STOCHASTIC SIMULATIONS FOR AGGREGATING SYSTEMS WITH NON-CONSTANT REACTION RATES

by

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Abstract

Stochastic simulations for aggregating systems with non-constant reaction rates

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In this thesis, reactive multi-particle collision dynamics (RMPC) is used for the simulation of aggregation and aggregation-fragmentation systems. RMPC dynamics consists of collisions, reactions, and free streaming. Aggregation and fragmentation is modelled using a reactive mechanism. An infinite system of ODEs called the Smoluchowski differential equations has been used for comparison in the well mixed case. The exact solution for the infinite system is also compared with a finite system RK4 solution that is more appropriate for finite system RMPC simulations. The maximum cluster size is taken to be five, and the domain for stochastic simulations is cubic with periodic boundary conditions. Constant, additive, and multiplicative rates are discussed, and the affects of variations in aggregation and break-up rates are observed. Non-zero, monomer-only initial conditions are used, and the solution for aggregation is obtained with a monomer only initial-concentration equal to 1, as well as \( b \), where \( b \) is a constant. The solution for aggregation and break-up is calculated using a monomer-only initial concentration equal to \( b \). The RMPC simulations showed that the RMPC results had a good agreement with the finite-system RK4 solution specially for smaller particle sizes. There was stochastic noise in the RMPC results for all cases that became more pronounced with increase in break-up rate. The novelty of this work consists of RMPC simulation results for additive and multiplicative rates, which has not been simulated using RMPC before. For the system size considered in this work, stochastic effects can be further extended for larger cluster sizes, and to analyse different choices for aggregation and break-up rates.
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List of Symbols

DPD  Dissipative particle dynamics
LBM  Lattice Boltzmann method
MPC  Multi-particle collision dynamics
RBCs Red blood cells
RMPC Reactive multi-particle collision dynamics
SPH  Smoothed particle hydrodynamics
Chapter 1

Introduction

1.1 Motivation

Blood flow has been analysed for centuries for different medical, biological, physical, chemical, and mathematical applications. It is an organized system that provides the oxygenated blood containing nutrients to all cells in the body and removes de-oxygenated blood from all organs. The arteries take blood away from the heart; the veins carry it back to the heart.

Blood itself is a two-phase suspension of structured elements consisting of red blood cells [RBCs], white blood cells [WBCs], and platelets suspended in an aqueous solution of organic molecules, proteins, and salts named plasma. The blood behaves as a non-Newtonian fluid, meaning that the apparent viscosity of blood is based on the existing shear forces. The factors that determine the blood viscosity include hematocrit, plasma viscosity, RBC aggregation, and the mechanical properties of RBCs. RBCs are enormously deformable, and this physical property highly aids blood flow both under bulk flow conditions and in the micro-circulation. The propensity of RBCs to experience reversible aggregation is an important factor to determine the apparent viscosity as the size of the RBC aggregates is inversely proportional to the magnitude of shear forces, meaning that the aggregates are diffused with increasing shear forces, and then regenerated under low-flow or static conditions. RBC aggregation is primarily determined by plasma protein composition and surface properties of RBCs [3, 4].

“At the beginning of the 20th century, a Scandinavian pathologist Robin Fahraeus started exploring the flow properties of blood. He found out that the suspension stability and fluidity of blood were changed during disease process, described the humoral pathology concepts by modern scientific ideas, and furnished a basis for understanding medical practices of previous centuries” [4]. It is well recognized that in the blood flow, the joint interactions of the RBCs with each other and with platelets contribute to the organization of these sole blood components such that red blood cells tend to accumulate at the centreline of the blood vessels (the Fahraeus-Lindquist effect) and platelets are noticed to be evicted towards the walls of the vessels in a non-diffusive manner [5].

A lot of research work has been done for aggregation and blood flow simulations. O. K. Baskurt [4]
presented a detailed discussion on Blood Rheology and the effects of Pathological alterations on RBC aggregation. YJ. Kang [10] worked on microfluidic-based techniques for measuring RBC aggregation and blood viscosity by comparing the proposed aggregation index and the conventional aggregation index. The recent work is done by L. L. Xiao [24] on the effects of RBC aggregation on the blood flow in a symmetrical stenosed microvessel.

The Smoluchowski coagulation equation was introduced by Merian Smoluchowski in 1916, describing the time evolution of the number density of the particles as they coagulate [19]. A lot of research has been done to solve the equation. D. J. Aldous [2] presented a nice collection of exact solutions for constant, additive, and multiplicative rates commonly also called kernels. An overview of the Smoluchowski equation, including solution techniques can be found in Krapivsky et al [12]. R. Durret [6] worked on the equilibrium behaviour of coagulation-fragmentation processes.

1.2 Particle-based methods for RBC aggregation

Particle-based methods are commonly used to solve the flow problems for biofluids due to the ease and flexibility to model complex structures. These methods keep track of positions and velocities of particles and then find their time evolutions. (DPD) Dissipative particle dynamics [8], (SPH) smoothed particle hydrodynamics [7], (LBM) lattice Boltzmann method [21, 16], (MPC) multiparticle collision dynamics [14, 9] are often used for RBC simulation, depending on microscopic, mesoscopic, or macroscopic length scale. For numerical results in this thesis, we have used (RMPC) reactive multiparticle collision dynamics [18], an extension of MPC and a mesoscopic method, that incorporates reaction mechanisms as well. RMPC is a three step method consisting of particle collisions at discrete time steps, reactions, and free-streaming.

Malevants and Kapral [14] introduced MPC in 1999. It is a method that conserves mass, energy, and momentum throughout the system. RMPC is the MPC dynamics combined with reaction events. Some applications include diffusion-infused reaction dynamics [22], diffusion-infused signalling pathways [20], reaction-diffusion fronts [23], and pattern-forming chemically reacting systems [11].

1.3 Aim and Methodology

This research is to examine interactions between particles, namely cluster formation called aggregation, and break-up called fragmentation. The goal for this thesis is to study aggregation between particles at no-flow conditions, and how changes in aggregation and reaction rates affect the system properties. We have presented simulation results for aggregation and fragmentation for constant, additive, and multiplicative aggregation and break-up rates. We have analysed numerical results and discussed conclusions and future work.
1.4 Thesis Organization

The thesis is organized as follows: Chapter 2 presents the background of an RMPC system describing the relevant details. In chapter 3, we have first presented the exact solution for Smoluchowski equations for an infinite system for constant, multiplicative, and additive rates for aggregation and then found the exact solutions for aggregation and aggregation-fragmentation processes. Chapter 4 outlines numerical results for aggregation as well as aggregation and break-up for constant, additive, and multiplicative rates. Finally, in Chapter 5, we provide conclusions of our results, as well as ideas for future work.
Chapter 2

Reactive Multi-particle Collision Dynamics (RMPC)

2.1 Definition

The RMPC consists of three main steps: collisions between particles at discrete time steps, reactions, and free-streaming. Note that collisions and reactions take place locally in subvolumes, whereas free-streaming takes place ballistically.

2.2 Construction

Let the system volume $V$ be partitioned into $N_c$ subvolumes of equal volumes $V_c$. Further, assume that there are $L_x$, $L_y$, and $L_z$ subvolumes in the respective $x$, $y$, $z$ directions. Then, the total number of subvolumes comes out to be $N_c = (L_x)(L_y)(L_z)$, and $V = N_cV_c$. The system is updated to associate collisions, then reactions, and finally free-streaming, at discrete time steps $\tau$. As collisions and reactions take place locally, or somewhat in local subvolumes $V_c$, a subscript $\xi \in \{1, ..., N_c\}$ is usually used for subvolume number. Each $V_c$ has volume $(dx)(dy)(dz)$, where $dx$, $dy$, $dz$ are the lengths in the respective, $x$, $y$, and $z$ directions.

2.3 Collision Rule

Collisions for multi-species MPC systems are generally comprised of an all-species collision rule and a subsequent single species collision [14]. Assume that the system has $s$ different species of particles. If $\alpha_i \in \{1, 2, ..., s\}$ is the species type of particle $i$, then one can write the combined collision rule as

\[
\vec{v}_i = \vec{V}_\xi + \hat{\omega}_\xi (\vec{V}_{\alpha_i}^{\prime\prime} - \vec{V}_\xi') + \hat{\omega}_{\alpha_i}' \hat{\omega}_\xi (\vec{V}_i - \vec{V}_{\alpha_i}^{\prime\prime}')
\]  

(2.1)
where $v_i$ is the post-collision velocity of the particle $i$ positioned in subvolume $\xi$ coming from the combined collision rule, $V'_\xi$ is the pre-collision center of mass velocity of all particles in subvolume $\xi$, and $V'^{\alpha'_i}_\xi$ is the pre-collision center of mass velocity of particles of species $\alpha'_i$ in the subvolume. $\hat{\omega}_\xi$ are the random rotation operators taken from a set $\Omega$ for the all-species collision rule applied to all particles in the subvolume, and $\hat{\omega}^{\alpha'_i}_\xi \in \Omega'_\alpha$ is a random rotation operator selected independently for species $\alpha'_i$ executed only on particles of that species in the subvolume. The set $\Omega'_\alpha$ does not have to be the same as $\Omega$, and hence the random rotation operators change from subvolume to subvolume, from one species to another, and differ with every time step.

