Efficient simulations of gas-grain chemistry in interstellar clouds

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Abstract

Chemical reactions on dust grains are of crucial importance in interstellar chemistry because they produce molecular hydrogen and various organic molecules. Due to the submicron size of the grains and the low flux, the surface populations of reactive species are small and strongly fluctuate. Under these conditions rate equations fail and the master equation is needed for modeling these reactions. However, the number of equations in the master equation grows exponentially with the number of reactive species, severely limiting its feasibility. Here we present a method which dramatically reduces the number of equations, thus enabling the incorporation of the master equation in models of interstellar chemistry.

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The chemistry of interstellar clouds consists of reactions taking place in the gas phase as well as on the surfaces of dust grains. Surface reactions include the formation of molecular hydrogen and reaction networks producing various organic molecules. The simulations of grain-surface chemistry are typically done using rate equation models. These models consist of coupled ordinary differential equations that provide the time derivatives of the populations of the reactive species on the grains. Rate equations are highly efficient for the simulation of reactions on macroscopic surfaces. However, in the limit of small grains under low flux, rate equations fail because they ignore the discrete nature of the populations of reactive species and their fluctuations.

Recently, a master equation approach for the simulation of reaction networks on small grains was proposed. It takes into account the discreteness and fluctuations in the surface populations of reactive species and provides accurate results for the reaction rates. For example, in the case of hydrogen recombination, its dynamical variables are the probabilities $P(N)$ that there are $N$ hydrogen atoms on a grain. The time derivatives $\dot{P}(N)$, $N = 0, 1, 2, \ldots$, are expressed in terms of the adsorption, reaction and desorption terms. The master equation was applied to the study of reaction networks involving multiple species that appear in models of interstellar chemistry. The master equation can be solved either by direct integration or by using a Monte Carlo (MC) method. A significant advantage of direct integration over the MC approach is that the equations can be easily coupled to the rate equations of gas-phase chemistry. However, the number of coupled equations increases exponentially with the number of reactive species, making direct integration infeasible for complex reaction networks of multiple species.

In this paper we introduce the multi-plane method, in which the number of equations is dramatically reduced, thus enabling the incorporation of the master equation in models of interstellar chemistry. The multi-plane method is tested by comparing its results to those obtained from the complete master equation set, showing excellent agreement. To demonstrate the method we consider a reaction network that involves three reactive species: H and O atoms and OH molecules. For simplicity we denote the reactive species by $X_1 = \text{H}$, $X_2 = \text{O}$, $X_3 = \text{OH}$, and the resulting non-reactive species by $X_4 = \text{H}_2$, $X_5 = \text{O}_2$, $X_6 = \text{H}_2\text{O}$. The reactions that take place in this network include $\text{H} + \text{O} \rightarrow \text{OH}$ ($X_1 + X_2 \rightarrow X_3$), $\text{H} + \text{H} \rightarrow \text{H}_2$ ($X_1 + X_1 \rightarrow X_4$), $\text{O} + \text{O} \rightarrow \text{O}_2$ ($X_2 + X_2 \rightarrow X_5$), and $\text{H} + \text{OH} \rightarrow \text{H}_2\text{O}$ ($X_1 + X_3 \rightarrow X_6$).
Consider a small spherical grain of diameter $d$, exposed to fluxes of H and O atoms and OH molecules. The cross-section of the grain is $\sigma = \pi d^2 / 4$ and its surface area is $\pi d^2$. The density of adsorption sites on the surface is denoted by $s$ (sites $\text{cm}^{-2}$). Thus, the number of adsorption sites on the grain is $S = \pi d^2 s$. The desorption rates of atomic and molecular species on the grain are given by $W_i = \nu \cdot \exp[-E_1(i)/k_B T]$, where $\nu$ is the attempt rate (standardly taken to be $10^{12} \text{ s}^{-1}$), $E_1(i)$ is the activation energy barrier for desorption of specie $X_i$ and $T$ (K) is the surface temperature. The hopping rate of adsorbed atoms between adjacent sites on the surface is $a_i = \nu \cdot \exp[-E_0(i)/k_B T]$, where $E_0(i)$ is the activation energy barrier for hopping of $X_i$ atoms (or molecules). Here we assume that diffusion occurs only by thermal hopping, in agreement with experimental results [19]. For small grains, it is convenient to replace the hopping rate $a_i$ (hops s$^{-1}$) by the sweeping rate $A_i = a_i / S$, which is approximately the inverse of the time it takes for an $X_i$ atom to visit nearly all the adsorption sites on the grain surface (up to a logarithmic correction [20]).

