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A Fast Stratified Sampling Simulation of Coagulation Processes

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Abstract

We develop a new version of the direct simulation Monte Carlo method [3] for coagulation processes governed by homogeneous Smoluchowsky equations. The method is based on a subdivision of the set of particle pairs into classes, and on an efficient algorithm for sampling from a discrete distribution, the so-called Walker's alias method [4]. The efficiency of the new method is drastically increased compared to the conventional methods, especially when the coagulation kernel is strongly varying. The method is applied to solving a problem of islands formation on a surface due to a diffusion controlled coagulation.

1 Introduction

Formation of clusters and their growth through aggregation is the main feature of many physical processes, from polymerization and gelation in polymer science, flocculation and coagulation in aerosol and colloidal chemistry, percolation and coarsening in phase transitions and critical phenomena, formation of aerosol particles in combustion processes, agglutination and cell adhesion in biology, to island nucleation and thin film growth in material science (e.g., see [5], [6], [10], [16], [9]).

The Smoluchowsky equation reads

$$\frac{\partial n_l}{\partial t} = \frac{1}{2}\sum_{i+j=l} K_{ij} n_i n_j - n_l \sum_{i=1}^{\infty} K_{li} n_i, \tag{1}$$

where n_l is the number density of the $\{l\}$-clusters (the particles containing i monomers), $K_{ij} = K_{ji}$ is a coagulation coefficient characterizing the frequency collision between an $\{i\}$- and $\{j\}$-clusters; it is assumed that the initial size distribution $n_l(t_0) = L(t_0, l)$ is given. Due to homogeneity in space, it is convenient to deal with n_l - the number of $\{l\}$-clusters per unit volume, hence we assume this normalization throughout the paper if otherwise not specified.

This equation governs the aggregation (coagulation) of a set of clusters in bulk, hence the solution does not depend on the spatial coordinates. More general forms of the coagulation equation can be found in [17], in particular, we studied in [15] the case

$$\frac{\partial n_l(r,t)}{\partial t} + v \cdot \nabla n_l(r,t) = \frac{1}{2}\sum_{i+j=l} K_{ij} n_i n_j - n_l \sum_{i=1}^{\infty} K_{li} n_i + D_l \Delta n_l + F_l(t),$$

where v is the velocity of the host gas, D_l is the diffusion coefficient, and $F_l(t)$ is the intensity of source of l-clusters.

We have suggested in [15] a stochastic Lagrangian method for solving the inhomogeneous equation by a special averaging over the solutions of homogeneous Smoluchowski equation in the case when the diffusion coefficients do not depend on the size of the particle. Here we focus on the homogeneous case (1).

1.1 Method of Majorant Frequency (MMF)

Direct stochastic simulation of coagulation was probably first applied in some physics applications, e.g., see [5], [6], [11], [12]. Let us describe the well known Method of Majorant Frequency (MMF) (e.g., see [2], [3], [8], [7]) which is quite straightforward and very simple. It considers the dynamics of states as a Markov process, and simulates this process by small time steps. The only one notion which is introduced is the majorant coagulation kernel: it is assumed that a constant K_{max} can be found so that $K_{max} \geq K_{ij}$ is true for all i and j. Even if the kernel is an unbounded function, the values of K_{ij} for a finite time are always finite.

So we start with the initial state of our system which is given. It means that at $t = 0$ we know the concentrations $n_l(0)$. Then, given the state of the system at time t_k, its state at time t_{k+1} is evaluated as follows:

1. Simulate a random time interval Δt according to the exponential distribution $p(\tau) = \lambda \exp(-\lambda\tau)$, and put $t_{k+1} = t_k + \Delta t$ where $\lambda = N(N-1)K_{max}/2N_0$.

Here N_0 is the initial number of test particles, $N(t)$ is the updated (current) number of particles.

This means, Δt is random: $\Delta t = -(1/\lambda)\ln(\alpha)$ where α is a random number uniformly distributed on $(0, 1)$. Note that since N is taken quite large, $1/\lambda$ is small, so it is reasonably simply to choose the time step deterministically as $\Delta t = 1/\lambda$.

2. Sample a pair of clusters uniformly among the $N(N-1)$ pairs, say clusters with i and j monomers.

3. With the probability $p_{ij} = K_{ij}/K_{max}$ the clusters i and j coagulate, i.e., the numbers n_i and n_j are decreased by one, the number n_{i+j} is increased by one, and N, the number of particles in the system is decreased by one. Otherwise (i.e., with probability $1 - p_{ij}$) the state of the system is not changed. Then we go to the next time step of the system evaluation.

It is clear that the number of clusters in the system will be decreasing in time. When the number N decreases to say 50% of the initial number of simulated clusters, we enrich the statistics by doubling the system. It means that a copy of the current system is added to the particle system. Accordingly, N_0 and N are increased by a factor of 2. After this, the system evolve further as described above. It can be shown that the process converges in a probabilistic sense to the solution of the Smoluchowski equation.

