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Stochastic algorithms for studying coagulation dynamics and gelation phenomena

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1. Introduction

Smoluchowski's coagulation equation [30]

$$\frac{\partial}{\partial t}\, c(t,x) = \frac{1}{2}\sum_{y=1}^{x-1} K(x-y,y)\, c(t,x-y)\, c(t,y) - \sum_{y=1}^{\infty} K(x,y)\, c(t,x)\, c(t,y)\,, \tag{1}$$

where $t \geq 0$ and $x = 1, 2, \ldots$, describes the time evolution of the average concentration of particles of a given size in some physical system. Concentration of particles of size x increases as a result of coagulation of particles of sizes $x-y$ and y. It decreases if particles of size x merge with any other particles. The intensity of the process is governed by the coagulation kernel K. The phenomenon of coagulation occurs in a wide range of applications, e.g., in astrophysics, biology, chemistry and meteorology (see the survey paper [7]).

Stochastic particle systems play an important role in the study and numerical treatment of equation (1). The standard stochastic model related to the coagulation equation is a Markov jump process where two different clusters of size x and y coagulate to a single cluster of size $x+y$ with rate $K(x,y)$. This model is called Marcus-Lushnikov process (cf. [23], [13], [22], [2]). The basic relationship between the stochastic model and the deterministic equation is given by the law of large numbers. Also qualitative properties of the coagulation equation and its generalizations have been successfully studied using the stochastic approach. We refer to [17], [15], [18], [24], [8], [25], [9] concerning recent results, and especially to [2] as an excellent review. Sufficiently fast increasing coagulation kernels lead to solutions exhibiting gelation, i.e. a loss of mass in finite time

$$t_{\mathrm{gel}} = \inf\left\{t \geq 0 :\ m_1(t) < m_1(0)\right\}, \quad \text{where} \quad m_1(t) = \sum_{x=1}^{\infty} x\, c(t,x)\,. \tag{2}$$

According to [2, Section 5.2], the general interpretation of gelation in terms of stochastic models is "perhaps the most interesting aspect of the subject".

The purpose of this paper is to study the gelation phenomenon using Monte Carlo simulations. In Section 2 we introduce two stochastic algorithms. One is based on the Marcus-Lushnikov process. The other is new and based on transfer of mass instead of concentration. In Section 3 we apply the stochastic algorithms to different kernels, and use the numerical results to discuss some conjectures concerning gelation.

2. Stochastic algorithms

Many stochastic algorithms for the coagulation equation (1) and its generalizations are based on the classical **Marcus-Lushnikov process** (cf. [13], [14], [6], [29], [12], [10], [16]). Various numerical methods for the coagulation equation are reviewed in [28], where also an extended list of references is given. Some stochastic algorithms contain an additional approximation parameter (time step), thus providing solutions to time discretized versions of the coagulation equation (1) (cf. [21], [20], [27], [26], [19]). Let the process be represented in the form

$$\big(x_1(t),\dots,x_{N(t)}(t)\big)\,,\qquad t\geq 0\,,\qquad N(0)=n\,, \tag{3}$$

where $N(t)$ denotes the variable number of particles in the system. Its jump process dynamics is given by the following algorithm.

Direct simulation algorithm (DSA)

0. Initialize the system $z=(x_1,\dots,x_n)$ according to the initial condition.

1. Given a state $z=(x_1,\dots,x_N)$ wait an exponentially distributed time, with parameter

$$\lambda(z)=\frac{1}{2n}\sum_{1\leq i\neq j\leq N}K(x_i,x_j)\,.$$

2. Choose indices $i\neq j$ according to the probabilities

$$\frac{1}{2n\,\lambda(z)}K(x_i,x_j)\,.$$

3. Replace x_i,x_j by x_i+x_j and go to **1.**

The Marcus-Lushnikov model corresponds to the "direct physical simulation" of the coagulation process. Assuming unit initial mass, functionals of the solution to equation (1) are approximated as

$$\sum_{x=1}^{\infty}\varphi(x)\,c(t,x)\;\sim\;\frac{1}{n}\sum_{i=1}^{N(t)}\varphi(x_i(t))=\sum_{x=1}^{\infty}\varphi(x)\,\frac{N_x(t)}{n}\,,$$

where $N_x(t)$ denotes the number of particles of size x.

