A stochastic model and Monte Carlo algorithm for fluctuation-induced $H_2$ formation on the surface of interstellar dust grains

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Abstract. A stochastic algorithm for simulation of fluctuation-induced kinetics of $H_2$ formation on grain surfaces is suggested as a generalization of the technique developed in our recent studies [15] where this method was developed to describe the annihilation of spatially separate electrons and holes in a disordered semiconductor. The stochastic model is based on the spatially inhomogeneous, nonlinear integro-differential Smoluchowski equations with random source term. In this paper we derive the general system of Smoluchowski type equations for the formation of $H_2$ from two hydrogen atoms on the surface of interstellar dust grains with physisorption and chemisorption sites. We focus in this study on the spatial distribution, and numerically investigate the segregation in the case of a source with a continuous generation in time and randomly distributed in space. The stochastic particle method presented is based on a probabilistic interpretation of the underlying process as a stochastic Markov process of interacting particle system in discrete but randomly progressed time instances. The segregation is analyzed through the correlation analysis of the vector random field of concentrations which appears to be isotropic in space and stationary in time.

Keywords: semi-analytic modeling, galaxy formation

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1 Introduction

In the literature, there exist several theoretical models and methods to study the surface chemistry that occurs on interstellar dust grains under different astrophysical conditions. We mention here the following approaches: the conventional rate equation method which can be implemented using the master equation, direct Monte Carlo methods which are able to simulate the diffusive reactions on surfaces. The kinetic Monte Carlo technique in different forms has been applied in all branches of astrochemistry studies, see, e.g. [3–6, 10, 20], and seems to be the most popular in practical calculations. The moment equation approach presents a nice analytical approach, however it is much weakened by the closer assumptions [11].

The fluctuation impact on the kinetics in the interstellar chemistry has not been studied thoroughly before, in spite the fact that in chemical kinetics, the segregation has been studied by many authors, see, for instance [10] where the segregation phenomenon has been described from a general point of view in the case of a source, random in space and continuous in time. Note that the Monte Carlo methods used in studies mentioned above are of different type: they do not deal with the spatial fluctuations of the source, actually, they suggest a randomized solution of deterministic rate equations which do not govern the segregation phenomenon. In other words, to properly take into account the impact of the spatial fluctuations of the source, one needs to simulate spatially inhomogeneous reaction and diffusion processes.

Let us explain this by a simple example by considering a reaction of two types of particles, $A$ and $B$, leading to a product $P$: $A + B \rightarrow P$. The simplest kinetic approach to this reaction first considered by Smoluchowski [19] is based on the rate equations

$$dn_A/dt = -g n_A(t)n_B(t), \quad dn_B/dt = -g n_A(t)n_B(t), \quad n_A(0) = a_0, n_B(0) = b_0$$

where $g$ is the reaction rate. For diffusion-controlled reactions in $\mathbb{R}^3$, Smoluchowski obtained $g = 4\pi Dr_0$, where $r_0$ is the particle radius and $D$ is the relative diffusion coefficient. This equation can be easily solved explicitly: $n_A(t) = a_0/(1 + a_0gt)$ for $a_0 = b_0$, and $n_A(t) = a_0f_0/[b_0 \exp(f_0gt) - a_0]$ for $a_0 < b_0$, where $f_0 = b_0 - a_0$.

Such description of chemical reactions implies conditions such that the rate at which the reactants approach each other (the diffusion rate) is much larger than the rate at which they react chemically. Hence, the basic assumption underlying this reaction model is a
homogeneous spatial distribution of particles during the reaction at any time instant, i.e., the components $A$ and $B$ should be always perfectly mixed. Independent of the dimension $d$, this assumption results in solutions with a long-time asymptotics $\sim \exp(-f_0 gt)$ if $a_0 \neq b_0$, and $\sim 1/\sqrt{t}$ if $a_0 = b_0$.

In this approach, the diffusion is treated macroscopically, ignoring density fluctuations. In the absence of nonlinear interactions such as chemical reactions, the macroscopic diffusion equations govern uniform concentration distributions. Thermal fluctuations, initial density inhomogeneities, and the randomness of reaction events lead to non-uniform concentration fields and changes the solution structure drastically, in particular, the time dependence of the mean solution for asymptotically long times.

