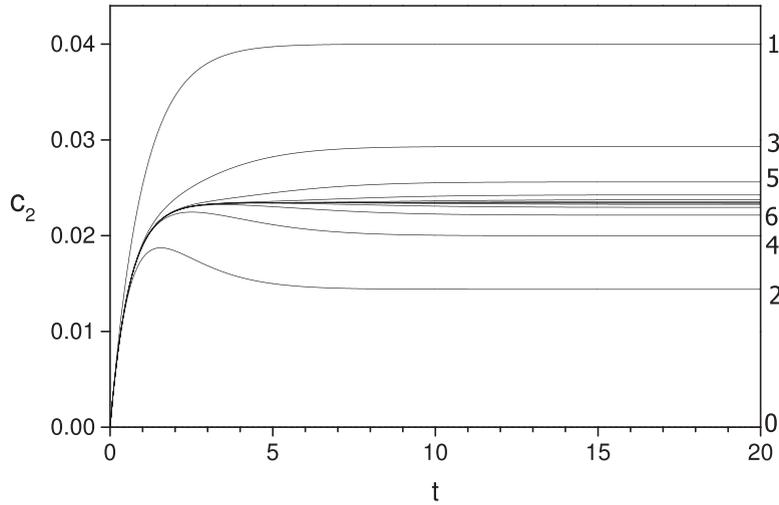
Fig. 1. The quantitative values of concentration c_2 of the dimers in the monomer-dimer mixture with the time-independent coefficients described in Example 5.1 in the case where $c_{o.2} = 0$ (and, thus, $c_{o.1} = c = 0.2$). The plots comprise the exact dependence (4.14) and a few approximations according to the AN/SA method (5.26)–(5.29). The lines in the figure show the kth approximations at $k = 0, 1, \ldots, 6, 9, 12$. The values of k are indicated to the right of the frame. The exact analytical solution agrees well with the 12th approximation.
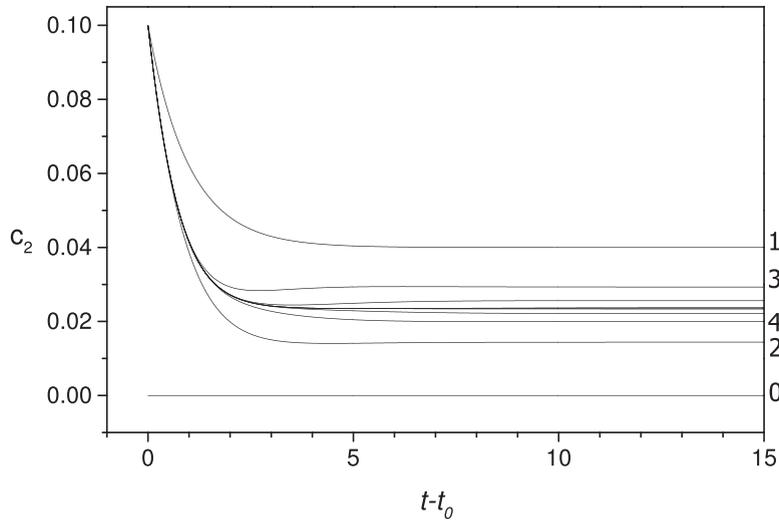
Fig. 2. The quantitative values of concentration c_2 of the dimers in the monomer-dimer mixture with the time-independent coefficients described in Example 5.1 in the case where $c_{o.2} = c/2 = 0.1$ (and, thus, $c_{o.1} = 0$). The plots comprise the exact dependence (4.14) and a few approximations according to the AN/SA method (5.26)–(5.29). The lines in the figure show the kth approximations at $k = 0, 1, \ldots, 6, 9, 12$. The values of k are indicated to the right of the frame. The exact analytical solution agrees well with the 12th approximation.

Figs. 1 and 2 show quantitative time behaviors of concentration c_2 of the dimers in the related monomer-dimer mixture at different values of $c_{o.2}$ and (see (4.15)) $c_{o.1} = c - 2c_{o.2}$, which assure that monomer concentration c_1 is non-negative, i.e., the settings are physically meaningful. The values of $c_{o.2}$ for Figs. 1 and 2 are $c_{o.2} = 0$ and $c_{o.2} = 0.2$, respectively. The time dependences in Figs. 1 and 2 illustrate the convergence in assertion (ii) of Theorem 5.2.

