Direct simulation Monte Carlo for new regimes in aggregation-fragmentation kinetics

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Abstract

We revisit two basic Direct Simulation Monte Carlo Methods to model aggregation kinetics and extend them for aggregation processes with collisional fragmentation (shattering). We test the performance and accuracy of the extended methods and compare their performance with efficient deterministic finite-difference method applied to the same model. We validate the stochastic methods on the test problems and apply them to verify the existence of oscillating regimes in the aggregation-fragmentation kinetics recently detected in deterministic simulations. We confirm the emergence of steady oscillations of densities in such systems and prove the stability of the oscillations with respect to fluctuations and noise.

1 Introduction

Aggregation kinetics – the process where particles (elementary units) join together to form larger agglomerates – has been successfully explored experimentally and analytically for more than a century and numerically for a couple of decades. The physical nature of an elementary unit may be very different, ranging from molecules and colloids to fibrils and dust grains [1-9]. Moreover, aggregation is observed in networks such as Internet or business/social networks [10]. Self-assembly – an
important natural phenomenon – is also associated with aggregation \[1\]-\[13\]. The history of the field commenced in 1914 from the seminal work of Smoluchowski \[14\], where the aggregation of colloidal particles in solution was put in a mathematical framework. Namely, famous Smoluchowski equations for concentrations \(n_s(t)\) of aggregates of size \(s\) have been formulated:

\[
\frac{dn_s}{dt} = \frac{1}{2} \sum_{i=1}^{s-1} K_{i,s-i} n_i n_{s-i} - n_s \sum_{i=1}^{\infty} K_{i,s} n_i. \tag{1}
\]

Eqs. (1) is an infinite system of the first-order ODE. The first term on the r.h.s. of (1) gives the rate of the process when two particles of size \(i\) and \((s-i)\) coalesce, giving rise to a particle of size \(s\). The summation accounts for all such processes, which increase the concentration \(n_s\). The coefficient \(K_{i,s-i}\) quantifies the coagulation rate and the factor \(1/2\) excludes double counting. Similarly, the second term on the r.h.s. of (1) describes the aggregation of particles of size \(s\) with all particles of size \(i\) with the rates \(K_{i,s}\), which leads to the decrease of the concentration \(n_s(t)\).

Hence, the rates \(K_{ij}\) describe binary inter-particle reactions symbolically written as

\([i] + [j] \rightarrow [i + j]\).

The dependence of \(K_{ij}\) on \(i\) and \(j\) is determined by the physical nature of the process \[1,2,15-17\].

The solution of the system (1) is challenging, as it is an infinite system of equations. Still for the simplest case of a constant kernel \(K_{i,j} = 1\) it may be solved for the mono-disperse initial conditions, \(n_s(t = 0) = \delta_s\) \[1\], with the result:

\[n_i(t) = \frac{4}{(t + 2)^2} \left( \frac{t}{t + 2} \right)^{j-1} .\]

This solution was first obtained and analyzed by Smoluchowski \[14\] and is currently known as the ”theory of a rapid coagulation”. Later on, a couple of other exact solutions have been obtained for the sum, \(K_{i,j} = i + j\), and product, \(K_{i,j} = i \cdot j\), kernels \[1,2\]. Generally, an exact solution is available for the kernels of the form \[1,2\]:

\(K_{i,j} = 1 + A(i + j) + B(i \cdot j),\)

where \(A\) and \(B\) are constants.

When the kinetic rates \(K_{ij}\) are homogeneous functions of their arguments \(i\) and \(j\), there exist also scaling solutions providing the large-time asymptotic \(t \rightarrow \infty\) for

\[1\] Actually, the constant kernel reads, \(K_{i,j} = A\), however the multiplicative constant \(A\) may be always chosen as unity by re-scaling of time. The same is true for multiplicative constants in other kernels.

\[2\] \(\delta_{k,1}\) is the Kronecker symbol.
the densities $n_s$. The most prominent examples of such kernels are the generalized product kernel, $K_{i,j} = (i \cdot j)^\mu$ and the ballistic kernel \cite{1,2}:

$$K_{i,j} = (i^{1/3} + j^{1/3})^2 \sqrt{\frac{1}{i} + \frac{1}{j}}. \quad (2)$$

Generally, however, Smoluchowski equations may be solved only numerically.