From the description of the algorithm it is clear that it may happen that its cost will be very high. Indeed, if the variation of the coagulation kernel K_{ij} is high, the probability

of the coagulation event in the algorithm above (see p.3) is small which implies, we will have a large number of small time steps till the next change of the state. As an important example, we mention the coagulation of charged particles where the coagulation kernel is strongly varying to many orders of magnitude [17].

The method described can be improved by using a finer majorant, instead of the crude majorant K_{max}. Assume, we have chosen a function $\hat{K}_{ij}$ such that $\hat{K}_{ij} \geq K_{ij}$ for all i, j. Then the simulation algorithm above is generalized to the following scheme:

1. Simulate a random time interval Δt according to the exponential distribution $p(\tau) = \hat{\lambda} \exp(-\hat{\lambda}\tau)$, and put $t_{k+1} = t_k + \Delta t$ where

$$\hat{\lambda} = \frac{1}{2N_0} \sum_{1 \leq i \neq j \leq N} \hat{K}_{ij}$$

2. Sample of a pair of indices according to the distribution

$$\frac{\hat{K}_{ij}}{2N_0}, \qquad 1 \leq i \neq j \leq N$$

3. With the probability $p_{ij} = K_{ij}/\hat{K}_{ij}$ the clusters i and j coagulate, i.e., the numbers n_i and n_j are decreased by one, the number n_{i+j} is increased by one, and N, the number of particles in the system is decreased by one. Otherwise (i.e., with probability $1 - p_{ij}$) the state of the system is not changed. Then we go to the next time step of the system evaluation.

This method however assumes that $\hat{K}_{ij}/2N_0$ is simple enough to carry out efficient sampling from this distribution. For instance in [2], an example with a linear majorant function was considered, and in [8], all the particles are divided into groups, so that inside the group, the majorant technique is used. This is done after each happened coagulation event. In addition, in this algorithm the authors use (again, after each coagulation event) the conventional sampling technique for the discrete distribution to simulate the index of the group. All this is time consuming, especially for strongly varying coagulation kernels.

2 Stratified sampling with large probabilities (SLP)

To explain the main idea behind the new method, let us suppose we have an extremely efficient method (EEM) of sampling from an arbitrary discrete distribution. Then we could imagine that we keep the table of the pair collision probabilities and sample the collision pairs from this table using the above mentioned method, EEM. Bad news is that after each coagulation event, we have to recalculate the table of probabilities. The crucial point of our new method is that the change in the table can be done quite rarely, and the choice of the class of pair particles is done by the method suggested by Walker [4]. Thus instead of using the rejection method where the coagulation event happens with small probabilities, we turn to a stratified sampling which ends up with a coagulation having large probability, so we call the method shortly SLP (stratified sampling with large probabilities).

Summarizing, the general scheme for solving (1) can be described as follows:

- First step: we choose the current particle distribution as a given initial distribution $L(t_0, l)$.
- Second step: take N particles according to the current distribution, choose a subdivision of the set of all particle pairs into (many) classes; this subdivision is generated by a subdivision of the whole sizes into a set of size bins; the random index of the class is sampled by EEM, while inside the sampled class the von Neumann rejection method is applied. The majorant of the rejection method is fixed: Each coagulation event $\{i\} + \{j\} = \{k\}$ leads to the corresponding change in the arrays containing the clusters $\{i\}, \{j\}, \{k\}$; sample the time step Δt according to the exponential distribution. The process simulations proceed till the number of particles in the size bins is twice decreased or increased. After that we go to step 2.

The algorithm can be described in steps, in more details:

The system of N_0 particles with the given initial size distribution $n_l(0)$ is considered. The state at the time t is defined by the vector

$$L(t) = \{l_1(t), ..., l_{N_0}(t)\},$$

where $l_i(t) \quad (i = 1, ..., N_0)$ is the size of the particle $\{i\}$.

We divide the set of particle pairs into classes $M(t) = \{(l_i, l_j) : i > j\} = \cup M_k(t)$. Let us assume that the probabilities P_k that a collision happens in the class M_k are given; the same for P_{kij}, the conditional probabilities that a collision of the particle pair (l_i, l_j) happens in the sampled class M_k. The change of the state happens in random time steps τ.

At each time step, so randomly chosen particles pair (l_i, l_j) collide according to probabilities p_{kij}, which born particles of larger size. In the Markov chain of collisions, the random time step τ is sampled according to the exponential distribution density

$$p_\tau = \rho \exp(-\rho\tau), \qquad \rho = \max_{k,(l_i,l_j)\in M_k} \frac{K_{l_i l_j}}{P_k P_{kij}}. \tag{2}$$

The probabilities p_{kij} can be defined by

$$p_{kij} = \frac{K_{l_i l_j}}{\rho P_k P_{kij}}. \tag{3}$$

This choice is quite natural since it takes the time scale ρ^{-1} as the minimum over all classes. It implies also that

$$< \tau > K_{l_i l_j} = P_k P_{kij} p_{kij} \tag{4}$$

for $\langle\tau\rangle = 1/\rho$.