The velocity distribution of the particles is taken from the Maxwell-Boltzmann distribution given by

$$p(v) = \left(\frac{m}{2\pi k_B T}\right)^\frac{3}{2} \exp\left(-\frac{m v^2}{2k_B T}\right)$$

with zero mean and standard deviation $\frac{k_B T}{m}$. $k_B$ is the Boltzmann constant, $m$ is the mass of a particle, and $T$ is the system temperature.

### 2.4 Implementation of random rotation operators in MPC dynamics

Random rotation operators in MPC dynamics can be imposed in many different ways. We use the following rule that was presented in [18, 17] that is

$$\hat{\omega}_\xi = \begin{bmatrix} R_{11} & R_{12} & R_{13} \\ R_{21} & R_{22} & R_{23} \\ R_{31} & R_{32} & R_{33} \end{bmatrix} = \begin{bmatrix} l_x^2 + (1 - l_y^2) c_\psi & l_x l_y (1 - c_\psi) - l_z s_\psi & l_x l_z (1 - c_\psi) + l_y s_\psi \\ l_x l_y (1 - c_\psi) + l_z s_\psi & l_y^2 + (1 - l_x^2) c_\psi & l_y l_z (1 - c_\psi) - l_x s_\psi \\ l_x l_z (1 - c_\psi) - l_y s_\psi & l_y l_z (1 - c_\psi) + l_x s_\psi & l_z^2 + (1 - l_y^2) c_\psi \end{bmatrix}$$ (2.2)

where $l_x = \sqrt{1 - \theta^2} \cos \phi, l_y = \sqrt{1 - \theta^2} \sin \phi, l_z = \phi$, $\phi$ is a random angle on the interval $[0, 2\pi]$, and $\theta$ is a random number in the interval $[-1, 1]$. The short form $c_\psi = \cos \psi$ and $s_\psi = \sin \psi$ is used for convenience. $\psi$ denotes the collision angle for all-species collision and if $\psi = \psi_\alpha \in \Omega_\alpha$, then (2.2) results in the single-species collision $\hat{\omega}_\alpha^{\alpha'_i}$, with $\alpha \in \{1, 2, ..., s\}$ representing the species type, where $\psi_\alpha$ represents collision angle for the single-species collision and $\Omega_\alpha$ set of single-species collision rule. If $\psi \in \Omega$, then (2.2) gives the all-species collision $\hat{\omega}_\xi$ [20, 18].

### 2.5 Reactive Mechanism

A reactive mechanism usually takes the form

$$R_\mu : \sum_{i=1}^s \nu^{\mu}_{i} X_i \xrightarrow{k_\mu} \sum_{i=1}^s \bar{\nu}^{\mu}_{i} X_i,$$

and it transforms the species types of the reacting particles locally in the subvolume at a rate $k_\mu$ for the
chemical reaction $R_\mu$, for all $\mu = 1, ..., r$ possible reactions, where $X_l(l = 1, ..., r)$ are the $s$ chemical species and $\nu_l^\mu$ and $\bar{\nu}_l^\mu$ are the stoichiometric coefficients for reaction $\mu$.

## 2.6 Free Streaming

The free-streaming restores particle positions based on their post-collision and post-reactive velocities according to

$$x_i = x'_i + \tau v_i,$$

with periodic boundary conditions.
Chapter 3

Aggregation and Fragmentation

3.1 Aggregation

Aggregation refers to irreversible joining of reactive clusters. Some real life examples include milk curdling, blood coagulation, and star formation by gravitational acceleration. The primary process for aggregation is often represented as

\[ A_i + A_j \xrightarrow{K_{i,j}} A_{i+j} \]

which shows that two clusters of mass \( i \) and \( j \) irreversibly join at rate \( K_{i,j} \) (called kernels) and form a cluster of mass \( i + j \). A cluster of size \( k \) is often called a \( k \)-mer.

3.2 The master equations

We assume that mass \( k \) takes positive integer values and the kernels are symmetric that is, \( K_{i,j} = K_{j,i} \).

If \( c_k(t) \) stands for the concentration of clusters of mass \( k \) at time \( t \), we have the infinite set of master equations for the time evolution of concentrations given by [12]

\[
\frac{dc_k}{dt} = \frac{1}{2} \sum_{i+j=k} K_{i,j} c_i c_j - c_k \sum_{i \geq 1} K_{i,k} c_i, \quad k = 1, 2, \ldots
\]  

(3.1)

The first term on the right-hand side indicates the creation of a \( k \)-mer (cluster of mass \( k \)) as a result of coalescence of two clusters of masses \( i \) and \( j \) with \( i + j = k \). The pre-factor \( \frac{1}{2} \) in the gain term is required to avoid double counting. The loss term on the right-hand side represents reactions of a \( k \)-mer with other clusters.
3.3 Exact Solution

We consider aggregation with monomer-only initial condition that is

\[ c_1(0) = 1, \quad c_i(0) = 0, \quad i = 2, 3, 4, \ldots \]  \hspace{1cm} (3.2)

There are different methods to find the exact solution of equation (3.1) with initial conditions (3.2). The solutions are summarized in Table 3.1, and we discuss the solution techniques in this section.

### 3.3.1 Case 1: \( K_{i,j} = 2 \)

For constant kernel, we choose \( K_{i,j} = 2 \) for convenience, and the master equations become

\[ \frac{dc_k}{dt} = \sum_{i+j=k} c_i c_j - 2c_k \sum_{i \geq 1} c_i \]  \hspace{1cm} (3.3)

Note that the mass is conserved in this system, that is, \( \frac{d}{dt} \sum_k k c_k = 0 \).

#### Exponential ansatz

Suppose that the appropriate exponential ansatz is

\[ c_k(t) = A a^{k-1} \]  \hspace{1cm} (3.4)

The initial conditions (3.2) imply \( A(0) = 1 \) and \( a(0) = 0 \) with \( A(t) \) and \( a(t) \) to be determined.

Substituting ansatz (3.4) into equation (3.3) gives

\[ \dot{A} a^{k-1} + A(k - 1) \dot{a} a^{k-2} = \sum_{i+j=k} A^2 a^{i+j-2} - 2 A a^{k-1} \sum_{i \geq 1} A a^{i-1}. \]  \hspace{1cm} (3.5)

Dividing both sides by \( c_k(t) = A a^{k-1} \) and using \( \sum_{i+j=k} a^{i+j-2} = (k-1) a^{k-2} \) and \( \sum_{i=1}^{\infty} a^{i-1} = \frac{1}{1-a} \), we have

\[ \frac{\dot{A}}{A} + (k - 1) \frac{\dot{a}}{a} = (k - 1) \frac{A}{a} - \frac{2A}{1 - a} \]  \hspace{1cm} (3.6)
To ensure the validity of the exponential ansatz, the $k$-dependent and $k$-independent components of this equation should separately vanish. Therefore, we have the following coupled differential equations to solve:

$$\dot{A} = -\frac{2A^2}{1-a}, \dot{a} = A. \tag{3.7}$$

Since $\sum_{k \geq 1} kc_k = A \sum_{k \geq 1} ka^{k-1} = A[1 + 2a + 3a^2 + ...] = A(1-a)^{-2}$, mass conservation implies

$$A = (1-a)^2 \tag{3.8}$$

since $\sum_k kc_k(0) = 1$ from the monomer only initial conditions. Substituting (3.8) into the second equation in (3.7) gives

$$\dot{a} = (1-a)^2$$

This is a separable DE that can be solved as follows:

$$\int \frac{\dot{a}}{(1-a)^2} dt = \int 1 dt$$

$$\int \frac{1}{(1-a)^2} da = \int 1 dt$$

$$\frac{1}{1-a} = t + c$$

$a(0) = 0 \implies c = 1$

$$\frac{1}{1-a} = t + 1$$

$$1-a = \frac{1}{t+1}$$

$$a(t) = \frac{t}{t+1} \tag{3.9}$$

Substituting (3.9) into (3.8) gives

$$A(t) = \frac{1}{(1+t)^2} \tag{3.10}$$

Substituting (3.9) and (3.10) into (3.4) gives

$$c_k(t) = \frac{tk^{-1}}{(1+t)^{k+1}} \tag{3.11}$$
3.3.2 Case 2: $K_{i,j} = ij$

Equation (3.1) can be rewritten as [15]

$$\frac{dc_i}{dt} = \frac{1}{2} \sum_{j=1}^{i-1} K_{j,i-j} c_{i-j} - c_i \sum_{j=1}^\infty K_{i,j} c_j$$

(3.12)

with the initial conditions (3.2). We are assuming that $\sum i^2 c_i$ is absolutely and uniformly convergent for $t$ in some closed interval $[0, \theta]$. With this convergence assumption, we can multiply the $i$th equation by $i$ and add to obtain

$$\sum_{i=1}^\infty i \frac{dc_i}{dt} = \frac{1}{2} \sum_{i=1}^\infty \sum_{j=1}^{i-1} i j (i-j) c_{i-j} - \sum_{i=1}^\infty i^2 c_i \sum_{j=1}^\infty j c_j$$

(3.13)

provided that the first term on right-hand side converges. In fact, it converges absolutely because it is just a rearrangement of the second term, which converges absolutely. Note that, if either term is multiplied out, then the total coefficient of $c_i c_j$ is $(i+j)ij$. It follows therefore that

$$\sum_{i=1}^\infty i \frac{dc_i}{dt} = 0$$

(3.14)

the convergence being absolute and uniform for $t$ in $[0, \theta]$. It follows from (3.12) that each $c_i$ is continuous because it is differentiable, and that $\frac{dc_i}{dt}$ is continuous because it is the sum of a uniformly convergent series of continuous functions. Hence, we may integrate (3.14) term by term, and obtain, using the initial conditions, that

$$\sum_{i=1}^\infty i c_i = 1$$

(3.15)