For many practical applications, a coarse-grained description suffices. In this case the discrete variable $i$ indicating the size of an agglomerate may be treated as continuous and Smoluchowski equations acquire the integro-differential form \cite{15,18,21}:

$$\frac{\partial n(v,t)}{\partial t} = \frac{1}{2} \int_0^v K(v-u,u)n(v-u,t)n(u,t)du - n(v,t) \int_0^\infty K(v,u)n(u,t)du. \quad (3)$$

Due to the importance of Smoluchowski equations for industrial applications, such as synthesis of nanoparticles \cite{22,24}, soot formation, pharmacy processes \cite{25}, etc. and for natural phenomena, e.g. \cite{7,26,27}, a number of numerical approaches has been elaborated \cite{28,34}. Despite a rapid development of efficient finite-difference and other deterministic methods \cite{35,37}, the major methodology for solving the aggregation equations remains the stochastic one. A particle in cell and Direct Simulation Monte Carlo (DSMC) methods \cite{23,38} may be mentioned as the most prominent examples; they have been proved to be efficient and reliable tools to model aggregation kinetics \cite{23,24,30}.

Early works of Smoluchowski gave rise to the development of a new field of research associated with agglomeration and related phenomena. The according theoretical and numerical approaches have been elaborated to describe aggregation with source/sink terms \cite{39,41}, multi-particle aggregation \cite{42,43}, spontaneous (unary) fragmentation \cite{2,44}, exchange-driven aggregation \cite{45,46}, etc. One of the most recent extensions of the pure aggregation model was the aggregation-fragmentation model, where the agglomerates undergo collisional (binary) fragmentation \cite{7,35,44,47,48}. The aggregation-fragmentation kinetics may be symbolically written for the collisional decomposition into monomers (shattering) as:

$$[i] + [j] \xrightarrow{K_{i,j}} [i + j], \quad \text{aggregation}$$

$$[i] + [j] \xrightarrow{\lambda K_{i,j}} \underbrace{[1] + \ldots + [1]}_{i+j}, \quad \text{shattering},$$

where the scalar parameter $\lambda$ quantifies the shattering rate. It may be also shown that the shattering model is generic. Qualitatively, similar results are obtained for more general fragmentation models provided that monomers are predominant in
debris size distribution [7]. The corresponding rate equations read,

\[
\begin{align*}
\frac{dn_i}{dt} &= -n_i \sum_{i=1}^{\infty} K_{1,i} n_i + \lambda \sum_{i=2}^{\infty} \sum_{j=2}^{\infty} (i+j) K_{i,j} n_i n_j + \lambda n_1 \sum_{j=2}^{\infty} j K_{1,j} n_j \\
\frac{dn_k}{dt} &= \frac{1}{2} \sum_{i=1}^{k-1} K_{i,k-i} n_i n_{k-i} - (1 + \lambda) n_k \sum_{i=1}^{\infty} K_{k,i} n_i, \quad k = 2, \infty.
\end{align*}
\]

The aggregation-fragmentation equations (4) have been intensively investigated, analytically and numerically, mainly in the context of particles size distribution in Saturn’s rings [7, 35]. In these studies, new and efficient deterministic algorithms have been applied; allowing the handling of up to a few hundred thousand equations. With the use of various iterative methods a steady-state and quasi-steady state size distribution of particles were found [7,35,49]. The most surprising was, however, the detection of never-ending oscillations of particle densities [48]. They occur for some range of parameters and may possibly explain the periodic formation and decay of clumps in the F Ring of Saturn [48, 50]. The observation of steady oscillations in closed systems with aggregation and fragmentation was rather surprising, as it was expected that such systems could relax only to a steady or quasi-steady state. Although the numerical evidence of the steady oscillations was quite convincing [7], an analytical proof of their existence is still lacking. The recent efforts to prove theoretically the appearance of the oscillating regime look very promising [45,46,51], yet the problem remains unsolved.