We suppose now, that the particles are arranged into N_1 size bins

$$L_k = \{l_{mk} = l_m, \quad m = 1, ...N_2\}, \quad k = 1, ..., N_1$$

so that the initial number of particles is $N_0 = N_1 N_2$. The size boundaries of particles in the bins are fixed:

$$b_{k-1}(t) < l_{mk} < b_k(t), \quad \forall m = 1, ...N_2, \quad k = 1, ..., N_1. \tag{5}$$

The subdivision of the set $M(t) = \cup M_{\bar{i}\bar{j}}, \quad \bar{i} \le \bar{j} = 1, ..., N_1$ is defined by

$$M_{\bar{i}\bar{j}} = \begin{cases} (l_i, l_j) : l_i \in L_{\bar{i}},\ l_j \in L_{\bar{j}} & if\ \ \bar{i} \neq \bar{j} \\ (l_i, l_j) : l_i < l_j,\ l_i, l_j \in L_{\bar{i}} & if\ \ \bar{i} = \bar{j} \end{cases}$$

Using the majorants

$$K_{\bar{i}\bar{j}} = \begin{cases} \max\limits_{(l_i,l_j)\in M_{\bar{i}\bar{j}}} K_{l_i l_j} & if\ \ \bar{i} \neq \bar{j}, \\ \frac{1}{2} \max\limits_{(l_i,l_j)\in M_{\bar{i}\bar{i}}} K_{l_i l_j} & if\ \ \bar{i} = \bar{j} \end{cases} \tag{6}$$

the probability $P_{\bar{i}\bar{j}}$ that a collision happens in the set $M_{\bar{i}\bar{j}}$ (see P_k in (2), (3)), is calculated according to

$$P_{\bar{i}\bar{j}} = \frac{K_{\bar{i}\bar{j}}}{\bar{K}}, \text{ where } \bar{K} = \sum_{1\le\bar{m}\le\bar{n}\le N_1} K_{\bar{m}\bar{n}}. \tag{7}$$

In the sampled class $M_{\bar{i}\bar{j}}$ the number of particles is obviously $\nu_{\bar{i}\bar{j}} = \nu_{\bar{i}}(\nu_{\bar{j}} - \delta_{\bar{i}\bar{j}})$ where $\nu_{\bar{i}}$ is the number of nonzero elements in $L_{\bar{i}}$, and δ_{ij} is the Kronecker symbol. Therefore, sampling in $M_{\bar{i}\bar{j}}$ the pair $\bar{i}\bar{j}$ uniformly means that the probability p_{kij} mentioned in (3) is equal to $1/\nu_{\bar{i}\bar{j}}$.

Let us define

$$\Delta = \begin{cases} 0 & if\ there\ exists\ \bar{j} \neq \bar{i}\ such\ that\ \ \nu_{\bar{i}} = \nu_{\bar{j}} = \bar{\nu} = \max\limits_{1\le\bar{i}\le N_1} \nu_{\bar{i}}\ , \\ 1 & otherwise\ . \end{cases}$$

Thus all the probabilities are defined, and we can present the simulation procedure as follows.

1. Generate the initial state of particles system according to the given $n_l(0)$.
2. Arrange the set $L(t) = \cup L_k$ according to (5). Then the probabilities $P_{\bar{i}\bar{j}}$ are calculated by the formulae (6), (7).
3. Sample an exponentially distributed time step τ with parameter ρ taken as $\rho = \frac{\bar{K}\hat{\nu}}{\beta}$, where $0 < \beta \le 1,\ \hat{\nu} = \bar{\nu}(\bar{\nu} - \Delta),\ \bar{\nu} = \max\limits_{1\le\bar{i}\le N_1} \nu_{\bar{i}}$, and set $t_{k+1} = t_k + \tau$.
4. The pair of the class indices $\bar{i}, \bar{j}$ is chosen according to the probabilities $P_{\bar{i}\bar{j}}$. This can be done by Walker's alias method [4].
5. Sample the pair of particle indices $i, j :\ l_i \in L_{\bar{i}},\ l_j \in L_{\bar{j}}$ uniformly within the class $M_{\bar{i}\bar{j}}$. It can be carried out with one recall of α, a random generator.
6. With probability as defined in (3), namely, with