The equation (3.12) therefore reduces to

$$\frac{dc_i}{dt} = \frac{1}{2} \sum_{j=1}^{i-1} j (i-j) c_{i-j} - i c_i$$

(3.16)

We have

$$\frac{dc_1}{dt} = -c_1$$

$$\frac{1}{c_1} \frac{dc_1}{dt} = -1$$

$$\ln |c_1| = -t + d$$

$$c_1 = fe^{-t}$$

$$c_1(0) = 1 \implies f = 1$$
\[ c_1 = e^{-t} \]
\[ \frac{dc_2}{dt} = \frac{1}{2} c_1^2 - 2c_2 \]
\[ \frac{dc_2}{dt} = \frac{1}{2} e^{-2t} - 2c_2 \]
\[ \frac{dc_2}{dt} + 2c_2 = \frac{1}{2} e^{-2t} \]
\[ I.F. = e^{\int 2dt} = e^{2t} \]
\[ c_2 e^{2t} = \frac{1}{2} \int e^{-2t} e^{2t} dt + h \]
\[ c_2 e^{2t} = \frac{1}{2} t + h \]
\[ c_2 = \frac{1}{2} t e^{-2t} + h e^{-2t} \]
\[ c_2(0) = 0 \implies h = 0 \]
\[ c_2 = \frac{1}{2} t e^{-2t} \]

Let us suppose in general that, for \( j = 1, 2, ..., n \),
\[ c_j = A_j t^{-j} e^{-jt} \]  \hspace{1cm} (3.17)

Where \( A_j \) is independent of \( t \). Then, substituting in the \((n+1)st\) equation (3.16), we have
\[ \frac{dc_{n+1}}{dt} = -(n+1)c_{n+1} + \frac{1}{2} \sum_{j=1}^{n} A_j A_{n+1-j} t^{n-1} e^{-(n+1)t} \]

So that
\[ \frac{d}{dt}(e^{(n+1)t} c_{n+1}) = \frac{1}{2} t^{n-1} \sum_{j=1}^{n} A_j A_{n+1-j} \]

and
\[ e^{(n+1)t} c_{n+1} = \frac{t^n}{2n} \sum_{j=1}^{n} A_j A_{n+1-j} \]  \hspace{1cm} (3.18)

Hence (3.17) holds by induction for all \( j \) provided that \( A_1 = 1 \) and
\[ \frac{1}{2n} \sum_{j=1}^{n} A_j A_{n+1-j} = \frac{A_{n+1}}{n+1} \]  \hspace{1cm} (3.19)

Substituting (3.19) into (3.18) gives
\[ e^{(n+1)t} c_{n+1} = \frac{A_{n+1}}{n+1} t^n \]  \hspace{1cm} (3.20)
where
\[ A_{n+1} = \frac{(n+1)^{n-1}}{n!} \quad (n = 1, 2, 3, \ldots) \quad (3.21) \]
upon investigation. Substituting (3.21) into (3.20), we have
\[
e^{(n+1)t}c_{n+1} = \frac{(n+1)^{n-1}}{(n+1)n!} t^n
\]
\[
c_{n+1} = \frac{(n+1)^{n-1}}{(n+1)n!} t^n e^{-(n+1)t}
\]
\[
c_{n} = \frac{(n)^{n-2}}{n(n-1)!} t^{n-1} e^{-nt}
\]
\[
c_{n} = \frac{n^{n-3}}{(n-1)!} t^{n-1} e^{-nt} \quad (3.22)
\]
Note: Equation (3.22) gives solution for (3.16) with initial conditions (3.2), for all positive \( t \leq 1 \). For \( t > 1 \), we have
\[
c_{n} = \frac{n^{n-3}}{(n-1)!} \frac{e^{-n}}{t} \quad (3.23)
\]
(See [13] for the details).

3.3.3 Case 1: \( K_{i,j} = i + j \)

The solution for (3.1) with initial conditions (3.2) for sum kernel, \( K_{i,j} = i + j \) is given by
\[
c_{n}(t) = \frac{n^{n-1}}{n!} (1 - e^{-t})^{n-1} e^{-t} e^{-n(1-e^{-t})} \quad (3.24)
\]
It is valid for all \( t > 0 \) [5].

3.4 Exact Solution for simulations: Aggregation

For comparison with RMPC simulations, we will need the rates to be probabilistic (eg. less than 1), with initial monomer concentrations larger than 1. As such, we derive the appropriate exact solutions for this case next. We have the infinite system of ordinary differential equations given by
\[
\frac{dc_k}{dt} = \frac{1}{2} \sum_{i+j=k} K_{i,j} c_i c_j - c_k \sum_{i=1}^{\infty} K_{i,k} c_i \quad (3.25)
\]
Taking \( K_{i,j} = K_{i,k} = E \), where E is a constant, we have
\[
\frac{dc_k}{dt} = \frac{1}{2} \sum_{i+j=k} E c_i c_j - c_k \sum_{i=1}^{\infty} E c_i \quad (3.26)
\]
\[ ^1 \text{We are not proving it here.} \]
For constant kernel aggregation, we use the exponential ansatz given in (3.4), that is
\[ c_k(t) = A(t)(a(t))^{k-1} \] (3.27)
with as yet unknown \( A(t) \) and \( a(t) \). We are using an initial monomer concentration, that is \( c_1(0) = c_0^1 = b \) and \( c_k(0) = 0, k > 1 \), which implies \( A(0) = b \) and \( a(0) = 0 \). Note that \( E = 2 \) and \( b = 1 \) in the known solution given in section 3.3. Differentiating (3.27), we get
\[ \frac{dc_k}{dt} = \dot{A}a^{k-1} + (k-1)Aa^{k-2}\dot{a} \] (3.28)
Substituting (3.27) and (3.28) in (3.26) gives
\[ \dot{A}a^{k-1} + (k-1)Aa^{k-2}\dot{a} = \frac{1}{2} \sum_{i+j=k} EA^2a^{i+j-2} - Aa^{k-1} \sum_{i=1}^{\infty} EAA^{i-1} \] (3.29)
Dividing both sides of the equation by \( c_k(t) = Aa^{k-1} \), we have
\[ \frac{\dot{A}a^{k-1}}{Aa^{k-1}} + \frac{(k-1)Aa^{k-2}\dot{a}}{Aa^{k-1}} = \frac{1}{Aa^{k-1}} \left( \frac{1}{2} \sum_{i+j=k} EA^2a^{i+j-2} \right) - \frac{1}{Aa^{k-1}} \left( Aa^{k-1} \sum_{i=1}^{\infty} EAA^{i-1} \right) \]
using \( \sum_{i+j=k} a^{i+j-2} = (k-1)a^{k-2} \) and \( \sum_{i=1}^{\infty} a^{i-1} = \frac{1}{1-a} \) gives
\[ \frac{\dot{A}}{A} + \frac{(k-1)\dot{a}}{a} = \frac{EA(k-1)}{2a} - \frac{EA}{1-a} \]
Since this equation should hold for all values of \( k \), and \( A \) and \( a \) are independent of \( k \), all coefficients of powers of \( k \) should be zero. Equating coefficients of \( k \)-dependent and \( k \)-independent terms leads to
\[ \frac{\dot{A}}{A} = \frac{EA}{1-a} \] (3.30)
\[ \dot{a} = \frac{EA}{2a} \] (3.31)
To simplify, we can use conservation of mass in the Smoluchowski equation. Mass in the Smoluchowski equation is defined as \( \sum_{k \geq 1} kc_k \), which is conserved since multiplying (3.26) by \( k \) and summing over \( k \) gives
\[ \frac{d}{dt} \sum_{k \geq 1} kc_k = 0. \] Thus \( \sum_{k \geq 1} kc_k(t) = \sum_{k \geq 1} kc_k(0) = b \) based on the monomer-only initial condition in this section.
Substituting the ansatz (3.27) into this, we have

\[ \sum_{k \geq 1} k c_k = A \sum_{k \geq 1} k a^{k-1} \]

\[ b = A(1 - a)^{-2} \]

\[ A = b(1 - a)^2 \] (3.32)

Substituting this into (3.31) gives

\[ \dot{a} = \frac{E b}{2} (1 - a)^2 \]

\[ \frac{1}{(1 - a)^2} \frac{da}{dt} = \frac{1}{2} E b \]

\[ \frac{1}{1 - a} = \frac{1}{2} E b t + C \]

Applying the initial condition \( a(0) = 0 \) to find \( C \) gives

\[ C = 1 \]

\[ \frac{1}{1 - a} = \frac{1}{2} E b t + 1 \]

\[ 1 - a = \frac{2}{E b t + 2} \]

\[ a = \frac{E b t}{E b t + 2} \]

Using (3.32)

\[ A = b \left( \frac{2}{E b t + 2} \right)^2 \]

\[ A = \frac{4 b}{(E b t + 2)^2} \]

Substituting in (3.27)

\[ c_k(t) = \frac{4 b}{(E b t + 2)^2} \left( \frac{E b t}{E b t + 2} \right)^{k-1} \]

\[ = \frac{4 b^k E^{k-1} t^{k-1}}{(E b t + 2)^{k+1}} \]
3.5 Exact Solution for simulations: Aggregation and Fragmentation