To prove/disprove the emerging oscillations in aggregation-fragmentation processes is important not only for the fundamental understanding of these processes, but also for their practical applications. Hence it is worth to confirm the existence of density oscillations by an alternative numerical approach, e.g. by stochastic methods. Moreover, stochastic methods would provide an even more solid justification for this phenomenon due to unavoidable presence of noise. Indeed, the deterministic equations (4) is essentially an idealized model of a real process. The aggregation-fragmentation kinetics is inevitably accompanied by fluctuations (noise), owing to the discrete nature of microscopic events and a stochastic environment.

In spite of the importance of the addressed problem, the stochastic methods have not been widely applied to this class of systems yet. To the best of our knowledge, an application of the direct simulation Monte Carlo (DSMC) to aggregation with fragmentation has been reported in Ref. [24] only. Hence, the motivation of the present study is twofold: Firstly, we extend the existing DSMC methods for aggregation processes with the collisional fragmentation – here we probe and adopt two different DSMC methods [28,30]. Secondly, we apply the extended methods to justify the existence of the never-ending density oscillations. We confirm that
these oscillations are stable and are not sensitive to fluctuations stemming from the stochastic nature of DSMC.

2 Pure aggregation: two methods revisited

Applications of DSMC to study aggregation processes has been initiated by Gillespie [52] who constructed an effective stochastic method for the solution of continuous coagulation equations. During the last decades, the methods have been improved, dramatically increasing the computational speed and accuracy [28,31,33,53]. Currently, one may classify these methods into several major groups: constant-N Monte Carlo, constant-V Monte Carlo, inverse Monte Carlo, and others. For instance, in the classical case of binary aggregation, a celebrated acceptance-rejection method picks randomly a pair of particles up and accepts its aggregation with a probability proportional to the aggregation rate [28]. The pseudocode for one step of the acceptance-rejection method is presented in Algorithm 1, where \( s(i) \) denotes the size of \( i \)-th particle in the particle array. The computational cost of one

Algorithm 1 Acceptance-rejection method

1: procedure ARAGGREGATIONSTEP(particles)
2: Generate random number \( r \in (0,1) \)
3: Choose randomly a pair \((i,j)\)
4: Advance time: \( t := t + \tau \),
5: if \( r < \frac{K_{s(i),s(j)}}{K_{\text{max}}} \) then
6: Add particle of size \( s(i) + s(j) \) into array of particles (and delete two old),
7: Update \( K_{\text{max}} \) and \( \tau \) if \( s(i) + s(j) \) is larger than the previous largest particle.

step depends on the average aggregation acceptance probability \( P_{\text{acc}} = \frac{\langle K_{s(i),s(j)} \rangle}{K_{\text{max}}} \) and the cost of computing \( K_{\text{max}} \). If one possesses a complete information about the kernel (symmetry, homogeneity degree, etc.), it is easy to reduce the computational cost for \( K_{\text{max}} \) dramatically. Note that \( K_{\text{max}} \) can be defined as any number satisfying the relation,

\[
K_{\text{max}} \geq \max_{i,j} K_{s(i),s(j)},
\]

where \( s(i) \) and \( s(j) \) are currently available particle sizes. It can be limited if the constrain of the maximal particle size in the system is imposed, and is to be updated only if the size of an emerging aggregate exceeds the current value of \( K_{\text{max}} \). If we neglect the cost of \( K_{\text{max}} \) computation, then the one-step cost is bounded by the average number of trials before the acceptance, which may be estimated as \( 1/P_{\text{acc}} \). Hence, the cost of a single step is \( O(1/P_{\text{acc}}^{-1}) \).
An important part of the above algorithm, as well as of any DSMC method, is the evaluation rule for the time-shift $\tau$; it is discussed in detail elsewhere, see e.g. [28, 31, 52]. For a qualitative understanding of the whole concept, it is worth however, to sketch the main idea of the rule.