$$p_{kij} = \beta \frac{\nu_{\bar{i}\bar{j}}}{\hat{\nu}} \frac{K_{l_i l_j}}{K_{\bar{i}\bar{j}}}, \quad \nu_{\bar{i}\bar{j}} = \nu_{\bar{i}}(\nu_{\bar{j}} - \delta_{\bar{i}\bar{j}}) \tag{8}$$

a coagulation step is made, i.e., we remove the particles of sizes l_i and l_j and add one particle of size $l_k = l_i + l_j$. We renew the sets $L_{\bar{k}}$ containing these particles and recalculate the corresponding values $\nu_{\bar{k}}, \hat{\nu}$. Otherwise, the interaction is fictitious, i.e. nothing is changed. We note that the relation (4) keeps true at every time step.
7. If the number of particles in any set L_k is changed more than two times (increased or decreased) in comparison with the one given in the step 2, then we go to step 2. Otherwise, we go to step 3.

From this description it is seen that one adjusting parameter, β, appears in the evaluation of the time step. Decreasing this parameter, we can decrease the time scale to adjust the method to the type of the coagulation kernel. For practically relevant kernels like diffusion controlled coagulation, the free molecule regime, the collisions in turbulent flows, this parameter can be taken close to one, while for regimes of faster coagulation it is recommended to take this parameter smaller.

We should mention that a doubling procedure is useful for long time simulations: if the number of particles in the whole system becomes two times less we just take a copy of the rest of particles and add it to the simulated system to keep the number of particles constant, see, e.g., [3].

Remark. *In the above algorithm, we have for simplicity taken in all of N_1 bins an equal number of particles N_2 so that the system started with a total number of particles $N_0 = N_1 N_2$. For example, when the initial particle system consists only of monomers, this choice is quite reasonable. However when the system evolves, it is quite suggestive to put in different bins a different number of particles, depending on the coagulation activity of the relevant part of the spectrum.*

3 Testing calculations

In this section we present the results of numerical experiments with the developed SLP method. In Figure 1 we plot the size distribution (left panel) and the second moment (right panel) of the solution to Smoluchowski equation governing the coagulation of agglomerates of particles in free molecule regime, with taking into account the fractal dimension which was 1.2 (e.g., see [8]), with the kernel $K_{ij} = \sqrt{(1/i + 1/j)} \cdot (i^{1./2.1} + j^{1./2.1})^2$. The calculations are compared against the exact results: the solid lines are solutions obtained by a high accuracy finite element method we constructed in [3]. The error of SLP is about 0.1%, the number of particles was 100000, the number of sections 100.

In Table 1 we present a detailed comparison of MMF with the SLP method. All the particles were subdivided into M classes, and we give the results for $M = 5$, $M = 20$, $M = 100$, $M = 200$. The case $M = 1$ coincides actually with MMF. In the table, the numbers show the cost of the method measured in hundreds of thousands of MC steps. It is seen that the dependence of the cost on the size of subdivision is the following: first, the cost is decreasing when the number of classes is enlarged, and then, reaching a minimum, it starts to grow. This can be explained as follows: when we start to increase the number of classes, the number of rejections inside all classes is decreasing since the smaller the size of the class the better is the local majorant in each class. This is exactly we had in mind when introducing the stratified sampling over classes. But then, after reaching a certain size, the ratio $n_{\bar{i}\bar{j}}/\hat{n}$ in (8) is decreasing as the number of classes increases which implies that this factor may damp the second "well behaved" factor $K_{l_i,l_j}/K_{\bar{i},\bar{j}}$. This leads to the mentioned dependence of the cost on the number of classes, and an interesting problem is to find the optimal number of classes. The gain depends strongly on the number of particles: the larger the system, the higher is the gain. And of course, this gain will be even more pronounced for strongly varying kernels which we will demonstrate in the example presented in the next section.

Number of particles	$M = 1$(MMF)	$M = 5$	$M = 20$	$M = 100$	$M = 200$
5000	14.1	5.59	3.36	4.58	-
20000	62.1	28.5	12.2	16.7	21.2
100000	463.8	165.5	62.9	59.0	73.4
500000	46337.7	-	328.4	244.9	299.1

Table 1: The cost of the SLP method, in MC steps, for different subdivisions in M sections