The solution for the Smoluchowski equation in accordance with aggregation for the infinite system can be acquired with the addition of fragmentation as well, taking constant reaction rates and only monomers initially in the system. The evolution equation for the concentration of a cluster of size \( k \), \( c_k(t) \) for classical aggregation-fragmentation process is [12, 1]

\[
\frac{dc_k}{dt} = \frac{1}{2} \sum_{i+j=k} K_{i,j} c_i c_j - c_k \sum_{i=1}^{\infty} K_{i,k} c_i + \sum_{i=k+1}^{\infty} W_{i,k} c_i - \frac{1}{2} c_k \sum_{i=1}^{k-1} W_{k,i}, \quad k = 1, 2, \ldots \tag{3.33}
\]

Taking \( K_{i,j} = K_{j,i} = E \), and \( W_{i,k} = W_{k,i} = F \), where \( E \) and \( F \) are constants, the time evolution of the concentration \( c_k(t) \) for aggregation and breakup is given by

\[
\frac{dc_k}{dt} = \frac{1}{2} \sum_{i+j=k} Ec_i c_j - c_k \sum_{i=1}^{\infty} Ec_i + \sum_{i=k+1}^{\infty} Fc_i - \frac{1}{2} c_k \sum_{i=1}^{k-1} F, \quad k = 1, 2, \ldots \tag{3.34}
\]

We use the exponential ansatz to solve this equation as well, which is

\[
c_k(t) = A(t)(a(t))^{k-1} \tag{3.35}
\]

with \( A(t) \) and \( a(t) \) as unknown yet. The monomer-only initial condition again implies \( A(0) = b \) and \( a(0) = 0 \). Substituting (3.35) into (3.34) and using (3.28), we have

\[
\dot{A}a^{k-1} + (k-1)Aa^{k-2}\dot{a} = \frac{EA^2(k-1)a^{k-2}}{2} - \frac{EA^2 a^{k-1}}{1-a} + \frac{FAa^k}{1-a} - \frac{FA(k-1)a^{k-1}}{2}
\]

Dividing both sides by \( c_k(t) = Aa^{k-1} \) and rearrange

\[
\frac{\dot{A}}{A} + \frac{(k-1)\dot{a}}{a} = \frac{EA(k-1)}{2a} - \frac{EA}{1-a} + \frac{Fa}{1-a} - \frac{F(k-1)}{2}
\]

Since this equation should hold for all values of \( k \), and \( A(t) \) and \( a(t) \) are independent of \( k \), all coefficients of powers of \( k \) should be zero. Equating coefficients of \( k \)-dependent and \( k \)-independent terms leads to

\[
\frac{\dot{A}}{A} = \frac{-EA}{1-a} + \frac{Fa}{1-a} \tag{3.36}
\]

\[
\frac{\dot{a}}{a} = \frac{EA}{2a} - \frac{F}{2} \tag{3.37}
\]
Recall that this system can be simplified using conservation of mass, which holds with the fragmentation term as well. This implies $\frac{d}{dt} \sum_{k \geq 1} k c_k = 0$, giving $A = b(1 - a)^2$. Substituting in (3.37)

$$\frac{\dot{a}}{a} = \frac{Eb(1 - a)^2}{2a} - \frac{F}{2}$$

$$\dot{a} = \frac{Eb(1 - a)^2}{2} - \frac{Fa}{2}$$

$$\frac{da}{dt} = \frac{1}{2} E b a^2 + (-E b - \frac{F}{2})a + \frac{1}{2} E b$$

(3.38)

To solve this DE, we suppose

$$a = a_1 + u$$

(3.39)

where $a_1$ is a constant to be determined, and $u(t)$ is the new unknown function. In order to find $a_1$, we substitute (3.39) into (3.38)

$$\frac{du}{dt} = \frac{1}{2} E b (a_1 + u)^2 + (-E b - \frac{F}{2})(a_1 + u) + \frac{1}{2} E b$$

$$= \frac{1}{2} E b (a_1^2 + 2a_1 u + u^2) + (-E b - \frac{F}{2})(a_1 + u) + \frac{1}{2} E b$$

$$= \frac{1}{2} E b a_1^2 + (-E b - \frac{F}{2})a_1 + \frac{1}{2} E b$$

$$+ \frac{1}{2} E b a^2 + (-E b - \frac{F}{2})u + E b a_1 u$$

We consider

$$\frac{1}{2} E b a_1^2 + (-E b - \frac{F}{2})a_1 + \frac{1}{2} E b = 0$$

$$\implies a_1 = \frac{(E b + \frac{F}{2}) + \sqrt{E F b + \frac{F^2}{4}}}{E b}$$

(3.40)

using (3.40) leaves only $u$-dependent terms with resulting DE for $u$ given by

$$\frac{du}{dt} = \frac{1}{2} E b u^2 + (-E b - \frac{F}{2})u + E b a_1 u$$

This is a Bernoulli equation in the form

$$\frac{du}{dt} - (Q + 2a_1 R)u = R u^2$$
with $R = \frac{1}{2}Eb$ and $Q = (-Eb - \frac{F^2}{2})$. To solve it, we use the substitution $w = \frac{1}{u}$ to get

$$\frac{dw}{dt} + \left(-Eb - \frac{F^2}{2}\right) + 2 \left(\frac{Eb + \frac{F^2}{4}}{Eb}\right) \left(\frac{1}{2}Eb\right) w = -\frac{1}{2}Eb$$

$$\frac{dw}{dt} + \left(\sqrt{EFb + \frac{F^2}{4}}\right) w = -\frac{1}{2}Eb$$

$$I.F. = e^{\int \sqrt{EFb + \frac{F^2}{4}}\, dt} = e^{\left(\sqrt{EFb + \frac{F^2}{4}}\right) t}$$

$$e^{\left(\sqrt{EFb + \frac{F^2}{4}}\right) t} \frac{dw}{dt} + \left(\sqrt{EFb + \frac{F^2}{4}}\right) e^{\left(\sqrt{EFb + \frac{F^2}{4}}\right) t} w = -\frac{1}{2}Ebe^{\left(\sqrt{EFb + \frac{F^2}{4}}\right) t}$$

$$\frac{d}{dt} \left(we^{\left(\sqrt{EFb + \frac{F^2}{4}}\right) t}\right) = -\frac{1}{2}Ebe^{\left(\sqrt{EFb + \frac{F^2}{4}}\right) t}$$

$$we^{\left(\sqrt{EFb + \frac{F^2}{4}}\right) t} = -\frac{1}{2}Ebe^{\left(\sqrt{EFb + \frac{F^2}{4}}\right) t} + C$$

$$w = \frac{-Eb}{2\sqrt{EFb + \frac{F^2}{4}}} + \frac{C}{e^{\left(\sqrt{EFb + \frac{F^2}{4}}\right) t}}$$

$$\frac{1}{u} = \frac{-Ebe^{\left(\sqrt{EFb + \frac{F^2}{4}}\right) t} + 2C\sqrt{EFb + \frac{F^2}{4}}}{2\left(\sqrt{EFb + \frac{F^2}{4}}\right) e^{\left(\sqrt{EFb + \frac{F^2}{4}}\right) t}}$$

$$u = Ebe^{\left(\sqrt{EFb + \frac{F^2}{4}}\right) t} - 2C\sqrt{EFb + \frac{F^2}{4}}$$

$$u(0) = \frac{-2\sqrt{EFb + \frac{F^2}{4}}}{Eb - 2C\sqrt{EFb + \frac{F^2}{4}}}$$

$$a(0) = 0 \implies (a_1 + u)|_{t=0} = 0$$
\[
\frac{(Eb + \frac{F^2}{4}) + \sqrt{EFb + \frac{F^2}{4}}}{Eb} = \frac{2\sqrt{EFb + \frac{F^2}{4}}}{Eb - 2C\sqrt{EFb + \frac{F^2}{4}}}
\]
\[
\frac{Eb - 2C\sqrt{EFb + \frac{F^2}{4}}}{2\sqrt{EFb + \frac{F^2}{4}}} = \frac{E_b}{(Eb + \frac{F^2}{2}) + \sqrt{EFb + \frac{F^2}{4}}}
\]
\[
\frac{Eb - 2C\sqrt{EFb + \frac{F^2}{4}}}{2\sqrt{EFb + \frac{F^2}{4}}} = \frac{2Eb\sqrt{EFb + \frac{F^2}{4}}}{(Eb + \frac{F^2}{2}) + \sqrt{EFb + \frac{F^2}{4}}}
\]
\[
\frac{2C\sqrt{EFb + \frac{F^2}{4}}}{4} = \frac{Eb - \frac{2Eb\sqrt{EFb + \frac{F^2}{4}}}{(Eb + \frac{F^2}{2}) + \sqrt{EFb + \frac{F^2}{4}}}}{(Eb + \frac{F^2}{2}) + \sqrt{EFb + \frac{F^2}{4}}}
\]
\[
\frac{2C\sqrt{EFb + \frac{F^2}{4}}}{4} = \frac{(E^2b^2 + \frac{EFb}{2}) - Eb\sqrt{EFb + \frac{F^2}{4}}}{(Eb + \frac{F^2}{2}) + \sqrt{EFb + \frac{F^2}{4}}}
\]
\[
C = \frac{(E^2b^2 + \frac{EFb}{2}) - Eb\sqrt{EFb + \frac{F^2}{4}}}{2\sqrt{EFb + \frac{F^2}{4}} \left( (Eb + \frac{F^2}{2}) + \sqrt{EFb + \frac{F^2}{4}} \right)}
\]
\[ u(t) = \frac{-2 \left( E + \frac{F^2}{4} \right) e^{\left( \sqrt{EFb + \frac{F^2}{4}} \right)^t}}{Ebe^{\left( \sqrt{EFb + \frac{F^2}{4}} \right)^t} - 2 \left( \frac{(E + \frac{F^2}{4}) - Eb\sqrt{EFb + \frac{F^2}{4}}}{\left( \sqrt{EFb + \frac{F^2}{4}} \right)^t + \sqrt{EFb + \frac{F^2}{4}}} \right)} \left( \sqrt{EFb + \frac{F^2}{4}} \right)^t \left( (Eb + \frac{F^2}{4}) + \sqrt{EFb + \frac{F^2}{4}} \right) - (E^2b^2 + \frac{Fb^2}{2}) + Eb\sqrt{EFb + \frac{F^2}{4}} \]