Let $n(t) = \sum_{i=1}^{\infty} n_i(t)$ be the total density of particles and $N$ – their total number at time $t$, $N = nV$, where $V$ is the system volume. These quantities are related to the initial values at $t = 0$ as

$$\hat{n}(N) = \frac{N}{N(t = 0)} n(t = 0).$$

Consider a small time interval $\Delta t$. According to the definition of the reaction rates, the number of collisions (reactions) between particles of size $i$ and $j$ in the volume $V$ reads, $K_{i,j}n_in_j\Delta tV$. The total number of collisions (reactions) between all particles may be written then as $(1/2)\sum_{i=1}^{\infty}\sum_{j=1}^{\infty} K_{i,j}n_in_j\Delta tV$. To obtain the collision frequency $\tau_{\text{coll}}^{-1}$ one needs to divide the number of collisions by the respective time interval $\Delta t$. Then we obtain:

$$\frac{1}{\tau_{\text{coll}}} = \frac{1}{2} \sum_{i=1}^{\infty} \sum_{j=1}^{\infty} K_{i,j}n_in_jV = \frac{1}{2} \sum_{i=1}^{\infty} \sum_{j=1}^{\infty} \frac{K_{i,j}}{V} N_iN_j = \frac{1}{2V} N(N-1) \langle K_{s(i),s(j)} \rangle$$

$$= K_{\text{max}} P_{\text{acc}} \cdot \frac{N(N-1)}{2} = K_{\text{max}} P_{\text{acc}} \cdot \hat{n}(N) \cdot \frac{(N-1)}{2},$$

(5)

where $N_{i/j} = n_{i/j}V$ and $\langle K_{s(i),s(j)} \rangle$ is the average reaction rate, which is related to the average acceptance probability as $P_{\text{acc}} = \langle K_{s(i),s(j)} \rangle / K_{\text{max}}$. Hence the average time increment $\tau$ may be found as

$$\tau = \tau_{\text{coll}} \cdot P_{\text{acc}}.$$

Correspondingly, the time-shift for each trial reads,

$$\tau = \frac{2}{\hat{n}(N) \cdot (N-1) \cdot K_{\text{max}}},$$

(6)

In our simulations we start with the unit density of particles $n(t = 0) = 1$ and monodisperse initial conditions, which implies that all particles are monomers.

The efficiency of the DSMC can be significantly improved by changing the sampling steps. Instead of sampling a new pair of particles at each time step, one can split this procedure into two separate stages as illustrated in Algorithm 2. Firstly, an initial particle is to be chosen for the aggregation event, then a second particle is sampled among the rest $N - 1$ particles. This trick allows us to decrease a number of useless rejection events and is known as Fast DSMC (FDSMC).
Algorithm 2 Fast DSMC method

1: procedure FDSMCAggregationStep\((particles)\)
2: \[ \text{Compute collision frequencies for each particle } S_i = \sum_{j \neq i} K_{s(i),s(j)}. \]
3: \[ \text{Choose random } r \in \left(0, \sum_{k=1}^{N} S_i\right). \]
4: \[ \text{Find } i \text{ s.t. } \sum_{k=1}^{i-1} S_k \leq r \leq \sum_{k=1}^{i} S_k \quad \triangleright \text{first particle selection} \]
5: \[ \text{Find } j \text{ s.t. } \sum_{k=1}^{j-1} K_{s(i),s(k)} \leq r - \sum_{k=1}^{i-1} S_k \leq \sum_{k=1}^{j} K_{s(i),s(k)} \quad \triangleright \text{second particle selection} \]
6: \[ \text{Create particle } s(i) + s(j) \text{ and delete } s(i) \text{ and } s(j). \]
7: \[ \text{Advance time } t := t + \tau. \]

This trick requires to compute, store and efficiently update the partial sums \( S(i) \). Additional acceleration of such types of methods can be achieved by using majorants of the kernel coefficients to approximate the evaluations of the sums (see [31]). One can also apply grouping of particles of the fixed size into the “buckets” and achieve extra speedup; this allows to deal with billions of particles.