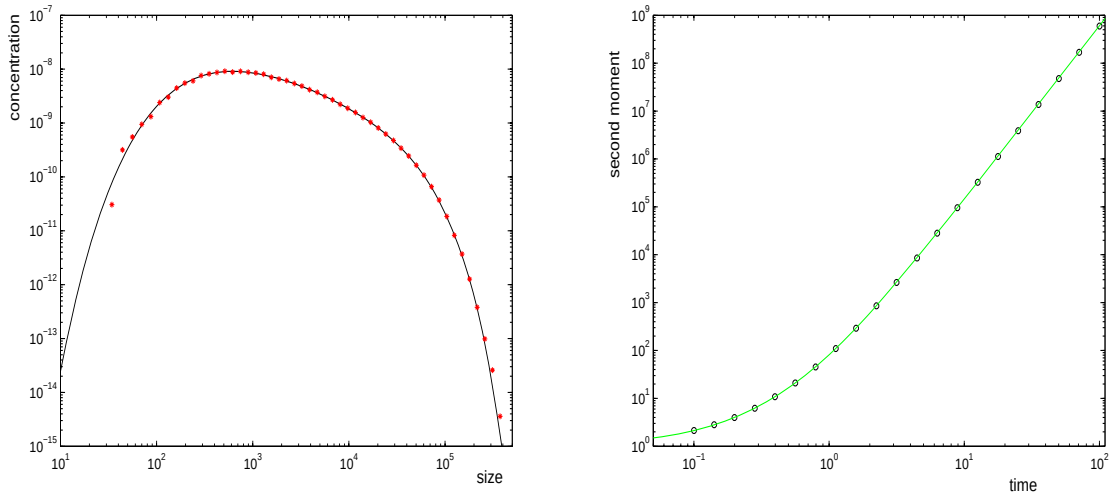

Figure 1: The size spectrum at the time $t = 100$ (left panel), and its second statistical moment (right panel)

4 Two-dimensional coagulation: diffusion of clusters on a plane surface

It is well understood that the diffusion on a surface is essentially different from the diffusion in space. In practice, one often uses uncritically the coagulation coefficients derived for 3D also in problems dealing with a coagulation process on a surface (e.g, see [1]). In this section we derive the coagulation kernel for particles moving on a plane, with the diffusion controlled coagulation regime. It turns out that a new correction term is dependent on the mean size, and hence, the coagulation kernel is dependent on time. This is the case where the cost of MMF will be strongly increasing in time, so our SLP method seems to be an extremely useful technique to improve the simulation efficiency. Numerical results have confirmed this assumption.

4.1 Evaluation of the diffusion controlled coagulation coefficient

Let us recall that in 3D, the diffusion controlled coagulation coefficient is derived explicitly, starting from the evaluation of the flux of diffusing particles on the surface of a fixed sphere.

Let us consider a cluster of radius R which is located as the origin, and calculate the flux of particles which are diffusing with a diffusion coefficient D. In the steady state regime, the concentration of diffusing particles is found from the Dirichlet problem:

$$\Delta c(r) = 0, \quad r > R,$$

with boundary conditions

$$c(r) = \bar{c} \quad r = \infty, \quad c(r)|_{r=R} = c_{eq}. \tag{9}$$

Hence the solution is $c(r) = \bar{c} + [c_{eq}(R) - \bar{c}]R/r$. Therefore, the flux of diffusing particles on the sphere is then calculated as

$$J = 4\pi R^2 \, D\nabla c|_{r=R} = 4\pi \, R \, D \, [\bar{c} - c_{eq}(R)].$$

Now, it is clear that the flux of diffusing j-clusters to a fixed i-cluster is

$$J_{ij} = 4\pi D(R_i + R_j)\bar{c}$$

if time is sufficiently large in the sense that $t >> (R_i + R_j)^2/D$.

If both particles are diffusing, the diffusion constant for the relative motion is $D_{ij} = D_i + D_j$, so the collision frequency is given by

$$K_{ij} = J_{ij}/\bar{c} = 4\pi(D_i + D_j)(R_i + R_j)$$

which was first derived by Smoluchowski.

In 2D, this approach does not work. Indeed, the general solution of the diffusion equation is here $c(r) = a + b\log(r)$, and the boundary condition at $r = \infty$ cannot be satisfied. It implies, the time dependent solution in 2D does not have a nonzero steady state limit.

In [13], the diffusion problem in 2D for a system of particles have been solved as follows. Assume that a particle of radius R is surrounded by a set of particles with the size distribution $n(r,t)$ for cluster sizes which equals the number of clusters of radius R per unit area. We seek the flux in the form:

$$J(R) = k(R)[\bar{c} - c_{eq}(R)].$$

The time evolution of the concentration is

$$\frac{\partial \bar{c}(t)}{\partial t} = -\Big\{ \int_0^\infty k(R)n(R,t)dR \Big\} \bar{c}(t) + \int_0^\infty k(R)c_{eq}(R)n(R,t)dR.$$

The local concentration $c(r,t)$ solves the equation

$$\frac{\partial c(r,t)}{\partial t} = D\Delta c(r,t) - D\xi^{-2} \, c(r,t) + S$$

where by definition

$$D\xi^{-2} = \int_0^\infty k(R) \, n(R,t)dR \tag{10}$$

is the sink term, and

$$S = \int_0^\infty k(R)\, c_{eq}(R)\, n(R,t)\, dR \tag{11}$$

is a source term. In steady state conditions $S = D\xi^{-2}\bar{c}$. This implies, that in steady state,

$$\{\Delta - \xi^{-2}\}\,[c(r) - \bar{c}] = 0 \tag{12}$$

and $c(r)$ satisfies the boundary conditions (9).