Fluctuations are responsible for the spatial correlations, and in particular, they may lead to segregation, i.e., the formation of spatially separated clusters composed entirely of particles of either type $A$ or $B$. In this paper we show by computer simulation of the reaction kinetics that the spatial inhomogeneity leads to segregation, and moreover, the segregation holds even in the stationary regime, with characteristic spatial correlations.

It was first shown by Ovchinnikov and Zeldovich [12] that in the fluctuation-induced reactions, the long-time asymptotics is $\sim t^{-d/4}$ if $a_0 = b_0$. Generally, for $a_0 = b_0$, the asymptotics $\sim t^{-d/4}$ is valid for any dimensionality $d \leq 4$, while for $d \geq 4$, $\sim t^{-1}$. This law was obtained by several authors using different arguments (see, e.g., refs. [1, 9, 12], and [15]). If the densities of the components are not equal, the asymptotics is different. For instance, if $a_0 < b_0$, $n_A \sim a_0 \exp(-\sqrt{t})$ for $d = 1$, $n_A \sim a_0 \exp\{-t/\log(t)\}$ for $d = 2$, while for $d \geq 3$, the asymptotic law again coincides with the homogeneous case: $n_A \sim a_0 \exp(-t)$ [1].

This difference between the homogeneous and fluctuation-limited kinetics holds regardless of the type of reaction between the particles. It applies, for instance, to the Smoluchowski coagulation equation. Coagulation, or coalescence, is a process by which two particles collide and adhere, or coagulate. There are many different mechanisms that bring two particles to each other: molecular diffusion, gravitational sedimentation, free molecule collisions, turbulent motion of the host gas, acoustic waves, density, concentration and temperature gradients, electric charges, etc. (see, e.g., refs. [21] and [7]). Let us consider the Smoluchowski equation governing the coagulation of particles of different type having different masses $m_i$: (e.g., see [17]):

$$\frac{\partial n(m, t)}{\partial t} = \frac{1}{2} \int_0^{m_1} \cdots \int_0^{m_s} R(u, m - u)n(m - u, t)n(u, t)du$$

$$- n(m, t) \int_0^{\infty} \cdots \int_0^{\infty} R(u, m)n(u, t)du. \tag{1.1}$$

Here, $m_i$ is the mass of the $i$-th component in a particle, and $m$ is a vector of compositions $(m_1, \ldots, m_s)$, where $s$ is the total number of components; $n(m, t)dm$ is the number of particles having mass of component $i$ in the range $[m_i, m_i + dm_i]$ at time $t$, and $R(u, m) = R(m, u)$ is the binary coagulation coefficient.

The numerical solution of the inhomogeneous Smoluchowski equations is a highly challenging problem even for only a few particle types. We deal in this paper with three particle types (physiosorbed H ($H_p$, chemisorbed H ($H_C$), and molecular hydrogen $H_2$). We construct the processes using a grid space treatment model where the physi- and chemisorption sites are presampled (uniformly and independently on the grid), thus these two types of sites are not spatially coincident.
The main difficulties in the problem we solve, can be formulated as follows:

1. The major difficulty arises from the inhomogeneity in space.
2. The second difficulty of our problem is caused by the low and singular particle densities.
3. Third, we are interested in the particle kinetics for very long times, to reach and study a quasi-stationary regime.
4. Finally, we deal with stochastic source term for physisorbed H, and we have to take the average over a reach ensemble of source realizations. In addition, other parameters of the governing equations may fluctuate randomly and have a large impact on the kinetics of the processes studied.

Conventional numerical methods are not applicable for handling problems of this kind, and we therefore use the Monte Carlo methods we have developed in our recent papers [15] and [16] which were based on the approach previously suggested in our publications refs. [8, 14], and [18].