Noteworthy, DSMC can be rather efficiently deployed on parallel computers. The according theoretical analysis can be found in Ref. [33] and the discussion of the experimental implementation in Ref. [54] for CPU-based clusters and in Refs. [55, 56] for modern GPUs.

Regardless of the chosen algorithm, a user has to decide what to do when only a few particles are left in the system. One possible and very natural choice is to clone all sampled particles from time to time without a significant loss of accuracy [29].

Certainly, cloning of particles can be done in many ways [8, 53]. The most straightforward way is to increase the volume of the system – this keeps the number of particles approximately constant; the simulation accuracy is also kept at the target level. For instance, one can duplicate the amount of the existing particles once their number drops down below half of the initial number. This mimics the doubling of the volume of the simulation cell, conserving the total mass density.

3 Application to collisional shattering

The modification of both methods for the case of (binary) collisional shattering may be done by taking into account that the particle array updates are decoupled from the pair selection procedure. Since the shattering rate \( \lambda \) does not depend on the particle densities and their size, we can choose the type of interaction – aggregation or fragmentation, afterwards, after the pair has been picked up.

Algorithms 3 and 4 illustrate the extension of the acceptance-rejection and
FDSMC algorithms by incorporating binary shattering process. The decision on
the type of process (aggregation or fragmentation) chosen is included as a separate
procedure PairInteraction. The procedure can be used as a drop-in replacement
for updates in lines 6 in both Algorithms 1 and 2. These additional pairwise
interactions may be directly added to the procedure in an obvious manner.

Algorithm 3 Acceptance-rejection method for binary scattering

1: procedure ARAGGREGATIONFRAGMENTATIONStep(particles)
2:    Generate random number \( r \in (0, 1) \)
3:    Choose random pair \((i, j)\)
4:    Advance time: \( t := t + \tau \)
5:    if \( r < \frac{K_{s(i), s(j)}}{K_{max}} \) then
6:        PairInteraction\((i, j)\)
7: end

PairInteraction\((i, j)\)
8: Generate random number \( r \in (0, 1) \)
9: if \( r < \frac{\lambda}{1 + \lambda} \) then \( \triangleright \) fragmentation
10:    Add \( s(i) + s(j) \) monomers into array of particles.
11: else \( \triangleright \) aggregation
12:    Add particle of size \( s(i) + s(j) \) into array of particles.
13:    Update \( K_{max} \) if \( s(i) + s(j) \) is larger than the previous largest particle.
14:    Recompute \( \tau \).
15: Delete particles \( i \) and \( j \).

The other significant change in this modification is the updated rule for time-
shift calculation, which now reads,

\[
\tau = \frac{2}{\hat{n}(N)(N - 1)K_{max}} \cdot \frac{1}{1 + \lambda}.
\]  

The same factor \( \frac{1}{1 + \lambda} \) has to be used to update the time-shifts in the FDSMC
algorithm.

While Algorithms 3 and 4 rely on two independent random numbers for the
pair selection and then for the event selection, it is possible to use only one random
number, by generating \( r \) uniformly distributed in \((0, 1 + \lambda)\). The range \((0, 1)\) then
corresponds to the aggregation event and the range \((1, 1 + \lambda)\) to the fragmentation
event.

4 Particle grouping

The following feature of the shattering algorithms hinders their efficiency – the
need to store a large number of newly created monomers right after the fragmenta-
tion event.
Algorithm 4 Fast DSMC method for binary shattering

1: procedure FDSMCAggregationFragmentationStep(particles)
2:  Compute collision frequencies for each particle \( S_i = \sum_{j \neq i} K_{s(i),s(j)} \).
3:  Choose random \( r \in \left(0, \sum_{k=1}^{N} S_k\right)\).
4:  Find \( i \) s.t. \( \sum_{k=1}^{i-1} S_k \leq r \leq \sum_{k=1}^{i} S_k \) \( \triangleright \) first particle selection
5:  Find \( j \) s.t. \( \sum_{k=1}^{j-1} K_{s(i),s(k)} \leq r - \sum_{k=1}^{i-1} S_k \leq \sum_{k=1}^{j} K_{s(i),s(k)} \) \( \triangleright \) second particle selection
6:  PairInteraction(\( i, j \)). \( \triangleright \) reused from Algorithm 3
7:  Advance time \( t := t + \tau \).