Here we consider an **alternative stochastic model** for the treatment of the coagulation equation, which was introduced in [3], [11]. In this model mass units (instead of physical particles) are simulated by stochastic point measures, and the approximate transfer of concentrations is replaced by a transfer of mass. The dynamics of the corresponding Markov process, which has also the form (3), is given by the following algorithm.

Mass flow algorithm (MFA)

0. Initialize the system $z=(x_1,\dots,x_n)$ according to the initial condition.

1. Given a state $z=(x_1,\dots,x_N)$ wait an exponentially distributed time, with parameter

$$\lambda(z)=\frac{1}{n}\sum_{1\leq i\neq j\leq N}\frac{K(x_i,x_j)}{x_j}$$

2. Choose indices $i \neq j$ according to the probabilities

$$\frac{1}{n\,\lambda(z)}\,\frac{K(x_i,x_j)}{x_j}$$

3. Remove x_i , add $x_i + x_j$ (if $x_i + x_j \leq b_n$) and go to **1.**

This process approximates (as $n \to \infty$ and $b_n \to \infty$) a transformation of the solution to equation (1), namely $\hat{c}(t,x) := x\,c(t,x)$. Consequently, functionals of the solution are approximated as

$$\sum_{x=1}^{\infty} \varphi(x)\,c(t,x) \;\sim\; \frac{1}{n}\sum_{i=1}^{N(t)} \frac{\varphi(x_i(t))}{x_i(t)}\,, \tag{4}$$

for appropriate test functions φ and $t \geq 0$, where unit initial mass is assumed.

3. Conjectures and numerical tests

We study the problem how to determine the time evolution of the mass m_1 (cf. (2)) for general coagulation kernels using stochastic algorithms. Homogeneous kernels, i.e. kernels satisfying

$$K(Cx,Cy) \;=\; C^{\lambda}K(x,y)\,, \qquad \forall C>0\,, \tag{5}$$

are expected to be gelling if $\lambda > 1$. As test examples, we consider the class of kernels

$$K(x,y) \;=\; \frac{2\,(x\,y)^{\gamma}}{(x+y)^{\gamma}-x^{\gamma}-y^{\gamma}}\,, \qquad 1<\gamma\leq 2\,, \tag{6}$$

which are homogeneous with exponent $\lambda = \gamma$, and the class of kernels

$$K(x,y) \;=\; (x\,y)^{\alpha}\,, \qquad 0.5<\alpha\leq 1\,, \tag{7}$$

which are homogeneous with exponent $\lambda = 2\,\alpha$.

Note that the multiplicative kernel

$$K(x,y) = x\,y \tag{8}$$

is contained in both classes (6) ($\gamma = 2$) and (7) ($\alpha = 1$). This special case has been intensively studied in the framework of random graph theory (see [2, Section 4.4]). The unique solution to the coagulation equation (1) with monodisperse initial condition

$$c(0,1) = 1\,, \qquad c(0,k) = 0\,, \quad k \geq 2\,, \tag{9}$$

is explicitly known. In particular, the mass is given by

$$m_1(t) \;=\; \begin{cases} 1 & : \; 0 \leq t \leq 1\,, \\ t^{-1} & : \; 1 < t\,, \end{cases} \tag{10}$$

so that $t_{\mathrm{gel}} = 1$. Moreover, it has been established that the asymptotic behaviour of the maximal component in the DSA-system changes qualitatively at the gelation point, namely

$$M_1^{(n)}(t) \;\sim\; \begin{cases} \log n & , \text{ if } \; t<1\,, \\ n^{\frac{2}{3}} & , \text{ if } \; t=1\,, \\ n & , \text{ if } \; t>1\,. \end{cases}$$

It was shown in [5] that, for the kernel (8), the Marcus-Lushnikov process converges to a deterministic limit, which coincides with the solution *before* the gelation point, but is different from the solution *after* that point. Thus, for the kernel (8), one obtains

$$\lim_{n\to\infty} \frac{M_1^{(n)}(t)}{n} > 0\,, \qquad \forall t > t_{\text{gel}}\,, \tag{11}$$

but the property, which one might naively expect,

$$m_1(t) \;=\; 1 - \lim_{n\to\infty} \frac{M_1^{(n)}(t)}{n}\,, \qquad \forall t \geq 0\,, \tag{12}$$

does not hold.