In the reaction network described above, the dynamical variables of the master equation are the probabilities $P(N_1, N_2, N_3)$ of having a population that includes $N_i$ atoms of specie $X_i$ on the grain. Only the reactive species are included in the master equation, from which the production rates of the non-reactive species can be obtained. The master equation for the H, O and OH system takes the form

$$
\dot{P}(N_1, N_2, N_3) = \sum_{i=1}^{3} F_i [P(\ldots, N_i - 1, \ldots) - P(N_1, N_2, N_3)] \\
+ \sum_{i=1}^{3} W_i [(N_i + 1)P(\ldots, N_i + 1, \ldots) - N_i P(N_1, N_2, N_3)] \\
+ \sum_{i=1}^{2} A_i [(N_i + 2)(N_i + 1)P(\ldots, N_i + 2, \ldots) - N_i(N_i - 1)P(N_1, N_2, N_3)] \\
+ (A_1 + A_2) [(N_1 + 1)(N_2 + 1)P(N_1 + 1, N_2 + 1, N_3 - 1) - N_1 N_2 P(N_1, N_2, N_3)] \\
+ (A_1 + A_3) [(N_1 + 1)(N_3 + 1)P(N_1 + 1, N_2, N_3 + 1) - N_1 N_3 P(N_1, N_2, N_3)].
$$

(1)

The terms in the first sum describe the incoming flux, where $F_i$ (atoms s$^{-1}$) is the flux per grain of the specie $X_i$. The probability $P(\ldots, N_i, \ldots)$ increases due to adsorption of an $X_i$ atom on grains that already have $N_i - 1$ such atoms on their surfaces, and decreases due to adsorption on grains that have $N_i$ atoms. Similarly, the second sum describes the effect of desorption. The third sum describes the effect of diffusion mediated reactions between two atoms of the same specie and the last two terms account for reactions between different
species. Each reaction rate is proportional to the number of pairs of atoms of the two species involved, and to the sum of their sweeping rates. The average population size of the $X_i$ specie on the grain is $\langle N_i \rangle = \sum_{N_1,N_2,N_3} N_i P(N_1,N_2,N_3)$, where $N_i = 0,1,2,\ldots$, and $i = 1, 2$ or $3$. The production rate per grain $R(X_k)$ (molecules s$^{-1}$) of $X_k$ molecules produced by the reaction $X_i + X_j \to X_k$ is given by $R(X_k) = (A_i + A_j)\langle N_i N_j \rangle$, or by $R(X_k) = A_i \langle N_i(N_i-1) \rangle$ in case that $i = j$.

In numerical simulations the master equation must be truncated in order to keep the number of equations finite. A convenient way to achieve this is to assign upper cutoffs $N_i^{\text{max}}$, $i = 1, \ldots, J$ on the population sizes, where $J$ is the number of reactive species. The number of coupled equations is thus

$$N_E = \prod_{i=1}^{J}(N_i^{\text{max}} + 1).$$

The truncated master equation is valid if the probability to have larger populations beyond the cutoffs is vanishingly small. However, the number of equations, $N_E$, grows exponentially as the number of reactive species increases. This severely limits the applicability of the master equation to interstellar chemistry. To exemplify the magnitude of this difficulty, note that the upper cutoffs must satisfy $N_i^{\text{max}} \geq 1$ for the $J'$ species that do not react with themselves and $N_i^{\text{max}} \geq 2$ for the $J''$ species that do react with themselves. Therefore, $N_E \geq 2^{J'}3^{J''}$ [10].

The chemistry taking place on interstellar dust grains is dominated by hydrogen atoms for three reasons. First, hydrogen is the most abundant specie; Second, it hops on the surface much faster than other species; Third, it is the most reactive specie, namely it reacts with many other species which do not react with each other. If two species such as $X_2$ and $X_3$ do not react with each other it is not crucial to maintain the correlation between their population sizes on a grain. Therefore, the probability distribution of the population sizes can be approximated by

$$P(N_1,N_2,N_3) = P(N_1)P(N_2/N_1)P(N_3/N_1),$$

where $P(N_i/N_1)$ is the conditional probability for a population size $N_i$ of specie $X_i$, given that the population size of $X_1$ atoms is $N_1$.