The main idea of Monte Carlo methods for solving the spatially homogeneous Smoluchowski equation lies in the probabilistic interpretation of the evolution of the interacting particles as a Markov chain (see, e.g., ref. [8]). In refs. [7] and [18], we have applied the Monte Carlo technique to the inhomogeneous Smoluchowski equation. In this paper, we consider the general inhomogeneous case with diffusion. Note that the direct Monte Carlo simulation of the particle interactions and diffusion jumps on a grid is computationally expensive, because one has to consider a huge number of jumps per one particle interaction. In [15] we suggest a new Monte Carlo method for this case, introducing “long diffusion jumps” which accelerate the simulation process significantly. However this approach being very efficient for calculating most important statistical characteristics of the solution, is not well adjusted when there is a need to analyze the spatial distribution, in particular, the segregation process. Therefore, we use a detailed Monte Carlo scheme where in each random time step, all processes including the diffusion jumps are directly simulated on a grid with presampled physi- and chemisorption sides.

It should be stressed, that the spatial correlations are of our interest not only because they lead to segregation phenomena, but also that the correlations may have a dramatic impact on the average concentrations and hence on the rate formation of $\langle H_2 \rangle$. The spatial correlations are calculated in our model by averaging over an ensemble of statistically independent runs of the model. This differs from the kinetic MC models described in the literature (e.g., see [3, 5, 6, 20]). This can be clearly seen from the representation given by (2.3) below: taking the mathematical expectation, spatial auto-correlation functions of $H_P$ and $H_C$ appear under the integrals in the right-hand side, as well as the cross-correlations between $H_P$ and $H_C$. This is a crucial issue when studying fluctuating spatially inhomogeneous reactions. Indeed, taking the expectation of the equation (2.3) yields for $\langle H_2(r;t) \rangle$:

$$\frac{\partial \langle H_2(r;t) \rangle}{\partial t} = \int \alpha_{PP}(|x|) \text{Corr}_{PP}(x;t) dx + \int \alpha_{PC}(|x|) \text{Corr}_{CP}(x;t) dx$$

$$+ \int \alpha_{CP}(|x|) \text{Corr}_{PC}(x;t) dx + \int \alpha_{CC}(|x|) \text{Corr}_{CC}(x;t) dx$$

(1.2)

where $\text{Corr}_{PP}(x;t), \text{Corr}_{CC}(x;t)$ are auto-correlations and $\text{Corr}_{CP}(x;t)$ is the cross-correlation of $H_P$ and $H_C$ concentrations. This clearly shows that the correlations have considerable impact on the yield of $\langle H_2(r;t) \rangle$. 


Thus the main difference of the new model and existing Monte Carlo algorithms can be shortly explained as follows. Being all based on the kinetic Monte Carlo scheme, the existing methods do not treat the chemical reactions as fluctuation-controlled processes. In our method, we consider the spatial concentration fluctuations, so to obtain the mean concentrations, we have to average the results over a set of independent realizations of the processes studied. It should be stressed that even small spatial correlations of the deposited atoms may lead to large correlations of the steady-state concentrations. This phenomena (e.g., well described in the paper [10]) is not well understood by professional practitioners of chemical engineering. Indeed, in 3D, this phenomena is negligible, while in 2D it always exists, and the segregation index is completely determined by the ratio \( D \ast L^2/B \) where \( D \) is the diffusion coefficient, \( L \) is the correlation length, and \( B \) is the reaction rate. Thus the chemical segregation might arise as a consequence of the interplay of the three counteracting mechanisms: (1) Diffusion mixes the species, while (2) the reaction annihilates \( (H_P + H_C = H_2) \) the mixed regions, thus favoring spatially separated regions. And third, (3) the sources tend to create spatially nonuniform patches on a scale determined by the density of sources. The latter stochastic mechanism is simulated in our algorithm exactly.