Using the fact that particles of the same size are indistinguishable, we suggest to group the particles into “buckets”. Each bucket comprises particles of one size only and keeps their number along with other information, such as total probability \( S(i) \). We store the buckets in a static array allocated ahead in time. Each index of the array directly corresponds to the particle size, allowing for a quick search of the bucket for a correct size during the insertions. To support the particles’ unbounded growth and avoid a huge number of empty buckets in the preallocated array, we group only particles, whose size does not exceed \( B \). If a particle is larger than \( B \), it is added to a dynamic vector as a separate particle.

With this hybrid static-dynamic approach, the addition of the monomers requires just an update of the counter in the bucket and a single traversal over all buckets and particles in the dynamic array; this allows to update all interaction probabilities.

Tuning the parameter \( B \), one achieves a trade-off between a cost of bucket array traversal and a cost of storing particles as separate units. In the extreme case of \( B \rightarrow \infty \), most of the buckets will be empty and any particle insertion/removal will incur a cost proportional to the size of the biggest particle. Another extreme case \( B = 0 \) corresponds to the lack of grouping, and any particle update will incur a cost proportional to the number of particles, as stated in the original algorithm. The choice of \( B \sim 1000 \) guarantees a good performance for most of the practical applications.
Figure 1: Particle size distribution at $t = 10$ for the ballistic kernel obtained by MC algorithms for the initial number of particles $N = 10^5$ (dots) and by the finite-difference method (lines) with the step size $\Delta t = 10^{-3}$ and 5000 equations. The shattering rate $\lambda = 0.01$ and mono-disperse initial conditions are used. Right panel: Fast DSMC. Left panel: The acceptance-rejection method.

5 Numerical experiments

5.1 Performance and accuracy testing on the basic problems

The very first test measures the accuracy of the aggregation-shattering Monte Carlo algorithms for the case of the constant kernel,

$$K_{i,j} = 1$$

and monodisperse initial conditions $n_s(t = 0) = \delta_{s,1}$: an analytical solution for this case is available, see e.g. [7]. In Table 1 we present the results for the accuracy of the method, quantified by the Euclidean norm of the error of the final particle size distribution (recall that the exact solution is known). The results indicate a good accuracy of the method and convergence to the analytical solution. No significant difference between the acceptance-rejection and FDSMC schemes is observed. Noteworthy, the error converges as $O(N^{-1/2})$.

Next we report the benchmarks for the case of the ballistic kernel,

$$K_{i,j} = (i^{1/3} + j^{1/3})^2 \sqrt{\frac{1}{i} + \frac{1}{j}},$$

with the same initial conditions. For this problem, the analytical solution is not known and the kernel itself requires more “heavy” computations. In Table 2 we
Table 1: The Euclidean norm of the error of the solution obtained by the acceptance-rejection (A-R) and FDMSC algorithms with the constant kernel, monodisperse initial conditions and \( \lambda = 0.1 \).

| Method | Parameters | \( t = 1 \) | \( t = 10 \) | \( t = 100 \) |
|--------|------------|------------|------------|------------|
| \( A-R \) | \( N = 10^4 \) | 0.012 | 0.008 | 0.017 |
| \( FDSMC \) | \( N = 10^4 \) | 0.010 | 0.019 | 0.034 |
| \( A-R \) | \( N = 10^5 \) | 0.005 | 0.009 | 0.009 |
| \( FDSMC \) | \( N = 10^5 \) | 0.003 | 0.004 | 0.008 |
| \( A-R \) | \( N = 10^6 \) | 0.002 | 0.007 | 0.0023 |
| \( FDSMC \) | \( N = 10^6 \) | 0.015 | 0.001 | 0.0024 |
| \( A-R \) | \( N = 10^7 \) | 0.0004 | 0.0005 | 0.0012 |
| \( FDSMC \) | \( N = 10^7 \) | 0.0003 | 0.0005 | 0.0005 |