\[ a(t) = a_1 + u(t) \]

\[ a(t) = \frac{(Eb + \frac{F^2}{4}) + \sqrt{EFb + \frac{F^2}{4}}}{Eb} \]

\[ A(t) = b(1 - a)^2 \]

\[ A(t) = b \left[ 1 - \frac{(Eb + \frac{F^2}{4}) + \sqrt{EFb + \frac{F^2}{4}}}{Eb} \right] \]

\[ c_k(t) = A(t)(a(t))^{k-1} \]

\[ c_k(t) = \frac{2 \left( \sqrt{EFb + \frac{F^2}{4}} \right)^t \left( (Eb + \frac{F^2}{4}) + \sqrt{EFb + \frac{F^2}{4}} \right) - (E^2b^2 + \frac{Fb^2}{2}) + Eb\sqrt{EFb + \frac{F^2}{4}} \left( \frac{(Eb + \frac{F^2}{4}) + \sqrt{EFb + \frac{F^2}{4}}}{Eb} \right) - \left( \frac{(Eb + \frac{F^2}{4}) + \sqrt{EFb + \frac{F^2}{4}}}{Eb} \right)^2 \left( \frac{(Eb + \frac{F^2}{4}) + \sqrt{EFb + \frac{F^2}{4}}}{Eb} \right)^{k-1}}{Ebe^{\left( \sqrt{EFb + \frac{F^2}{4}} \right)^t} - 2 \left( \frac{(E + \frac{F^2}{4}) - Eb\sqrt{EFb + \frac{F^2}{4}}}{\left( \sqrt{EFb + \frac{F^2}{4}} \right)^t + \sqrt{EFb + \frac{F^2}{4}}} \right)} \left( \sqrt{EFb + \frac{F^2}{4}} \right)^t \left( (Eb + \frac{F^2}{4}) + \sqrt{EFb + \frac{F^2}{4}} \right) - (E^2b^2 + \frac{Fb^2}{2}) + Eb\sqrt{EFb + \frac{F^2}{4}} \]
Taking $E \to 2$, $F \to 0$, and $b \to 1$ gives the exact solution of section 3.3.
Chapter 4

Numerical Results

4.1 Finite system ODE solution

We consider the finite system with a maximum cluster size $N$. The Smoluchowski equations for aggregation-fragmentation for the concentration of a cluster of size $k$, $c_k(t)$, at time $t$ is

$$\frac{dc_k}{dt} = \frac{1}{2} \sum_{i+j=k} K_{ij} c_i c_j - c_k \sum_{i=1}^{N-k} K_{ik} c_i + \sum_{i=k+1}^{N} W_{ik} c_i - \frac{1}{2} c_k \sum_{i=1}^{k-1} W_{ki}, \quad k = 1, 2, ..., N \quad (4.1)$$

For convenience, we have dropped the commas in the rates and written $K_{i,j}$ as $K_{ij}$ and $W_{i,j}$ as $W_{ij}$. Note that this equation is like equation (3.32) with finite upper limits rather than $\infty$. For example, we list the first five finite system evolutions

$$\frac{dc_1}{dt} = -K_{11} c_1^2 - K_{21} c_1 c_2 - K_{31} c_1 c_3 - K_{41} c_1 c_4 + W_{21} c_2 + W_{31} c_3 + W_{41} c_4 + W_{51} c_5$$

$$\frac{dc_2}{dt} = \frac{1}{2} K_{11} c_1^2 - K_{12} c_1 c_2 - K_{22} c_2^2 - K_{32} c_2 c_3 + W_{32} c_3 + W_{42} c_4 + W_{52} c_5 - \frac{1}{2} W_{21} c_2$$

$$\frac{dc_3}{dt} = \frac{1}{2} K_{12} c_1 c_2 + \frac{1}{2} K_{21} c_2 c_1 - K_{13} c_1 c_3 - K_{23} c_2 c_3 + W_{33} c_3 + W_{43} c_4 + W_{53} c_5 - \frac{1}{2} W_{31} c_3 - \frac{1}{2} W_{32} c_3$$

$$\frac{dc_4}{dt} = \frac{1}{2} K_{22} c_2^2 + \frac{1}{2} K_{31} c_3 c_1 + \frac{1}{2} K_{13} c_1 c_3 - K_{14} c_1 c_4 + W_{44} c_4 - \frac{1}{2} W_{41} c_4 - \frac{1}{2} W_{42} c_4 - \frac{1}{2} W_{43} c_4$$

$$\frac{dc_5}{dt} = \frac{1}{2} K_{32} c_2 c_3 + \frac{1}{2} K_{31} c_3 c_1 + \frac{1}{2} K_{14} c_1 c_4 + \frac{1}{2} K_{41} c_4 c_1 - \frac{1}{2} W_{51} c_5 - \frac{1}{2} W_{52} c_5 - \frac{1}{2} W_{53} c_5 - \frac{1}{2} W_{54} c_5$$

Note that we assume $K_{ij} = K_{ji}$ and $W_{ij} = W_{ji}$. We have used RK4 ($4^{th}$-order Runge Kutta) method for numerical ODE solution, with monomer-only initial condition. We have worked on various cases for the rates with a step size of 0.1 for all cases, and changing time range for different cases if necessary.
4.2 RMPC simulations

For RMPC simulations, we have used a set of parameters described in this section. The system volume is defined as 

\[ \text{volume} = L_x dx \times L_y dy \times L_z dz \]

we take \( dx = 1, dy = 1, \) and \( dz = 1, \) and \( L_x = 10, L_y = 10, \) and \( L_z = 10. \) We take the time step as \( \tau = 1. \) The initial concentration of monomers is set as \( b = 10. \) We take values for the velocity distribution of particles from a Maxwell-Boltzmann distribution with \( k_B T/m = 0.3. \)

4.3 Results for constant rates

For theoretical results for the infinite system, we refer back to the Smoluchowski equation for the aggregation-fragmentation process solved in section 3.5. Aggregation rates are taken as \( K_{ij} = E \) and break up rates as \( W_{ij} = F, \) where \( E \) and \( F \) are constants. In this section, we will discuss variation in \( E \) and \( F. \)

We have obtained these graphs over a time span of \([0\ 200]\) or \([0\ 1000]\) with a step size of 0.1. The RMPC solution is obtained using fortran simulations. We have used the infinite system solution from Chapter 3, and plotted it using Matlab. For comparison, we have also plotted the RK4 solution for the finite system with the help of Matlab.

4.3.1 Effects of varying break-up rates

We have taken \( E = 0.001, \) and observed effects of increments in \( F. \) At first \( F = 0 \) is taken, which is aggregation only. Then, we have increased \( F \) up until \( F = 0.02, \) so that \( F = 20E, \) that is, the break-up rate is 20 times larger than the aggregation rate.
Figure 4.3.1: RMPC, Infinite and RK4 solutions for monomers and dimers, \( K_{ij} = E, W_{ij} = F, E = 0.001, F = 0 \)

Figure 4.3.2: RMPC, Infinite and RK4 solutions for trimers and 4-mers, \( K_{ij} = E, W_{ij} = F, E = 0.001, F = 0 \)
In the aggregation only case ($F = 0$), we first compare the RMPC solution to both the infinite system solution from the previous chapter as well as the finite system RK4 solution.

Figure 4.3.1 shows that there is a fair agreement between all three solutions for monomers and dimers. The solutions for trimers and 4-mers agree well at first with the infinite system and RK4 solutions (Figure 4.3.2) but settle to a different equilibrium value. The agreement for 5-mers is fairly poor (see Figure 4.3.3).

In general, the RMPC solutions seem to have a better agreement with the finite RK4 solutions than the infinite system solutions.
Figure 4.3.4: RMPC, Infinite and RK4 solutions for monomers and dimers, $K_{ij} = E$, $W_{ij} = F$, $E = 0.001$, $F = 0.005$

Figure 4.3.5: RMPC, Infinite and RK4 solutions for trimers and 4-mers, $K_{ij} = E$, $W_{ij} = F$, $E = 0.001$, $F = 0.005$
Figure 4.3.6: RMPC, Infinite and RK4 solutions for 5-mers, $K_{ij} = E$, $W_{ij} = F$, $E = 0.001$, $F = 0.005$

We can see from the Figures 4.3.4 − 4.3.6 that for non-zero break-up rate, the agreement between the RMPC solutions and the infinite system and finite system RK4-solutions improve. Note that the RMPC solutions for trimers and 4-mers (Figure 4.3.5) have some stochastic noise.