2 The inhomogeneous nonlinear Smoluchowski equation based model

We assume that hydrogen atoms absorbed on a grain site can move to another site via tunneling or thermal diffusion. We define \( H_P, H_C \) and \( H_2 \) as the physisorbed, chemisorbed H and molecular hydrogen concentrations, respectively. We consider the granular surfaces to be square lattices with four nearest neighbor sites, as on fcc[100] plane. In this paper we use a model where the physi- and chemisorption sites are presampled (uniformly and independently on the grid), thus the sites are not spatially coincident. We remark that due to the stochastic nature of the model, it is also possible to sample the relevant sites not in advance, but on demand, when tracking the random trajectory of the atom, since the system is ergodic, and our result is obtained by averaging over a family of independent realizations. This approach dramatically reduces the memory and computer time needed, and makes it possible to simulate the \( H_2 \) formation of very large grain surfaces. Numerical comparison of these two models show a full agreement. But to make the presentation not too complicated, we present the results only for the grid space treatment model.

Different energy barriers occur between different pairs of sites which can be sites in which H atoms are weakly bound, due to physisorption (weak Van der Waals interaction), or strongly covalent bound, due to chemisorption. We assume the number of physisorbed and chemisorbed sites on a grain to be identical. We denote by \( D_P \) the diffusion coefficient for the physisorption, and by \( D_C \) the chemisorption diffusion coefficient. The recombination of spatially separate sites distributed in a grain \( G \) due to tunneling from a physisorption to physisorption site is defined by the rate \( \alpha_{PP}(r) \), from a chemisorption to physisorption site it is defined by \( \alpha_{CP}(r) \). Analogously, the tunneling from a chemisorption to chemisorption site is defined by the rate \( \alpha_{CC}(r) \), from a physisorption to chemisorption site is defined by the rate \( \alpha_{PC}(r) \). These tunneling coefficients have the form \( \alpha_{ij}(r) = \alpha_{ij}^0 \exp(-|x|/a_{ij}) \) where \( |x| \) is the distance between the two interacting sites. Here \( a_{ij} \) is the characteristic distance of tunneling, and \( \alpha_{ij}^0 \) (ij=P,C) are the frequencies of the relevant events which are described in details in [6], see also [2]. Note that the desorption of physi- and chemisorption atoms are taken into account by the terms \( W_{H_P} \) and \( W_{H_C} \) below. There is no desorption term in the
equation for $H_2$ because all of the produced molecules $H_2$ are desorbed immediately. Thus the yield of $\langle H_2 \rangle$ is calculated.

The source $F(r)$ is the accretion rate. In this study we assume that $F(r)$ is a spatial random field, and in simplest case we use the Poissonian distribution.

Altogether, the concentrations $H_P(r,t)$ and $H_C(r,t)$ are governed by the following system of two coupled nonlinear Smoluchowski equation

$$
\frac{\partial H_P(r;t)}{\partial t} = D_P(r) \Delta H_P(r;t) - \alpha_{PC} H_P - H_P(r;t) \int \alpha_{PC}(|x|) H_P(r+x;t) dx
+ \alpha_{CP} H_C - H_P(r;t) \int \alpha_{CP}(|x|) H_C(r+x;t) dx - W_{HP} H_P + F(r),
$$

(2.1)

$$
\frac{\partial H_C(r;t)}{\partial t} = D_C(r) \Delta H_C(r;t) - \alpha_{CP} H_C - H_C(r;t) \int \alpha_{CC}(|x|) H_C(r+x;t) dx
+ \alpha_{PC} H_P - H_C(r;t) \int \alpha_{PC}(|x|) H_P(r+x;t) dx - W_{HC} H_C.
$$

(2.2)

Without loss of generality, we assume that the total initial concentrations of $H_P$ and of $H_C$ are equal. At the initial time $t = 0$, the concentrations $H_P$ and $H_C$ are zero.

Since the source $F$ is a random field, so are the concentrations $H_P$ and $H_C$. Therefore, the experimentally measured is the mean concentration of the molecules $H_2$. The kinetics of $H_2$ concentration reads

$$
\frac{\partial H_2(r;t)}{\partial t} = H_P(r;t) \int \alpha_{PC}(|x|) H_P(r+x;t) dx + H_P(r;t) \int \alpha_{PC}(|x|) H_C(r+x;t) dx
+ H_C(r;t) \int \alpha_{CP}(|x|) H_P(r+x;t) dx + H_C(r;t) \int \alpha_{CC}(|x|) H_C(r+x;t) dx.
$$

(2.3)

Here is no desorption term in the equation for $H_2$ because all of the produced molecules $H_2$ are desorbed immediately (e.g. see the formula (17) and the relevant comments in [6]).