The above quantitative time behaviors of c_2 were also tested at value $c_{o.2} = 0.4$, which is in the domain of asymptotic stability (see (4.11)). These results also illustrate the convergence in assertion (ii) of Theorem 5.2. However, they are not included as figures because value $c_{o.2} = 0.4$ means that $c_{o.1} = -0.6$, which is not physically relevant. The corresponding calculations were implemented for the method testing only. In spite of that, the infinite-time case shows physically meaningful values. They are presented in Column 1 of Table 1.

In each of the three cases, $c_{o.2} = 0$, $c_{o.2} = 0.2$, and $c_{o.2} = 0.4$, the c_2-behaviors were also computed by means of the explicit Euler method at the fixed time step of 10^{-4}. In all of the three cases, results of the AN/SA method at higher k well agree with the results of the Euler method.

Table 1
The approximations for the steady-state solution (5.21) of ODE (4.7) obtained by means of the version of the proposed method (5.26)–(5.29) that corresponds to the case of Example 5.1 in the infinite-time limits of the solutions of initial-value problem (4.7), (4.15) at the initial values $c_{o.2} = 0.4$ and $c_{o.2} = 0.5$. Note that $c_{2.as} \approx 0.0234435$. All of the approximations were obtained at $t = 100$.

Ordinal number of the approximation	$c_{o.2} = 0.4$ 1	$c_{o.2} = 0.5$ 2
1	0.36002	0.04000
2	0.27045	0.01440
3	0.11622	0.02931
4	0.00105	0.01999
5	0.03916	0.02561
6	0.01480	0.02214
7	0.02903	0.02425
8	0.02015	0.02295
9	0.02550	0.02375
10	0.02220	0.02326
11	0.02421	0.02356
12	0.02298	0.02339

The case where $c_{o.2}$ is in the domain of instability (4.12) of ODE (4.7) is also of interest. One can show that, if $c_{o.2}$ is in this domain, then the solution of initial-value problem (4.7), (4.15) with the explicit or semi-implicit Euler method at arbitrary small fixed time step presents strictly monotonically increasing sequence of values of c_2. This behavior differs qualitatively from the behavior of the exact solution (4.14). The instability case can be exemplified with the value $c_{o.2} = 0.5$, which is in the instability domain (4.12). The quantitative-simulation results of the explicit Euler method at this value completely agree with the described behavior. The steady-state values listed in Column 2 of Table 1 illustrate the convergence in assertion (i) of Theorem 5.2 in the case of where assertion (iii) of this theorem holds. These data show that, even if the initial value is in the domain of instability, the AN/SA-method results include useful information, namely the steady-state solution, which is in the domain of asymptotic stability of ODE (4.7).

The above consideration on the AN/SA method presents a positive and specific answer to Research Question 3 (see Remark 1.3). The outcomes of the present section are summarized in the corresponding part of Section 6.

6. Conclusion

The present work deals with the ODE system for the association and dissociation reactions with time-dependent coefficients in finite mixtures of polymers dispersed in fluid media with solid components or, briefly, fluid-solid media. The polymers are regarded to be formed by identical units, polymer-forming units (PFUs) and, thus, present homopolymers. The model takes into account the porosity of the dispersion-medium/polymer-mixture system. The work obtains answers to each of the three research questions formulated in Remarks 1.1–1.3.

Summing up the work, we note the following results.

- It is shown how specifically the modeling of the above polymer mixtures can be formulated in terms of the concentrations common in theoretical-physics modeling, i.e., the concentrations of point (or volumeless) particles. The obtained formulation is used in the work.
- The ODE system for the association/dissociation reactions in finite polymer mixtures, which provides the conservation law of the total number of PFUs, is derived.
- The derived model presents a non-autonomous quadratic finite ODE system in a time-independent hyperplane in the closed first orthant of the finite-dimensional Euclidean state space. In spite of the fact that the system is derived for a fairly general family of polymer mixtures, it has three remarkable features: it is formally quasi-linear, its linear part corresponds to the dissociation-only case, and the matrix of the linear part is upper triangular. The latter feature allows analytical evaluation of the corresponding Cauchy matrix.
- A variety of engineering applications of the derived finite-mixture model are briefly discussed. One of the most important potential industrial applications is prospective production of spatially heterogeneous polymer products. The importance of stability analysis of the finite-mixture ODE system is noted. The discussed applications generally deal with asymptotically stable, stable, or unstable solutions. A need in the corresponding methods that can provide practically useful data on solutions of any of these types is emphasized.