As for the aggregation only case, the RMPC solutions compare better with the finite system RK4 solutions than the infinite system solutions.

Next, we compare the RMPC solutions for each particle size with fixed $E = 0.001$ and increasing $F$. We have considered $F = 0$, $F = 0.005$, $F = 0.01$, and $F = 0.02$, where $F = 20E$ in our last case considered. We present graphs for all particle sizes, starting with monomers in Figure 4.3.7, ending with 5-mers in Figure 4.3.11.
Figure 4.3.7: RMPC solutions for monomers, $K_{ij} = E$, $W_{ij} = F$, $E$ fixed, $F$ variable

Figure 4.3.8: RMPC solutions for dimers, $K_{ij} = E$, $W_{ij} = F$, $E$ fixed, $F$ variable
Figure 4.3.9: RMPC solutions for trimers, $K_{ij} = E$, $W_{ij} = F$, $E$ fixed, $F$ variable

Figure 4.3.10: RMPC solutions for 4-mers, $K_{ij} = E$, $W_{ij} = F$, $E$ fixed, $F$ variable
From Figure 4.3.7, we can observe that as the break-up rate $F$ increases, the RMPC solutions for monomers become less steep, and settle to a smaller concentration at equilibrium. The RMPC solutions for dimers and trimers (Figures 4.3.8 and 4.3.9) for $F = 0$ differ from the RMPC solutions for the non-zero values of $F$. For $F = 0$, the dimer and trimer curves initially increase, reach a maximum and then decrease, while $F \neq 0$ curves simply increase their equilibrium values. As $F$ increases from $F = 0.005$, the equilibrium values decrease. There is significant shift in the RMPC solutions for 4-mers and 5-mers (see Figures 4.3.10 and 4.3.11) as $F$ increases but the curves have a similar shape for all values of $F$. In general, the RMPC solutions for all particle sizes become less smooth as break-up rates increase, indicating stochastic noise in the system.

### 4.3.2 Effects of varying aggregation rates

We set $F = 0.001$, and observed effects of increment in $E$. At first, we take $E = 0.005$, since a zero aggregation rate with a monomer-only initial condition would not lead to cluster formation.
Figure 4.3.12: RMPC, Infinite and RK4 solutions for monomers and dimers, $K_{ij} = E$, $W_{ij} = F$, $E = 0.005$, $F = 0.001$

Figure 4.3.13: RMPC, Infinite and RK4 solutions for trimers and 4-mers, $K_{ij} = E$, $W_{ij} = F$, $E = 0.005$, $F = 0.001$
Figure 4.3.14: RMPC, Infinite and RK4 solutions for 5-mers, $K_{ij} = E$, $W_{ij} = F$, $E = 0.005$, $F = 0.001$

Figure 4.3.12 shows that the three solutions do not agree well. Note that the RMPC and the RK4 solutions for monomers and dimers cross each other, while infinite system solutions have different behaviour than the RMPC and the finite system RK4 solutions. From Figure 4.3.13, the RMPC and the finite system RK4 solutions for trimers and 4-mers compare better, and the infinite system solution have discrepancy. Note from Figure 4.3.14 that the RMPC, the infinite system, and the finite system RK4 solutions have disagreement.

Next in Figure 4.3.15 – 4.3.19, we have the RMPC solution for each particle size with fixed $F = 0.001$ and increasing $E$. We are taking $E = 0.005$, $E = 0.01$ and $E = 0.02$. In our last case considered, this gives $E = 20F$. 

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Figure 4.3.15: RMPC solutions for monomers, $K_{ij} = E$, $W_{ij} = F$, $E$ variable, $F$ fixed

Figure 4.3.16: RMPC solutions for dimers, $K_{ij} = E$, $W_{ij} = F$, $E$ variable, $F$ fixed
Figure 4.3.17: RMPC solutions for trimers, $K_{ij} = E$, $W_{ij} = F$, $E$ variable, $F$ fixed

Figure 4.3.18: RMPC solutions for 4-mers, $K_{ij} = E$, $W_{ij} = F$, $E$ variable, $F$ fixed
The RMPC solutions for monomers (Figure 4.3.15) gets less steep as aggregation rates increase and settle to a slightly smaller equilibrium value. Figures 4.3.16 and 4.3.17 show that the dimer and trimer peaks are lower and wider as $E$ decreases, leading to a smaller equilibrium concentration. From Figure 4.3.18 and 4.3.19, we see that the 4-mers and 5-mers do not have peaks. The equilibrium concentration for 4-mers (see Figure 4.3.18) first decreases as $E$ decreases from $E = 0.02$ to $E = 0.01$, and then increases for $E = 0.001$. The equilibrium concentrations for 5-mers increase with decrease in $E$.

Now, we increase the aggregation rate to $E = 0.02$ to observe the effect of a larger $E$, and compare the RMPC, Infinite system and the RK4 solutions.
Figure 4.3.20: RMPC, Infinite and RK4 solutions for monomers and dimers, $K_{ij} = E, W_{ij} = F, E = 0.02, F = 0.001$

Figure 4.3.21: RMPC, Infinite and RK4 solutions for trimers and 4-mers, $K_{ij} = E, W_{ij} = F, E = 0.02, F = 0.001$
Figure 4.3.22: RMPC, Infinite and RK4 solutions for 5-mers, $K_{ij} = E$, $W_{ij} = F$, $E = 0.02$, $F = 0.001$

We can see from Figures 4.3.20 – 4.3.22 that for largest E, the RMPC, Infinite system and RK4 solutions have significant disagreement.

4.4 Results for additive rates

We have taken $K_{i,j} = E(i + j)$, $W_{i,j} = F(j + (i - j)) = Fi$ where $W_{i,j}$ is the break-up of an $i$-mer into a $j$-mer and an $(i-j)$-mer.

4.4.1 Effects of varying break-up rates

At first, we compare the RMPC, the infinite system, and the RK4 solutions for the aggregation only case by taking $E = 0.001$ and $F = 0$. Then, we have increased $F$ up until $F = 0.02$, so that $F = 20E$, that is, the break-up rate is 20 times larger than the aggregation rate.
Figure 4.4.1: RMPC, Infinite and RK4 solutions for monomers and dimers, $K_{ij} = E(i + j)$, $W_{ij} = Fi$, $E = 0.001$, $F = 0$

Figure 4.4.2: RMPC, Infinite and RK4 solutions for trimers and 4-mers, $K_{ij} = E(i + j)$, $W_{ij} = Fi$, $E = 0.001$, $F = 0$
In the aggregation only case (F=0), we first compare the RMPC solution to both the infinite system solution and the finite system RK4 solution for additive rates. Figure 4.4.1 shows that there is a nice agreement between the RMPC, the infinite system, and the RK4 solutions for monomers and dimers. There is a poor agreement between three solutions for trimers and 4-mers (see Figure 4.4.2). The RMPC, the infinite system and the RK4 solutions for 5-mers show discrepancy from Figure 4.4.3. The RMPC solution compares better with the finite system RK4 solution.

For a non-zero break-up rate, we consider \( F = 0.005 \) and compare the RMPC, Infinite system, and RK4 solutions.
Figure 4.4.4: RMPC, Infinite and RK4 solutions for monomers and dimers, $K_{ij} = E(i + j)$, $W_{ij} = Fi$, $E = 0.001$, $F = 0.005$.

Figure 4.4.5: RMPC, Infinite and RK4 solutions for trimers and 4-mers, $K_{ij} = E(i + j)$, $W_{ij} = Fi$, $E = 0.001$, $F = 0.005$. 
Figure 4.4.6: RMPC, Infinite and RK4 solutions for 5-mers, \( K_{ij} = E(i+j) \), \( W_{ij} = Fi \), \( E = 0.001 \), \( F = 0.005 \)

Figures 4.4.4 – 4.4.6 show that there is a better agreement between the RMPC solutions and the infinite system and the finite system RK4-solutions for non-zero break-up rate than for \( F = 0 \) case. Note from Figure 4.4.4 that the RMPC solutions are more smooth for monomers and dimers indicating less stochastic noise, while the RMPC solutions for trimers and 4-mers (Figure 4.4.5) show increased stochastic noise as compared to the RMPC solution for 5-mers (Figure 4.4.6).

Now, we compare the RMPC solutions for each particle size with fixed \( E \) and increasing \( F \). We have taken \( E = 0.001 \) with \( F = 0 \), \( F = 0.005 \), \( F = 0.01 \), and \( F = 0.02 \), where \( F = 20E \) in our last case considered. We present graphs for each particle size, starting with Figure 4.4.7 for monomers, ending at Figure 4.4.11 for 5-mers.
Figure 4.4.7: RMPC solutions for monomers, $K_{ij} = E(i + j)$, $W_{ij} = Fi$, $E$ fixed, $F$ variable

Figure 4.4.8: RMPC solutions for dimers, $K_{ij} = E(i + j)$, $W_{ij} = Fi$, $E$ fixed, $F$ variable
Figure 4.4.9: RMPC solutions for trimers, $K_{ij} = E(i + j)$, $W_{ij} = Fi$, $E$ fixed, $F$ variable

Figure 4.4.10: RMPC solutions for 4-mers, $K_{ij} = E(i + j)$, $W_{ij} = Fi$, $E$ fixed, $F$ variable
Figure 4.4.11: RMPC solutions for 5-mers, $K_{ij} = E(i + j)$, $W_{ij} = F_i$, $E$ fixed, $F$ variable

From Figure 4.4.7, we can observe that as break-up rate increases, the RMPC solutions for monomers have more fluctuation. The RMPC solutions for dimers in Figure 4.3.8 for $F = 0$ differ from the RMPC solutions for the non-zero values of $F$. Figure 4.4.9 shows a poor agreement between the RMPC solutions for trimers. The RMPC solutions for 4-mers (see Figure 4.4.10) have similar shape for all values of $F$. In general, the RMPC solutions for all particle sizes have more fluctuation as break-up rates increase, demonstrating elevated stochastic noise in the system.