We are interested both in kinetics and the quasi-steady state which is reached in which the total mean surface population of $H$ atoms fluctuates around a constant value. After the steady-state has been reached the $H_2$ formation efficiency is then defined by the ratio of the means:

$$
\eta = \frac{1}{\langle f(G) d\mathbf{r} \rangle} \langle 2H_2(r) d\mathbf{r} \rangle.
$$

(2.4)

where the angle brackets stand for the ensemble average generated by the random source $F$.

3 Monte Carlo algorithms

The equations (2.1)–(2.2) have the structure of spatially inhomogeneous Smoluchowski coagulation equations, as mentioned in the introduction. The Smoluchowski equations can be interpreted probabilistically as an equation generated by Markov chains describing the evolution of pairwise interacting particle system. In ref. [7], we developed a Monte Carlo algorithm for inhomogeneous Smoluchowski equation, which we adapt in [15]. Here it will be used to solve eqs. (2.1)–(2.2) for the two-dimensional case $d = 2$, with the focus on the segregation problem.
3.1 Recombinations by tunneling, in the absence of diffusion

For simplicity, let us first consider the algorithm for the case when there is no diffusion. The direct simulation assumes that the process of interactions is pairwise and Markovian, i.e., having made a time step, the next time step is simulated independently. The interacting pair is sampled according to the kernel of the equation $B = B_0 \exp(-|x|/a)$ as described below.

The process is simulated in a square grid box with size $L \times L$ and periodic boundary conditions.

In the first step, we sample between the following possible events: (i) formation of $H_2$ by tunneling from $H_P$ to $H_P$, (ii) formation of $H_2$ by tunneling from $H_P$ to $H_C$, (iii) formation of $H_2$ by tunneling from $H_C$ to $H_C$, and (iv) formation of $H_2$ by tunneling from $H_C$ to $H_P$. The processes are described by the relevant probabilities $\alpha_{ij}(r) = \alpha_{ij}^0 \exp(-|x|/a_{ij})$. Thus, the simulation algorithm in the absence of diffusion can be described as follows.

(i) Put $t = 0$, and sample $n = n_0$ atoms $H_P$ and $p = n_0$ atoms $H_C$ at random, independently and uniformly from the relevant sets of physi- and chemisorption sites.

(ii) Sample one of the possible events: (i) $H_P + H_P$, (ii) $H_P + H_C$, (iii) $H_C + H_C$ and (iv) $H_C + H_P$. To do this, first calculate the majorant frequencies for the four events:

\[
\lambda_1 = \frac{n(n-1)}{2} \alpha_{PP}^0 \exp \left\{ - \frac{r_{pp,\text{min}}}{a_{PP}} \right\},
\]

\[
\lambda_2 = np \alpha_{PC}^0 \exp \left\{ - \frac{r_{np,\text{min}}}{a_{PC}} \right\},
\]

\[
\lambda_3 = np \alpha_{CP}^0 \exp \left\{ - \frac{r_{np,\text{min}}}{a_{CP}} \right\},
\]

\[
\lambda_4 = \frac{p(p-1)}{2} \alpha_{CC}^0 \exp \left\{ - \frac{r_{pp,\text{min}}}{a_{CC}} \right\},
\]

where $r_{np,\text{min}}$ is the minimal of all possible distances between $n$ $H_P$ atoms and $p$ $H_C$ atoms in the box, and analogously for other cases. From these frequencies, calculate the probabilities $p_1, p_2, p_3, p_4$ of the events (i), (ii), (iii) and (iv), respectively: $p_1 = \lambda_1/\lambda$, $p_2 = \lambda_2/\lambda$, $p_3 = \lambda_3/\lambda$ and $p_4 = 1 - p_1 - p_2 - p_3$, where $\lambda = \lambda_1 + \lambda_2 + \lambda_3 + \lambda_4$.