- The complete analysis of the derived finite-mixture model is presented in the simplest case, i.e., the one of monomer-dimer mixtures with time-independent reaction coefficients (see Example 4.1). The results of this analysis straightforwardly illustrate the phenomena described with the general model.
- The analytical-numerical (AN) method of the successive-approximations (SA) type is proposed for solving the derived finite-mixture model. The approximations present approximating functions of time. It includes explicit analytical expressions for each of the approximations in terms of the preceding approximation. The AN/SA method is exact in the dissociation-only case. The approximations are expected to converge if the association-reaction coefficients are not too large and the zeroth approximations are not very far from the solution. The AN/SA method comprises two sequences of the approximations.

  If the first one converges uniformly in the entire time axis, then the limit function is a steady-state (or "dynamic equilibrium") solution of the ODE system (see Theorem 5.1). Thus, the first sequence presents a constructive technique for calculation of steady-state solution of nonlinear (quadratic) ODE systems.

  The second sequence presumes that the first sequence is convergent in the aforementioned sense. The second sequence is intended for calculation of the solutions of initial-value problems for the above ODE system in a semi-infinite time interval. If the second sequence converges uniformly in this interval, then the limit function is the solution of the initial-value problem, this solution is asymptotically stable solution, and the corresponding initial value is in a domain of asymptotic stability of the system. If the initial value is not in this domain, the second sequence converges to the steady-state solution of the ODE system at least in the infinite-time limit (see Theorem 5.2 for both the cases).

  The main differences from common computational methods are formulated (see Remarks 5.1–5.3). The AN/SA method is quantitatively illustrated with a few examples of the settings in the aforementioned case of monomer-dimer mixtures. The corresponding quantitative approximations show rather fast convergence to the available exact analytical solution (see (4.14)) if the initial value is in the domain of asymptotic stability of the model (see (4.11)). Under this condition, the AN/SA-method curves agree well with the ones obtained the explicit Euler method. If the initial value is not in the mentioned domain, the quantitative approximations of the AN/SA method converge to the steady-state solution of the model at least in the infinite-time limit, whereas the Euler-method results qualitatively differ from the exact solution of the initial-value problem at all time-discretization points.
- The form of the AN/SA method allows especially efficient implementation on multi-processor/multi-core personal computers with graphic processing units even if the dimension of the state space is large.
- The developed model and method form a constructive framework for analysis or design of polymer mixtures dispersed in fluid-solid media.

The listed results present a constructive framework for analysis and design of polymer mixtures. The directions for future research can include a number of topics.

- Implementation of the proposed AN/SA method in a computer software and analysis of different polymer mixtures by the corresponding computer simulation.
- Analysis of stability of the derived non-autonomous quadratic finite-mixture ODE system in a time-independent hyperplane.
- Conditions sufficient for the convergence of the AN/SA method.

The outcomes would contribute to improvement and greater flexibility of the developed constructive framework.