4.4.2 Effects of varying aggregation rates

We fix $F = 0.001$, and increase $E$ to see how that affects the curves. At first, we set $E = 0.005$, since a zero aggregation rate with a monomer-only initial condition would not lead to cluster formation.
Figure 4.4.12: RMPC, Infinite and RK4 solutions for monomers and dimers, $K_{ij} = E(i + j)$, $W_{ij} = Fi$, $E = 0.005, F = 0.001$

Figure 4.4.13: RMPC, Infinite and RK4 solutions for trimers and 4-mers, $K_{ij} = E(i + j)$, $W_{ij} = Fi$, $E = 0.005, F = 0.001$
Figure 4.4.14: RMPC, Infinite and RK4 solutions for 5-mers, \( K_{ij} = E(i+j), W_{ij} = F_i, E = 0.005, F = 0.001 \)

Figure 4.4.12 compares the RMPC, the infinite system, and the RK4 solutions for monomers and dimers for aggregation-fragmentation process for additive rates. Note that the RMPC and the RK4 solutions have some overlap, while infinite system solutions have different behaviour than the RMPC and the finite system RK4 solutions. From Figure 4.4.13, the three solutions for trimers and 4-mers are different. Note from Figure 4.4.14 that the RMPC, the infinite system, and the finite system RK4 solutions have disagreement.

Next in Figures 4.4.15 – 4.4.19, we have the RMPC solution for each particle size with fixed \( F = 0.001 \) and increasing \( E \). We are taking \( E = 0.005, E = 0.01 \) and \( E = 0.02 \). In our last case considered, this gives \( E = 20F \).
Figure 4.4.15: RMPC solutions for monomers, $K_{ij} = E(i + j)$, $W_{ij} = Fi$, $E$ variable, $F$ fixed

Figure 4.4.16: RMPC solutions for dimers, $K_{ij} = E(i + j)$, $W_{ij} = Fi$, $E$ variable, $F$ fixed
Figure 4.4.17: RMPC solutions for trimers, $K_{ij} = E(i + j)$, $W_{ij} = F_i$, $E$ variable, $F$ fixed

Figure 4.4.18: RMPC solutions for 4-mers, $K_{ij} = E(i + j)$, $W_{ij} = F_i$, $E$ variable, $F$ fixed
Figure 4.4.19: RMPC solutions for 5-mers, $K_{ij} = E(i + j)$, $W_{ij} = Fi$, $E$ variable, $F$ fixed

Figure 4.4.15 shows that the RMPC solutions for monomers lead to faster decrease in concentrations for larger $E$ values. The RMPC solutions for dimers (see Figure 4.4.16) have peaks that are lower and wider as $E$ decreases, with largest equilibrium concentrations for the smallest $E$. The same is true for trimers (see Figure 4.4.17). The RMPC solutions for 4-mers and 5-mers have different behaviours (Figures 4.4.18 and 4.3.19) with curves crossing.

Now, we set the aggregation rate as $E = 0.02$ to check the effect of a larger $E$, and compare the RMPC, Infinite system and the RK4 solutions.
Figure 4.4.20: RMPC, Infinite and RK4 solutions for monomers and dimers, $K_{ij} = E(i + j)$, $W_{ij} = F_i$, $E = 0.02$, $F = 0.001$

Figure 4.4.21: RMPC, Infinite and RK4 solutions for trimers and 4-mers, $K_{ij} = E(i + j)$, $W_{ij} = F_i$, $E = 0.02$, $F = 0.001$
We can see from Figures 4.4.20 − 4.4.22 that for largest E, the RMPC, Infinite system and RK4 solutions agree fairly well for monomers, dimers, but show some differences for trimers, 4-mers, and 5-mers.

4.5 Results for multiplicative rates

In this section, we consider multiplicative rates in the form

\[ K_{ij} = E(i + j), \quad W_{ij} = Fi \]

Note the \( W_{ij} \) represents break-up of an \( a \) \( j \)-mer into an \( (i - j) \)-mer, so that the products \( j \) and \( (i - j) \) are used in the multiplicative break-up rates \( W_{ij} \).

4.5.1 Effects of varying break-up rates

We present the aggregation only case with \( E=0.001 \), and \( F=0 \) first.
Figure 4.5.1: RMPC, Infinite and RK4 solutions for monomers and dimers, $K_{i,j} = E_{ij}$, $W_{i,j} = F(j)(i - j)$, $E = 0.001, F = 0$

Figure 4.5.2: RMPC, Infinite and RK4 solutions for trimers and 4-mers, $K_{i,j} = E_{ij}$, $W_{i,j} = F(j)(i - j)$, $E = 0.001, F = 0$
Figure 4.5.3: RMPC, Infinite and RK4 solutions for 5-mers, $K_{i,j} = E_{ij}$, $W_{i,j} = F(j)(i - j)$, $E = 0.001$, $F = 0$

For the aggregation only case ($F = 0$) for multiplicative rates, Figure 4.5.1 shows that there is a good agreement between the RMPC, infinite system, and RK4 solutions for monomers and dimers. The solutions for trimers and 4-mers (Figure 4.5.2) compare well at first with curves crossing but settle to a different equilibrium value. There is not a good agreement for 5-mers (see Figure 4.5.3). From sections 4.3.1 and 4.4.1 respectively, the RMPC solutions for multiplicative kernel here also agree better with the finite system RK4 solutions than with the infinite system solutions.

To see the effect of increment in break-up rate, we plot the RMPC, Infinite system, and RK4 solutions by taking $E=0.001$ and $F=0.005$ in Figures 4.5.4 – 4.5.7.
Figure 4.5.4: RMPC, Infinite and RK4 solutions for monomers and dimers, \( K_{i,j} = E_{ij}, W_{i,j} = F(j)(i - j), \)
\( E = 0.001, F = 0.005 \)

Figure 4.5.5: RMPC, Infinite and RK4 solutions for trimers and 4-mers, \( K_{i,j} = E_{ij}, W_{i,j} = F(j)(i - j), \)
\( E = 0.001, F = 0.005 \)
Figure 4.5.6: RMPC, Infinite and RK4 solutions for 5-mers, \( K_{i,j} = E_{i,j}, W_{i,j} = F(j)(i - j), \) \( E = 0.001, F = 0.005. \)

Note from Figures 4.5.4 – 4.5.6 that for a non-zero break-up rate, the agreement between the RMPC, infinite system and RK4 solutions improves. The RMPC solutions have more fluctuation for trimers, 4-mers, and 5-mers, showing increased stochastic noise.

Next, we have the RMPC simulation curves for each particle size, with \( E = 0.001 \) and increasing \( F \) in Figures 4.5.7 to 4.5.11. We have considered \( F = 0, F = 0.005, F = 0.01 \) and \( F = 0.02 \), where \( F = 20E \) in our last case considered.
Figure 4.5.7: RMPC solutions for monomers, $K_{i,j} = E_{ij}$, $W_{i,j} = F(j)(i - j)$, $E$ fixed, $F$ variable

Figure 4.5.8: RMPC solutions for dimers, $K_{i,j} = E_{ij}$, $W_{i,j} = F(j)(i - j)$, $E$ fixed, $F$ variable
Figure 4.5.9: RMPC solutions for trimers, $K_{i,j} = E_{ij}$, $W_{i,j} = F(j)(i - j)$, $E$ fixed, $F$ variable

Figure 4.5.10: RMPC solutions for 4-mers, $K_{i,j} = E_{ij}$, $W_{i,j} = F(j)(i - j)$, $E$ fixed, $F$ variable
Figure 4.5.11: RMPC solutions for 5-mers, $K_{i,j} = E_{ij}$, $W_{i,j} = F(j)(i - j)$, $E$ fixed, $F$ variable

Figure 4.5.7 show that as the break-up rate $F$ increases, the RMPC solutions for monomers get less steep and settle to a smaller concentration at equilibrium. From Figures 4.5.8 – 4.5.10, the disagreement between the RMPC solutions for $F = 0$ and the non-zero values for $F$ is clear. For $F = 0$, the dimer, trimer, and 4-mers curves increase at first, reach a maximum and then decrease, while $F \neq 0$ curves simply increase their equilibrium values. As $F$ increases from $F = 0.005$, the equilibrium values decrease. The RMPC solutions for 5-mers (see Figure 4.5.11) shifts with increment in $F$ with similar shape for all values of $F$. The RMPC solutions for all particle sizes become less smooth as $F$ increases, indicating stochastic noise in the system.