Table 2: Comparison of the errors of the simulation results for zeroth \( M_0(t) = \sum_{s=1}^{\infty} n_s(t) \), second \( M_2(t) = \sum_{s=1}^{\infty} s^2 n_s(t) \) and third \( M_3(t) = \sum_{s=1}^{\infty} s^3 n_s(t) \) moments of the particle size distribution for the ballistic kernel and \( \lambda = 0.01 \). The average relative error (standard deviation) is shown for both MC algorithms and the finite-difference scheme. Different number of particles (for the MC algorithms) and different time steps (for the finite-difference scheme) are used.

| Method | Parameters | \( t = 1 \) | \( t = 10 \) | \( t = 100 \) |
|--------|------------|------------|------------|------------|
| \( A-R \) | \( N = 10^3 \) | 3\% | 16\% | 26\% |
| \( FDSMC \) | \( N = 10^3 \) | 5\% | 13\% | 21\% |
| \( A-R \) | \( N = 10^4 \) | 0.9\% | 5\% | 26\% |
| \( FDSMC \) | \( N = 10^4 \) | 22\% | 7\% | 21\% |
| \( A-R \) | \( N = 10^5 \) | 0.8\% | 2\% | 10\% |
| \( FDSMC \) | \( N = 10^5 \) | 0.8\% | 2\% | 10\% |
| \( A-R \) | \( N = 10^6 \) | 0.6\% | 0.6\% | 0.6\% |
| \( FDSMC \) | \( N = 10^6 \) | 0.08\% | 0.08\% | 0.08\% |
| \( FD \) | \( \Delta t = 0.05 \) | 3.8\% | 8.1\% | 0.17\% |
| \( \Delta t = 0.005 \) | 0.33\% | 0.81\% | 0.014\% |

\[ \Delta t = 0.005 \]
Table 3: Running time, in seconds, for the acceptance-rejection (A-R), Fast Direct Monte Carlo Simulation (FDSMC) and Finite-Difference (32 758 equations) algorithms for the constant kernel, monodisperse initial conditions and $\lambda = 0.1$.

|         | $t = 1$ | $t = 10$ | $t = 100$ |
|---------|---------|----------|-----------|
|         | A-R     | FDSMC    | A-R       | FDSMC  | A-R     | FDSMC    |
| $N = 10^3$ | 0.001 | 0.01 | 0.0001 | 0.07 | 0.0001 | 0.64    |
| $N = 10^4$ | 0.001 | 0.005 | 0.0006 | 0.09 | 0.0025 | 0.82    |
| $N = 10^5$ | 0.001 | 0.046 | 0.0059 | 0.13 | 0.025  | 1.97    |
| $N = 10^6$ | 0.011 | 0.09 | 0.046 | 0.71 | 0.26   | 15.13   |
| Finite-difference | 2.49 | 24.66 |       | 246.21 |

Table 4: Running time, in seconds, for the acceptance-rejection (A-R), Fast Direct Monte Carlo Simulation (FDSMC) and Finite-Difference algorithm (5 000 equations) for the ballistic kernel, monodisperse initial conditions and $\lambda = 0.01$.

|         | $t = 1$ | $t = 10$ | $t = 100$ |
|---------|---------|----------|-----------|
|         | A-R     | FDSMC    | A-R       | FDSMC  | A-R     | FDSMC    |
| $N = 10^3$ | 0.0001 | 0.017 | 0.0005 | 0.407 | 0.071  | 245.4   |
| $N = 10^4$ | 0.011 | 0.15 | 0.0064 | 3.4 | 1.11   | 439.0   |
| $N = 10^5$ | 0.013 | 1.67 | 0.076 | 34.82 | 14.15  | 5204    |
| $N = 10^6$ | 0.17 | 18.08 | 0.96 | 406.8 | 87.89  | 40335   |
| Finite-difference | 9.51 | 94.57 |       | 988.48 |

The data in Table 2 clearly illustrates that the accuracy of the finite-difference approach is higher.