Property (11) suggests to study the gelation problem for general coagulation kernels using the maximal component in the DSA-system. Let τ_ψ^n be the random moment at which a component of size bigger than $\psi(n)$ is formed for the first time. In [6] the convergence of τ_ψ^n for $\psi(n) = \frac{1}{2}\,n$ and various coagulation kernels was studied numerically. Correspondingly, gelation was interpreted as the emergence of a "superparticle" having mass proportional to the mass of the system. More general functions ψ have been considered in [4] and [17, Theorem 5]. A basic element of the convergence proofs for general kernels is uniqueness of the solution to the limiting equation. However this uniqueness has been established only up to the gelation point [24]. Thus, the problem of convergence after the gelation point is open for general kernels. There is **Aldous' conjecture** [2, Section 5.2] that $M_1^{(n)}(t) = o(n)$ after the gelation point, i.e. (11) does not hold, for homogeneous kernels (5) with exponent $1 < \lambda < 2$. **Spouge's conjecture** [29] says that for kernels (7) with $\alpha \in (0.5, 1)$ the mass of the gel is approximated by the maximal cluster, i.e. (12) and, in particular, (11), hold. For kernels (6) it has been proved in [1] that the moment of order γ explodes at $t = 1$, "strongly suggesting" that $t_{\text{gel}} = 1$ for all γ.

Since the new MFA-process is not mass-preserving (due to the truncation parameter b_n), one obtains a natural approximation of the mass (cf. (4)), namely **conjecture A**

$$m_1(t) \;=\; \lim_{n\to\infty} \frac{N^{(n)}(t)}{n}\,, \qquad \forall t \geq 0\,, \tag{13}$$

where $N^{(n)}(t)$ is the current particle number. Another interesting aspect of this model (for $b_n = \infty$) is the emergence of infinite clusters in finite time for gelling kernels. Our **conjecture B** is that the (random) explosion times of the stochastic system converge (as $n \to \infty$) to the gelation time. This would connect the gelation effect (a property of the limiting equation) with the explosion phenomenon of a stochastic process, thus representing the physical interpretation of gelation.

Numerical experiments have been carried out using MFA and DSA for different coagulation kernels. Both algorithms are initialized with monomers according to (9). The functionals

$$\frac{N^{(n)}(t)}{n}\,, \qquad t \geq 0\,, \tag{14}$$

for MFA (cf. (13)), and

$$1 - \frac{M_1^{(n)}(t)}{n}\,, \qquad t \geq 0\,, \tag{15}$$

for DSA (cf. (12)) are measured for different values on n. The results are averaged over a sufficiently large number of independent runs.

Figure 1 illustrates the theoretical results concerning the asymptotic behaviour of the largest cluster for DSA and the kernel (8). Corresponding numerical results for MFA show convergence of the mass approximation (14) to the analytic expression (10), thus confirming conjecture (13). Both numerical curves visually coincide with the corresponding theoretical values.

Figure 2 shows convergence of the mass approximations (14) and (15) for the kernel (6) with $\gamma = 1.5$. The limits are different, in analogy with the case (8). The MFA results support conjecture (13) as far as the existence of the limit at the right-hand side is concerned. The DSA results suggest **conjecture C** that (11) holds for the kernel (6) and all γ, contradicting Aldous' conjecture. At least, deviations from the order n are so small that they cannot be detected numerically.

Figure 3 shows convergence of the mass approximation (14) provided by MFA for the kernel (7) with $\alpha = 0.8$. As in the previous case, these results partly support conjecture (13). The corresponding results for DSA (cf. (15)) are given in Figure 4. These results do not allow us to make any suggestions concerning the controversial conjectures mentioned above. We do not see convergence even for very large n. At least, the order of the largest cluster clearly changes at the gelation point.

An interesting feature of MFA is the much better convergence behaviour (compared to DSA) after the gelation point for kernels of the form (7). Note that there is no gel-sol interaction in the mass flow algorithm, while there is such an interaction in the direct simulation algorithm. This makes us believe in conjecture (13). Note that the exponent of homogeneity (cf. (5)) varies between 1 and 2 for both classes of kernels (6) and (7), but kernels (6) are not of the order $o(x\,y)$ as $x + y \to \infty$. One might speculate that for kernels (7) the gel-sol interaction in DSA is not strong enough to be kept in the limit, but causes significant systematic error for finite particle systems, while for kernels (6) the gel-sol interaction is so strong that both algorithms converge to different limits.