4.5.2 Effects of varying aggregation rates

We set $F = 0.001$, and increase $E$ to observe the effects on curves. At first, we take $E = 0.005$, since a zero aggregation rate with a monomer-only initial condition would not lead to cluster formation.
Figure 4.5.12: RMPC, Infinite and RK4 solutions for monomers and dimers, $K_{i,j} = Eij, W_{i,j} = F(j)(i - j)$, $E = 0.005$, $F = 0.001$

Figure 4.5.13: RMPC, Infinite and RK4 solutions for trimers and 4-mers, $K_{i,j} = Eij, W_{i,j} = F(j)(i - j)$, $E = 0.005$, $F = 0.001$
Figures 4.5.12 – 4.5.14 compare the RMPC, the infinite system, and the RK4 solutions for aggregation-fragmentation process for multiplicative rates. Note that for monomers and dimers (Figure 4.5.12), three solutions agree quite well. Figure 4.5.13 shows that the RMPC, infinite system, and RK4 solutions for trimers and 4-mers have different behaviour and increased stochastic noise for the RMPC solutions. Figure 4.5.14 illustrates that the solutions for 5-mers have poor agreement with some stochastic noise for the RMPC solutions.

Next, we have the RMPC solution for each particle size with fixed $F = 0.001$ and increasing $E$ in Figures 4.5.15 – 4.5.19. We take $E = 0.005$, $E = 0.01$ and $E = 0.02$. In our last case considered, this gives $E = 20F$. 
Figure 4.5.15: RMPC solutions for monomers, $K_{i,j} = E_{ij}$, $W_{i,j} = F(j)(i - j)$, $E$ variable, $F$ fixed

Figure 4.5.16: RMPC solutions for dimers, $K_{i,j} = E_{ij}$, $W_{i,j} = F(j)(i - j)$, $E$ variable, $F$ fixed
Figure 4.5.17: RMPC solutions for trimers, $K_{i,j} = E^{ij}$, $W_{i,j} = F(j)(i - j)$, $E$ variable, $F$ fixed

Figure 4.5.18: RMPC solutions for 4-mers, $K_{i,j} = E^{ij}$, $W_{i,j} = F(j)(i - j)$, $E$ variable, $F$ fixed
Figure 4.5.19: RMPC solutions for 5-mers, $K_{i,j} = E_{ij}$, $W_{i,j} = F(j)(i - j)$, $E$ variable, $F$ fixed

Note from Figure 4.5.15 that the RMPC solutions for monomers show faster decrease in concentrations as $E$ increases. The RMPC solutions for dimers and trimers (Figures 4.5.16 and 4.5.17) have lower and wider peaks as $E$ decreases, with largest equilibrium concentration for the smallest $E$. Figure 4.5.18 show that the RMPC solution curve for $E = 0.005 \times F = 0.001$ does not have a peak, whereas the RMPC solutions for $E = 0.01 \times F = 0.001$ and $E = 0.02 \times F = 0.001$ do. The equilibrium concentration decreases with increment in $E$. The RMPC solutions for dimers, trimers, and 4-mers (Figures 4.5.16 – 4.5.18) have some stochastic noise. The RMPC solutions for 5-mers (Figure 4.5.19) do not have peak and increases for the largest value of $E$.

Now, we set the aggregation rate as $E = 0.02$ to check the effect of a larger $E$, and compare the RMPC, Infinite system and the RK4 solutions in Figures 4.5.20 – 4.5.22.
Figure 4.5.20: RMPC, Infinite and RK4 solutions for monomers and dimers, \( K_{i,j} = E_{i,j}, W_{i,j} = F(j)(i-j) \), \( E = 0.02, F = 0.001 \)

Figure 4.5.21: RMPC, Infinite and RK4 solutions for trimers and 4-mers, \( K_{i,j} = E_{i,j}, W_{i,j} = F(j)(i-j) \), \( E = 0.02, F = 0.001 \)
We can see from Figures 4.5.20 – 4.5.22 that a larger value of E, does not give a good agreement between the RMPC, Infinite system, and RK4 solutions.

4.6 Results

In the previous sections, we have compared the RMPC simulations, the infinite system solutions from Chapter 3, and the finite system RK4 solutions. We have considered constant, additive, and multiplicative rates in sections 4.3, 4.4, and 4.5 respectively. Each of the above mentioned sections is divided into two subsections: first, describing the effects of varying break-up rates $F$, and the second for the effects of varying aggregation rates $E$. For simplicity, we have added figures in the same order in each of the sections 4.3, 4.4, and 4.5.

At first, we have fixed the aggregation rate at $E = 0.001$ and varied $F$. We have compared the RMPC, the infinite system, and the RK4 solutions for $E = 0.001$, $F = 0$, which is the aggregation only case. Then, we have presented the three solutions for aggregation-fragmentation process for $E = 0.001$, $F = 0.005$. Next, we have added the RMPC solutions for monomers, dimers, trimers, 4-mers, and 5-mers for fixed $E$ and variable $F$. We have presented the RMPC solutions for $E = 0.001$, with $F = 0$, $F = 0.005$, $F = 0.01$, and $F = 0.02$.

Secondly, we have fixed the break-up rate as $F = 0.001$, and observed the effects of variation in $E$. For that, we have added the RMPC, the infinite system, and the finite system RK4 solutions for $E = 0.005$, $F = 0.001$ first. Then, the RMPC solutions for monomers, dimers, trimers, 4-mers, and 5-mers for variable $E$ and fixed $F$ are presented. For these, we have chosen $E = 0.005$, $E = 0.01$, and $E = 0.02$ with $F = 0.001$. Finally, we have observed the effect of increasing $E$. We have compared the three solutions for $E = 0.02$, $F = 0.001$, which gives $E = 20F$. Our main findings are
• For all cases considered (constant, additive, and multiplicative rates), RMPC results for monomers and dimers agree fairly well with the finite-system RK4 solution when $E > F$.

• RMPC results for trimers, 4-mers, and 5-mers show more discrepancies compared to the infinite system, as well as the RK4 finite system solutions for all cases considered in this Thesis. General features, such as existence of a local maximum or monotonic increase, is present in the RMPC results when present in the finite-system RK4 solution, but equilibrium values are quite different, with most discrepancy in the largest cluster size (5-mers).

• For all cases considered (constant, additive, and multiplicative rates), stochastic noise is present in the RMPC results, that becomes more pronounced as F increase, when $E < F$.

• When stochastic noise is present in the system, intermediate cluster sizes (dimers, trimers, and 4-mers) experience the most stochastic noise compared to the smallest (monomers) and largest (5-mers) clusters.

• Additive and multiplicative rates lead to more stochastic noise in the system compared to constant rates for the same E and F values.
Chapter 5

Conclusions and Future Work

5.1 Summary

The presence of red blood cells (RBCs) and their interactions determine the rheological behaviour of blood. RBCs are considered to be the main contributors to the non-Newtonian flow of blood. This is due to the fact that RBCs aggregate, and form three-dimensional clusters, affecting the overall density of blood flow in micro-circulation. This is the reason that study of RBC interactions is important and applicable to various medical and pharmaceutical procedures.

A mesoscopic method, reactive multi-particle collision dynamics is an extension of the multi-particle collision dynamics, that can be used to simulate reacting systems in equilibrium conditions. Since it incorporates collisions, reactions, and free-streaming, that makes it suitable for aggregation and aggregation-fragmentation simulations.

The analysis for this thesis starts with solving the Smoluchowski equation, which is the coupled system of ODEs for an infinite number of variables. The system was considered with constant, multiplicative, and additive rates for aggregation. The exact solution for constant and multiplicative rates were derived, and stated for additive rates. Then, the exact solution for simulation was obtained for aggregation as well as aggregation and fragmentation. Next, numerical results were added, that were extended for additive and multiplicative rates also. The affects of varying break-up rates $F$ and aggregation rates $E$ were observed respectively. The RMPC, the infinite system, and the finite system RK4 solutions were compared for various values of $E$ and $F$ with monomers and dimers on first, trimers and 4-mers on second, and 5-mers on third figure simultaneously. The changes in behaviour of curves for each particle size with $E$ fixed, $F$ variable and $E$ variable, $F$ fixed were also added.

These results were obtained for a maximum cluster size, $N = 5$. At first, the aggregation rate was fixed as $E = 0.001$, and the aggregation only case was presented with $E = 0.001, F = 0$, followed by aggregation-fragmentation case with $E = 0.001, F = 0.005$. Then, the RMPC solutions for each particle size with $E$ fixed, $F$ variable were added. Next, the break-up rate was fixed as $F = 0.001$, and the three solutions were compared for $E = 0.005, F = 0.001$, followed by the RMPC solutions for each particle size with $E$ variable,
Finally, $E$ was increased to $E = 20F$, which was our last case considered.

### 5.2 Conclusions

There is a good agreement between RMPC results and the finite-system RK4 solutions for monomers and dimers. In general, RMPC results for trimers, 4-mers, and 5-mers have different equilibrium values. As $F$ increases, there is noticeable stochastic noise in the RMPC results for all cases. There is more stochastic noise in the system for additive and multiplicative rates as compared to constant rates. The RMPC solution compares better with the finite system RK4 solution than the infinite system solution for most of the cases considered.

To summarize, the best agreement between the RMPC, the infinite, and the RK4 solutions is obtained for smaller particle sizes. The RMPC results have increased stochastic noise for trimers, 4-mers, and 5-mers, especially for larger value of $E$ in most cases.

### 5.3 Future work

Results for larger cluster sizes can be obtained using the same RMPC algorithm used to obtain results for this thesis. We have worked for $N = 5$, it would be interesting to compare these results with simulations for larger values of $N$. The aggregation and break-up rates can also be varied further to see how that would affect the output. To find the exact solution for multiplicative and additive rates for the aggregation-fragmentation process is a goal as well. This work can be further extended to find the best combination of $K_{i,j}$ and $W_{i,j}$ for different applications.
References