(iii) From the probabilities $p_1, p_2, p_3, p_4$, sample the event $k = i, ii, iii, iv$, calculate the time increment as $\Delta t = -\log(\text{rand})/\lambda$, and calculate $t := t + \Delta t$.

(iv) For the sampled event $k(= i, ii, iii, iv)$, choose uniformly the relevant interacting pair, and check if the interaction takes place. For instance, if $k = ii$, i.e., the sampled event happens to be recombination $H_P + H_C$, calculate $P_{np} = \exp \left\{ - \frac{r_{pp,\text{min}}}{a_{np}} \right\}$. If $\text{rand} < P_{np}$, then the event occurs. Hence, recalculate $n := n - 1$ and $p := p - 1$, and go back to step 2. Otherwise, nothing happens, the probabilities $p_1, p_2, p_3, p_4$ remain the same, and so return to step 3. Here $r$ is the distance between the sampled interacting pair. For the case $k = i$, put $n := n - 2$. If the concentrations $n$ and $p$ are calculated at some prescribed time instances $t_m, m = 1, \ldots, M$, just score the values $n(t_m), p(t_m)$, $m = 1, \ldots, M$. To calculate the concentration of $H_2$, say, at a time $t$ from the interval $t \in [t_1, t_2]$, count $M$, the number of all recombinations which have occurred during this time interval, and take the approximation $I(t) \approx M$.

(v) To carry out the average, run the steps 1–4 independently, say, $\nu$ times, with $\nu$ being a sufficiently large number, and take the arithmetic mean.
Note that there is no need to recalculate the value $r_{\text{min}}$ after each tunneling: this should be done only if the pair with $r_{\text{min}}$ reacts.

3.2 Recombination in the presence of diffusion

In the general case when the atoms $H_P$ and $H_C$ not only recombine, but also diffuse, the algorithm becomes more sophisticated. Usually, we would consider diffusion to occur by microscopic random jumps according to the law $dl = \omega \sqrt{D dt}$, where $dl$ is the length of the random jump, $\omega$ is a random (isotropic) direction, and $D$ is the diffusion coefficient. However, since the time between individual recombination events may be very large compared to $dt$, a huge number of diffusion jumps would be required to simulate the recombination dynamics.

To accelerate this algorithm, we have suggested in [15] a Random Walk on Spheres based algorithm (more details about the Random Walk on Spheres method can be found in ref. [13]). The idea behind this method is simple. Around each diffusing atom, we construct a disk of maximal radius which does not contain any atom $H_P$ or $H_C$. We then simulate the random exit times $\tau_k$ of the atom from these disks. We chose the atom which has a minimal exit time, and let this atom jump out of the disk, so that the new random position of the atom is uniformly distributed on the boundary of this disk. The distribution of the exit time is known (e.g., see [15], and we are thus able to simulate the random time $dt$ according to this distribution, giving us the time $t := t + dt$.

This method has shown high efficiency for calculation of the intensity, as reported in [15]. For our purpose however this approach cannot be directly applied: for viewing at the aggregation process where clusters of $H_P$ atoms are separated by the clusters of $H_C$ atoms, we need to simulate the process step by step, with sufficiently small time intervals. Therefore, we use again the grid space treatment model, and the atoms were diffusing over the grid with the frequency $\lambda_5 = D_n$ for $H_P$, and $\lambda_6 = D_p$ for $H_C$.

The general code described above remains the same. We have only to sample an additional event that the atom $H_P$ makes a jump with frequency $\lambda_5$, and the atom $H_C$ makes a jump with frequency $\lambda_6$. Then, taking $\lambda_5$ and $\lambda_6$ as described above, put $\lambda = \sum_{i=1}^{6} \lambda_i$, and calculate the probabilities as $p_i = \lambda_i / \lambda$, $i = 1, \ldots, 6$.

Analogously the resorption and exchange of $H_C$ and $H_P$ positions are simulated, using the rates $W_{H_P}$, $W_{H_C}$, and $\alpha_{PC}$, $\alpha_{CP}$, respectively, which introduces four more events. Finally, the event of appearance of a new $H_P$ atom is simulated according to the accretion rate, or flux $F$, of $H$ atoms onto the surface of a dust grain. Thus in total we have 11 events to be sampled at each time step.