In Tables 3 and 4 we present the CPU times of simulations by the DSMC algorithms for the constant and ballistic kernels. It is compared with the according simulation time for the fast finite-difference approach [36]. One can see that although the DSMC approach is less accurate, it provides faster simulations (see Table 4) ensuring the conservation of mass.
Figure 2: Time-dependence of the second moment of the particle size distribution function, $M_2(t) = \sum_{k=1}^{\infty} k^2 n_k(t)$ for the case of monodisperse initial conditions. (a) $a = 0.95$ and $\lambda = 0.01$, (b) $a = 0.98$ and $\lambda = 0.005$. Dots – Monte Carlo results, lines – the results of the finite-difference solution of 8192 equations. One can see the emergence of steady oscillations.

5.2 Oscillating regimes in the aggregation-fragmentation kinetics

Opposite to the plain relaxation behavior expected for the Smoluchowski-like equations, a surprising oscillation regime has been recently reported for the aggregation-fragmentation kinetics. It was observed that the kinetic equations (4) with the kernels

$$K_{i,j} = \left(\frac{i}{j}\right)^a + \left(\frac{j}{i}\right)^a$$

demonstrated for closed systems, with a lack of sources and sinks of particles, steady oscillations for $a > 0.5$ and $0 < \lambda < \lambda_{\text{crit}}$ \cite{48, 57}. Such oscillations have been detected numerically, by an efficient implementations of the finite-difference second-order Runge-Kutta time-integration scheme. Although the qualitative theory of Ref. \cite{57} supports the existence of the oscillating regimes, an additional independent verification of this phenomenon is highly desirable. Here we show that DSMC methods demonstrate the same oscillations of densities, as in Refs. \cite{48, 57} and the according numerical solutions converge, see Figure 2. Both, the acceptance-rejection and FDSMC approach demonstrate the emergent oscillations, thus verifying the results of the previous studies. Therefore, we conclude that the oscillatory solutions are robust and stable with respect to stochastic errors and fluctuations inherent for Monte Carlo methods.
In our experiments, we also observed an “extinction” effect, when all particles coalesce in a single final cluster; evolution of the systems ceases in this case. The extinction occurs for relatively long sequences of only-aggregative collisions. The probability of such sequences rapidly decreases with the systems size. Hence to observe the steady oscillations the system should be large enough. Still for any finite system the extinction effect is always possible, even if its probability is vanishingly small. Note that the possibility of this effect illustrates a very important difference between the stochastic Monte Carlo approach and the deterministic one of the finite difference method. The latter approach ignores the discrete nature of the process with inevitable fluctuations, and essentially models an infinitely large system in the thermodynamic limit. Hence the reported results confirm the existence of steady oscillations in aggregation-fragmentation kinetics in real systems, which are always finite and subjected to noise and fluctuations.

6 Conclusions

In the present study we report a straightforward generalization of two well-established Monte Carlo (MC) techniques for aggregation kinetics, supplemented by collisional fragmentation (shattering). We present a comprehensive validation of the proposed methodology. The MC results are compared with the known analytical solutions for the constant kernel and with the alternative efficient finite-difference scheme [36] for the ballistic kernel. We show that the basic MC methods – the acceptance-rejection and FDSMC method, formulated initially for a pure aggregation may be easily modified for a more complex model without losing the computational efficiency and good convergence. We implement both methods using the grouping of particles and demonstrate that it significantly outperforms, in terms of the CPU-time, the most efficient finite-difference method of Ref. [36].

We also demonstrate that the recent observations of the oscillatory regimes in the aggregation-fragmentation kinetics [48,57] for the generalized Brownian kernel may be validated by the stochastic methods. Thus, our experiments provide a convincing proof that the steady oscillations do exist and are stable with respect to fluctuations and noise.

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