Obviously, the sink term ξ plays the role of a screening length, and hence removes the divergence present in the single particle case.

Now, the solution to the problem (12),(9) is

$$c(r) = \bar{c} + [c_{eq}(R) - \bar{c}]\,\frac{K_0(r/\xi)}{K_0(R/\xi)}$$

where K_0 is the zeroth modified Bessel function. So the local flux into the cluster at the origin is:

$$J = 2\pi\, R\, \nabla c|_R = 2\pi D\,\frac{R}{\xi}\frac{K_1(R/\xi)}{K_0(R/\xi)}[\bar{c} - c_{eq}(R)]$$

where K_1 is the first modified Bessel function. So we substitute

$$k(R) = 2\pi D\,\frac{R}{\xi}\frac{K_1(R/\xi)}{K_0(R/\xi)} \tag{13}$$

in the equation (10), which yields

$$\xi^{-1} = 2\pi \int_0^\infty R\,\frac{K_1(R/\xi)}{K_0(R/\xi)}\, n(R,t)\, dR. \tag{14}$$

Thus given the size distribution of clusters $n(R,t)$, the sink term ξ can be obtained by solving the equation (14).

Now when we have the expression for the flux (13), we can derive the coagulation coefficient. Summing up the fluxes for two diffusing clusters of sizes R_i and R_j we obtain

$$K_{ij} = 2\pi\,(D_i + D_j)\,\frac{(R_i + R_j)}{\xi}\,\frac{K_1((R_i + R_j)/\xi)}{K_0((R_j + R_j)/\xi)}\,. \tag{15}$$

Note that the parameter ξ is defined by (14) through the unknown size distribution function $n(R,t)$.

Thus we come to the Smoluchowski equation

$$\frac{\partial n_l(t)}{\partial t} = \frac{1}{2}\sum_{i+j=l} K_{ij} n_i(t) n_j(t) - n_l(t)\sum_{i=1}^{\infty} K_{li} n_i(t), \tag{16}$$

coupled with the equation (14); here the size l of an l-cluster is related to its radius R as $R = R_0\sqrt{l}$ where R_o is the radius of the monomer.

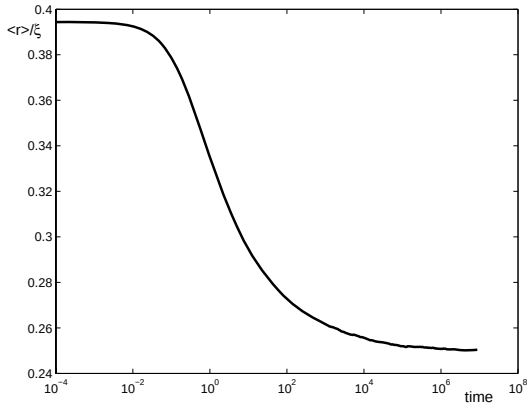

Figure 2: The quantity $\langle r\rangle/\xi$, as a function of time.

4.2 Monte Carlo algorithm

Let us describe the Monte Carlo algorithm for solving the Smoluchowski equation (16) coupled with (14).

Assume that initially, we have only monomers on the plane, the radius of the monomer being R_0, the area coverage being $q = \pi \int_0^\infty R^2\, n(R,\infty)\, dR$. As mentioned, the m-cluster of radius R consists of m monomers, and $R = R_0\sqrt{m}$. Hence, $dm = \frac{2R\, dR}{R_0^2}$. Let us denote $y = R_0/\xi$. So if we take the initial distribution as the delta-function $\delta(R - R_0)$, we get from (14):

$$y = 2q\frac{K_1(y)}{K_0(y)}$$

which can be easily solved numerically. For example, for $q = 0.1$ the solution is $y_0 \approx 0.395$. It means, that initially, the screen length ξ is given by $\xi \approx R_0/0.395$, so it is approximately 2.5 times larger than R_0.

With this value of ξ we can make our first step in the Monte Carlo method described above, till the first coagulation event which leads to the change in the distribution function. Then we calculate the new value of ξ by evaluating approximately the integral in (14) where in the integrand, the old value of ξ is taken. Calculations have shown, that this method converges very fast. Moreover, the recalculations of ξ can be made not after each coagulation, but after a number of coagulation events, when the distribution function is not changed much. In Figure 2 we show $\langle R\rangle/\xi$ as a function of time, for the coverage $q = 0.1$, and for $D = 1$.

It is clearly seen, that during the change of the size distribution, the value of $\langle R\rangle/\xi$ starts form the initial value of $\simeq 0.395$, then it is rapidly decreasing, and for large time, it approaches a steady state value of ≈ 0.25.