4 Simulation results

As mentioned in the introduction, inhomogeneous fluctuations lead to the formation of clusters. The clustering slows down the reaction considerably, because only particles near the boundary of the clusters are likely to react, while particles inside the cluster have to diffuse to the boundary before they have a chance to react with a particle of the other type. In other words, fluctuations induce the formation of a mosaic of continuously growing domains which contain only one of the two components, $H_P$ or $H_C$.

Our simulations are adapted to take place on a spatial and temporal scale comparable to that for the surface of interstellar dust grains, given in [6] and [2]. In figure 1 we show 6 samples of random concentration fields of $H_P$ and $H_C$ when the system reaches a stochastically stationary regime. The segregation phenomenon is clearly seen: large clusters of $H_P$ and $H_C$ are negatively correlated, and should be taken into account when evaluating the concentration of
Figure 1. Six samples of \( \text{H}_P \) and \( \text{H}_C \) atoms during the stochastically stationary regime on a grain of radius 0.1 \( \mu \text{m} \). It is seen, that a segregation is formed with a characteristic distance between large clusters of \( \text{H}_P \) (green) and \( \text{H}_C \) (blue) atoms.
the molecular hydrogen from the equation (2.3). Without this correction, the model would much overestimate the efficiency \( \eta \) given by (2.4). The evaluation of \( \eta \) in the framework of this model will be done in the forthcoming paper.

Important reason for the deviations from the results known from the literature, can be the spatial correlations, i.e., the segregation: this phenomenon can drastically change the mean value of the concentrations. In the models applied before, no spatial fluctuations have been taken into account. It should be stressed mention that we do not claim in this paper that the results obtained for the concentrations are closer to real physical values; the statement is that segregation is clearly seen, and that the spatial correlations may have a large impact on the mean concentrations. The figures in the paper show only some samples, and from these samples it is not possible to predict how large are the average concentrations. But to make accurate comparisons, there is a need to collect and choose carefully all the necessary rates of reactions, and the next publication will be dealing with this issue.

5 Summary and conclusion

Stochastic model and Monte Carlo simulation algorithm are constructed for solving a non-linear system of inhomogeneous 2D Smuluchowski equations with random source term for simulation of \( \text{H}_2 \) formation on grain surfaces. The general system of inhomogeneous Smolu-
chowski type equations is used to govern the formation of \( \text{H}_2 \) from two hydrogen atoms on the surface of interstellar dust grains with physisorption and chemisorption sites. Both tunneling and diffusion mechanisms are taken into account. We focus in this study on the spatial distribution, and numerically investigate the segregation in the case of a source with a continuous generation in time and randomly distributed in space. The stochastic particle method presented is based on a probabilistic interpretation of the underlying process as a stochastic Markov process of interacting particle system in discrete but randomly progressed time instances. The segregation is analyzed through the correlation analysis of the vector random field of concentrations which appears to be isotropic in space and stationary in time. Note that the suggested model can be easily extended to more general situations, in particular, additional capture centers may be introduced in the system where the \( \text{HP} \) and \( \text{HC} \) may recombine without giving a contribution to the molecular hydrogen. This model will be presented in the forthcoming paper.

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References

[1] M. Bramson and J.L. Lebowitz, *Asymptotic behavior of densities for two-particle annihilating random walks*, *J. Stat. Phys.* **62** (1991) 297.

[2] S. Cazaux, P. Caselli, A.G. G.M. Tielens, J. Le Bourlot and M.C. Walmsley, *Molecular hydrogen formation on grain surfaces*, *J. Phys. Conf. Ser.* **6** (2005) 155 [astro-ph/0502291] [insPIRE].

[3] Q. Chang, H.M. Cuppen and E. Herbst, *Gas-grain chemistry in cold interstellar cloud cores with a microscopic Monte Carlo approach to surface chemistry*, *Astron. Astrophys.* **469** (2007) 973 [arXiv:0704.2704] [insPIRE].
[4] S.B. Charnley, *Stochastic astrochemical kinetics*, *Astrophys. J.* **509** (1998) L121.