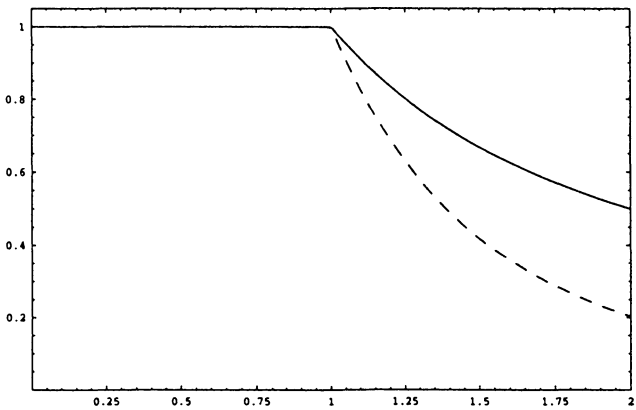

Figure 1: Mass approximation by MFA (solid line, $n = b_n = 10^5$) and DSA (dashed line, $n = 10^7$) for kernel (8).

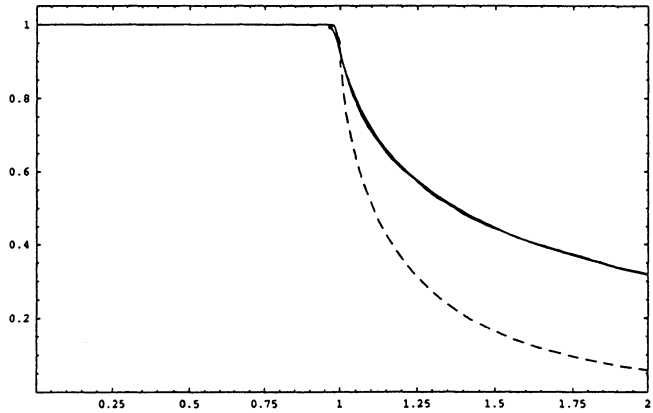

Figure 2: Mass approximation by MFA (solid lines, $n = 10^4, 10^5$, $b_n = 10^5$) and DSA (dashed lines, $n = 10^7, 10^8$) for kernel (6) with $\gamma = 1.5$.

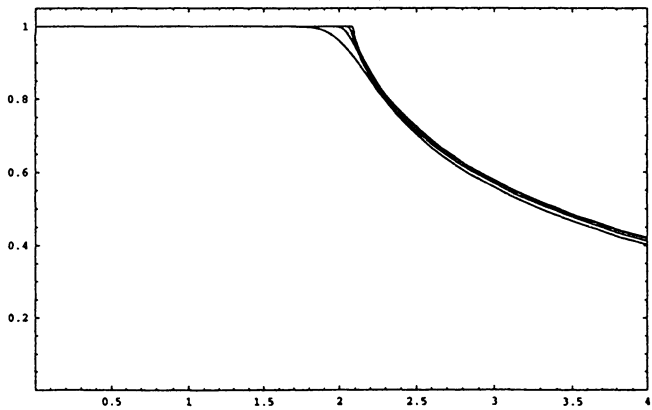

Figure 3: Mass approximation by MFA (solid lines, $n = 10^2 \to 10^5$, $b_n = 100\,n$) for kernel (7) with $\alpha = 0.8$.

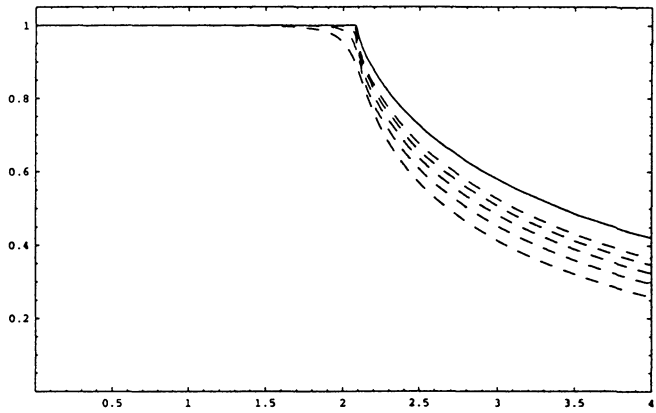

Figure 4: Mass approximation by MFA (solid line, $n = 10^5$, $b_n = 10^7$) and DSA (dashed lines, $n = 10^5 \to 10^9$) for kernel (7) with $\alpha = 0.8$.

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