As mentioned above, in the literature (e.g., see [1]) the diffusion controlled coagulation kernel is often taken as $K_{ij} \simeq D_i + D_j$. Compared to this, our kernel has now a correction term, see (15).

It is interesting to understand how this correction term affects the main properties of the cluster kinetics, in particular, the mean size and the size distribution.

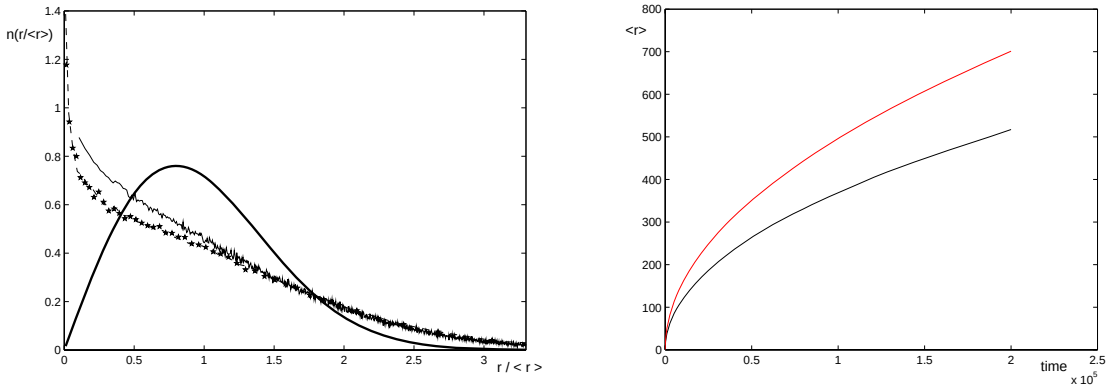

Figure 3: Left panel: The diffusion coefficient $D = 1$, the kernel with the correction term. The size spectra as functions of $r/\langle r\rangle$, for 3 different times: solid line – at a time when the mean size reached the value $\langle r\rangle = 10$; points - $\langle r\rangle = 38$, and the dash line $\langle r\rangle = 500$. For comparison, the exact solution for the kernel without the correction term is shown (bold solid line). Right panel: The average radius as a function of time: the coagulation kernel without (the upper curve) and with the correction term (lower curve).

We have made calculations for 3 types of diffusion controlled kernels: (1) $D_i = 1$, (2) $D_i = 1/i$, and (3) $D_i = a/(a+i)$, a being a constant.

Let us comment on the results, and we consider first the case $D = 1$. In Figure 3, right panel, we compare the mean cluster size: the upper curve corresponds to the kernel without correction, the lower curve is obtained for the kernel with the correction term. So it is seen that the correction term leads to a deceleration of the growth, but the asymptotics in time is the same: $\langle r\rangle \simeq t^{0.5}$.

However the correction term affects the size distribution dramatically: in the uncorrected case, the size distribution has a Gaussian-form distribution (which is known explicitly), while for the case of corrected kernel, the size distribution is a monotonically decaying function, see Figure 3, left panel. In this picture, we show the size distributions for three different time instances: solid line was obtained for a time when the mean radius was equal to 10; points: $\langle r\rangle = 38$, and the dash line: $\langle r\rangle = 500$. It is seen that the spectrum is preserved after reaching $\langle r\rangle = 38$.

For the kernel with $D_i = 1/i$ and $D = a/(a+i)$ the influence of the correction term is different: the size distributions for large times are almost the same as in the case of kernels without correction, see Figures 4 and 5, left panels. Note however that the correction terms in both these cases lead to an accelerated growth of the average size, and the asymptotics well agree with the theoretical behaviour $\langle r\rangle \simeq t^{0.25}$.

The coagulation process for $D = a/(a+i)$ with the correction term was simulated both by the MMF and SLP methods, to compare the costs in the case when the kernel is varying with time as described above. In Figure 6 we compare the costs of these methods measured in MC steps. It is seen that the gain of the new method compared to MMF is rapidly increasing in time.