[5] H.M. Cuppen, L.J. Karssemeijer and T. Lamberts, *The kinetic Monte Carlo method as a way to solve the master equation for interstellar grain chemistry*, *Chem. Rev.* **113** (2013) 8840.

[6] W. Iqbal, K. Acharyya and E. Herbst, *Kinetic Monte Carlo studies of H₂ formation on grain surfaces over a wide temperature range*, *Astrophys. J.* **751** (2012) 58.

[7] A.A. Kolodko and K.K. Sabelfeld, *Stochastic Lagrangian model for spatially inhomogeneous Smoluchowski equation governing coagulating and diffusing particles*, *Monte Carlo Meth. Appl.* **7** (2001) 223.

[8] A. Kolodko, K. Sabelfeld and W. Wagner, *A stochastic method for solving Smoluchowski’s coagulation equation*, *Math. Comput. Simulat.* **49** (1999) 57.

[9] E. Kotomin and V. Kuzovkov, *Modern aspects of diffusion-controlled reactions. Cooperative phenomena in bimolecular processes*, in *Chemical Kinetics Series* **34**, Elsevier, Amsterdam, Netherlands (1996), pg. 612.

[10] K. Lindenberg, B.J. West and R. Kopelman, *Steady-State Segregation in Diffusion-Limited Reactions*, *Phys. Rev. Lett.* **60** (1988) 1777.

[11] A. Lipshtat and O. Biham, *Moment equations for chemical reactions on interstellar dust grains*, *Astron. Astrophys.* **400** (2003) 585 [astro-ph/0212200] [SPIN].

[12] A.A. Ovchinnikov and Ya.B. Zeldovich, *Role of density fluctuations in bimolecular reaction kinetics*, *Chem. Phys.* **28** (1978) 215.

[13] K.K. Sabelfeld, *Monte Carlo methods in boundary value problems*, Springer Verlag, New York-Heidelberg-Berlin, (1991).

[14] K.K. Sabelfeld, S.V. Rogasinsky, A.A. Kolodko and A.I. Levykin, *Stochastic algorithms for solving Smoluchovskii coagulation equation and applications to aerosol growth simulation*, *Monte Carlo Meth. Appl.* **2** (1996) 41.

[15] K.K. Sabelfeld, O. Brandt and V.M. Kaganer, *Stochastic model for the fluctuation-limited reaction-diffusion kinetics in inhomogeneous media based on the nonlinear Smoluchowski equations*, *J. Math. Chem.* **53** (2015) 651.

[16] K.K. Sabelfeld, A.I. Levykin and A.E. Kireeva, *Stochastic simulation of fluctuation-induced reaction-diffusion kinetics governed by Smoluchowski equations*, *Monte Carlo Meth. Appl.* **21** (2015) 33.

[17] K.K. Sabelfeld, *Stochastic models for coagulation of aerosol particles in intermittent turbulent flows*, *Math. Comput. Simulat.* **47** (1998) 85.

[18] K.K. Sabelfeld and A.A. Kolodko, *Stochastic Lagrangian models and algorithms for spatially inhomogeneous Smoluchowski equation*, *Math. Comput. Simulat.* **61** (2003) 115.

[19] M. Smoluchowski, *Drei Vorträge über Diffusion, Brownsche Molekularbewegung und Koagulation von Kolloidteilchen*, *Physik Z.* **17** (1916) 557–585.

[20] A.I. Vasyunin, D.A. Semenov, D.S. Wiebe and T. Henning, *A Unified Monte Carlo Treatment of Gas-Grain Chemistry for Large Reaction Networks. I. Testing Validity of Rate Equations in Molecular Clouds*, *Astrophys. J.* **691** (2009) 1459 [arXiv:0810.1591] [SPIN].

[21] M.M.R. Williams and S.K. Loyalka. *Aerosol Science: Theory and Practice*, Pergamon, New York, U.S.A. (1991).