References

[1] L.H. Hartwell, J.J. Hopfield, S. Leibler, A.W. Murray, From molecular to modular cell biology, Nature 402 (1999) C47–C52.
[2] M. Smoluchowski, Drei vorträge über diffusion, brownsche molekularbewegung und koagulation von kolloidteilchen, Physik. Z. 17 (1916) 530–594 (in German).
[3] M. Smoluchowski, Versuch einer mathematischen theorie der koagulationskinetik kolloider lösungen, Physik. Z. 17 (1916) 595–639 (in German).
[4] F. Leyvraz, H.R. Tschudi, Singularities in the kinetics of coagulation processes, J. Phys. A Math. Gen. 14 (1981) 3389–3405.
[5] P. van Dongen, M.H. Ernst, Pre- and post-gel size distributions in (ir)reversible polymerisation, J. Phys. A Math. Gen. 16 (1983) L327–L332.
[6] A. Golovin, The solution of the coagulation equation for cloud droplets in a rising air current, Izv. Geophys. Ser. 5 (1963) 482–487.
[7] J. McLeod, On an infinite set of nonlinear differential equations, Quart. J. Math. Oxford 13 (1962) 119–128.
[8] D.J. Aldous, Deterministic and stochastic models for coalescence (aggregation and coagulation): a review of the mean-field theory for probabilists, Bernoulli 5 (1999) 3–48.
[9] P. Meakin, M.H. Ernst, Scaling in aggregation with breakup simulations and mean-field theory, Phys. Rev. Lett. 60 (1988) 2503–2506.
[10] P.G.J. van Dongen, M. H.Ernst, Scaling solution of Smoluchowski's coagulation equation, J. Statist. Phys. 50 (1988) 295–329.
[11] J.A.D. Wattis, An introduction to mathematical models of coagulation fragmentation processes: a discrete deterministic mean-field approach, Physica D 222 (2006) 1–20.
[12] N. Jamshidi, B. Palsson, Formulating genome-scale kinetic models in the post-genome era, Mol. Syst. Biol. 4 (1) (2008) 171/1–171/10.
[13] C. Gérard, A. Goldbeter, Temporal self-organization of the cyclin/cdk network driving the mammalian cell cycle, Proc. Natl. Acad. Sci. USA 106 (51) (2009) 21643–21648 (and 39 pp. of the supporting information).
[14] J.A. Pojman, Q. Tran-Kong-Miyata (Eds.), Nonlinear Dynamics with Polymers: Fundamentals, Methods and Applications, Wiley-VCH Verlag, Weinheim, 2010.
[15] E. Longo, N. Bellomo, The Boltzmann equation for dissipative disparate mixtures, Appl. Math. Lett 12 (6) (1999) 71–76.
[16] I.S. Ciuperca, L.I. Palade, The steady state configurational distribution diffusion equation of the standard FENE dumbbell polymer model: existence and uniqueness of solutions for arbitrary velocity gradients, Math. Models Methods Appl. Sci. 19 (11) (2009) 2039–2064.
[17] K. Hansen, Statistical Physics of Nanoparticles in the Gas Phase, Springer, Dordrecht, 2013.
[18] R.P. Treat, An exact solution of the discrete Smoluchowski equation and its correspondence to the solution of the continuous equation, J. Phys. A: Math. Gen. 23 (1990) 3003–3016.

[19] R. Simha, Kinetics of degradation and size distribution of long chain polymers, J. Appl. Phys. 12 (7) (1941) 569–578.
[20] T.A. Bak, O. Heilmann, A finite version of Smoluchowski's coagulation equation, J. Phys. A Math. Gen. 24 (20) (1991) 4889–4893.
[21] Y. Gabellini, J.-L. Meunier, Gel, self-similarity and universality in the discrete Smoluchowski equation with finite mass, J. Phys. A: Math. Gen. 25 (1992) 3683–3700.
[22] Report 2012. Additive manufacturing and 3d printing state of the industry, Annual Worldwide Progress Report, Wohelrs Associates, Fort Collins (CO, USA), 287 pp. http://wohlersassociates.com/.
[23] B.-J. de Gans, P.C. Duiveneld, U.S. Schubert, Inject printing of polymers: State of the art and future developments, Adv. Mater. 16 (3) (2004) 203–213.
[24] M. Macaré, Radiation curing: A key partner in 3D printing, IEN Europe 41 (1/2) (2015) 12–13.
[25] J.F. Bredt, New life for 3D printing, 2012. http://www.rdmag.com/articles/2012/04/new-life-3d-printing,19.
[26] V.J. Cahill, A short history and current development of UV-curing for ink jet printing, RadTech Report of RadTech International North America, July-August, 20–24, 2001. http://www.vcesolutions.com/wp-content/uploads/2014/09/A-Short-History-and-Current-Development-of-UV-Curing-for-Ink-Jet-Printing.pdf.
[27] R. Balescu, Statistical Dynamics: Matter out of Equilibrium, Imperial College Press, London, 1997.
[28] E. Mamontov, A specification of the maxwell-rayleigh-heisenberg approach to modelling fluids for bioelectronic applications, Mathl Comput. Model. 42 (3–4) (2005) 441–470.
[29] N.G. McCrum, C.P. Buckley, C.B. Bucknall, Principles of polymer engineering, Oxford University Press, Oxford, 1997.
[30] H.B. Dwight, Tables of Integrals and Other Mathematical Data, McMillan, New York, 1961.
[31] B.P. Demidovič, Lectures on the Mathematical Theory of Stability, Nauka, Moscow, 1967 (in Russian) (Math. Rev. 37 (1969) 1716).
[32] E. Mamontov, Dynamic-equilibrium solutions of ordinary differential equations and their role in applied problems, Appl. Math. Lett. 21 (4) (2008) 320–325.