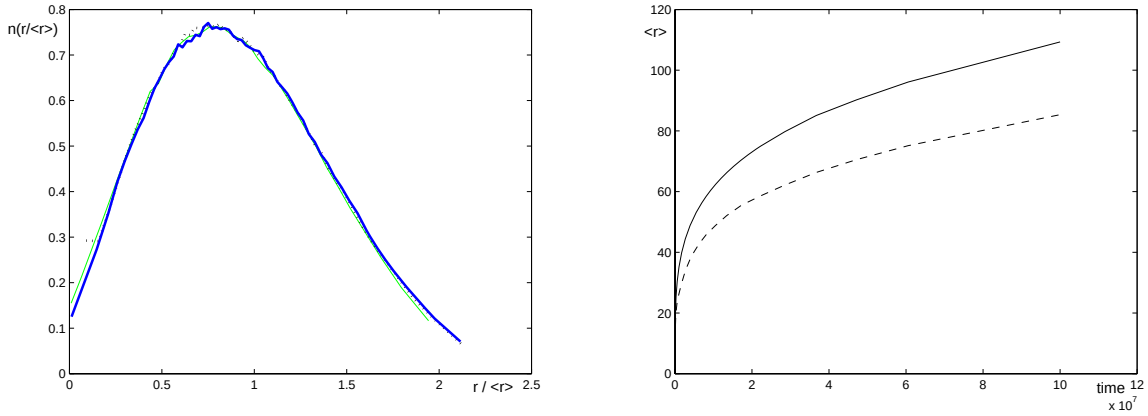

Figure 4: Left panel: The size spectra as functions of $r/\langle r\rangle$, for $D = 1/i$, without correction term (bold solid line, $\langle r\rangle = 85$), and with the correction term (solid line, $\langle r\rangle = 109$; dots, $\langle r\rangle = 11$). Right panel: The mean radius, as a function of time: the coagulation kernel without (dash line) and with the correction term (solid line).

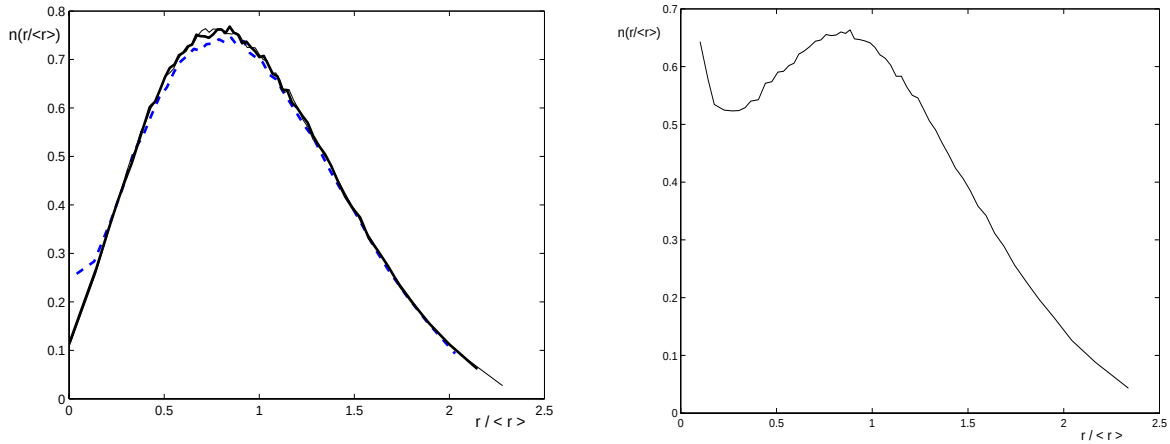

Figure 5: Left panel: The size spectra as functions of $r/\langle r\rangle$, for $D = 234/(234 + i)$, without correction term (bold solid line, $\langle r\rangle = 336$), and with the correction term (solid line - $\langle r\rangle = 456$; dash line - $\langle r\rangle = 25$). Right panel: The same as in the left panel, but for small time, when the average radius was $\langle r\rangle = 10$.

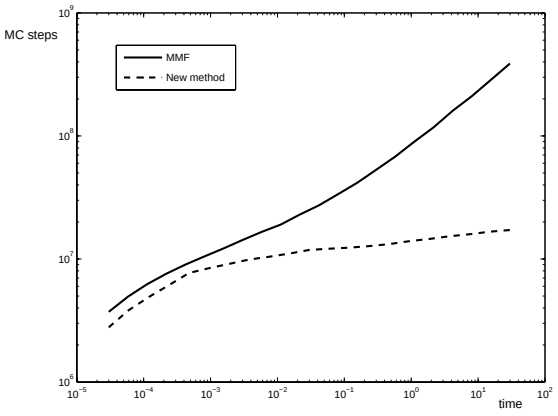

Figure 6: Comparison of the costs (in MC steps) of the MMF and the new developed method

5 Conclusion

SLP method, a new version of the Method of Majorant Frequency (MMF) for coagulation processes governed by homogeneous Smoluchowsky equations is developed. The SLP method is based on a subdivision of the set of particle pairs into classes, so that the local majorants in the classes are used to a stratified sampling to simulate the collissions with larger probabilities, so the title SLP. For sampling from discrete distributions, Walker's alias method is used. The efficiency of the new method is drastically increased compared to the conventional methods, especially when the coagulation kernel is strongly varying. The method is applied to solving a problem of islands formation on a surface due to a diffusion controlled coagulation. In this case, the coagulation kernel depends both on time, and on the solution itself. Comparison of the costs of MMF and the new method presented in Figure 6 shows that the gain of the SLP method compared to MMF rapidly increases in time.

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