The multi-plane method is derived as follows: inserting Eq. (3) into the master equation (1), we trace over $N_3$, using the fact that $\sum_{N_3} P(N_3/N_1) = 1$ and $\sum_{N_3} \dot{P}(N_3/N_1) = 0$. We
obtain the following set of equations:

\[
\dot{P}(N_1, N_2) = \sum_{i=1}^{2} F_i [P(\ldots, N_i - 1, \ldots) - P(N_1, N_2)] \\
+ \sum_{i=1}^{2} W_i [(N_i + 1)P(\ldots, N_i + 1, \ldots) - N_iP(N_1, N_2)] \\
+ \sum_{i=1}^{2} A_i [(N_i + 2)(N_i + 1)P(\ldots, N_i + 2, \ldots) - N_i(N_i - 1)P(N_1, N_2, N_3)] \\
+(A_1 + A_2) [(N_1 + 1)(N_2 + 1)P(N_1 + 1, N_2 + 1) - N_1N_2P(N_1, N_2)] \\
+(A_1 + A_3) [(N_1 + 1)P(N_1 + 1, N_3)\langle N_3 \rangle_{N_1+1} - N_1P(N_1, N_2)\langle N_3 \rangle_{N_1}],
\]

(4)

where \( \langle N_3 \rangle_{N_1} = \sum_{N_3} N_3 P(N_3/N_1) \). A similar procedure for tracing over \( N_2 \) yields

\[
\dot{P}(N_1, N_3) = \sum_{i=1,3} F_i [P(\ldots, N_i - 1, \ldots) - P(N_1, N_3)] \\
+ \sum_{i=1,3} W_i [(N_i + 1)P(\ldots, N_i + 1, \ldots) - N_iP(N_1, N_3)] \\
+A_1 [(N_1 + 2)(N_1 + 1)P(N_1 + 2, N_3) - N_1(N_1 - 1)P(N_1, N_3)] \\
+(A_1 + A_2) [(N_1 + 1)P(N_1 + 1, N_3 - 1)\langle N_2 \rangle_{N_1+1} - N_1P(N_1, N_3)\langle N_2 \rangle_{N_1}] \\
+(A_1 + A_3) [(N_1 + 1)(N_3 + 1)P(N_1 + 1, N_3 + 1) - N_1N_3P(N_1, N_3)].
\]

(5)

The production rates of the non-reactive species \( X_4, X_5 \) and \( X_6 \) are given by

\( R(X_{i+3}) = A_i \sum_{N_1,N_2} N_i(N_i - 1)P(N_1, N_2) \), where \( i = 1, 2 \), and \( R(X_6) = (A_1 + A_3) \sum_{N_1,N_3} N_1N_3P(N_1, N_3) \). The desorption rate of the reactive species \( X_3 \) is given by

\( R(X_3) = W_3 \sum_{N_1,N_3} N_3P(N_1, N_3) \). In simulations using the multi-plane method, one can choose any initial condition that can be expressed by Eq. \( 3 \). A convenient choice is of an empty grain, namely, \( P(N_1 = 0, N_2 = 0) = 1 \) in Eq. \( 4 \) and \( P(N_1 = 0, N_3 = 0) = 1 \) in Eq. \( 5 \), where all other probabilities vanish. The multi-plane method requires setting cutoffs, \( N_i^{\text{max}}, i = 1, 2, 3 \), where the same value of \( N_1^{\text{max}} \) is used in Eqs. \( 4 \) and \( 5 \).

The simulations presented here were done for spherical grains on which the density of adsorption sites is \( s = 5 \times 10^{13} \) (sites cm\(^{-2}\)), at a grain temperature of \( T = 10 \) K. The activation energies for diffusion and desorption of the reactive species H, O and OH were taken as \( E_0(1) = 22, E_1(1) = 32, E_0(2) = 25, E_1(2) = 32 \) and \( E_0(3) = 28, E_1(3) = 35 \) meV, respectively. The parameters for hydrogen are rounded values in the range of experimental results on silicate and ice surfaces \( 19 \). For the other species no concrete experimental results are available and the chosen values reflect the tendency of heavier species to be more
strongly bound to the surface. The flux of H atoms on a grain of $S$ sites was taken as $F_1 = 2.75 \times 10^{-9} S$ (s$^{-1}$), and the flux of O atoms was $F_2 = 0.01 F_1$. These parameters are suitable for dense molecular clouds where such reaction networks are likely to take place. For simplicity, the OH flux was neglected, taking $F_3 = 0$. In Fig. 1 we present the production rates of $H_2$ (circles), $O_2$ (squares), $H_2O$ (triangles) and the desorption rate of OH (×) per grain vs. grain size. The results of the multi-plane method (symbols) and the complete master equation (solid lines), both obtained by direct numerical integration, are in excellent agreement. The results of the rate equations, that for small grains deviate significantly from the master equation results are also shown (dashed line).

In a complex reaction network of $J$ reactive species, $X_i$, $i = 1, \ldots, J$, the distribution of surface populations is given by $P(N_1, \ldots, N_J)$. If the only reactions are of the form $X_1 + X_i \rightarrow X_p$ and $X_i + X_i \rightarrow X_q$ (no matter if $X_p$ and $X_q$ are reactive or not), then the system can be reduced to $J - 1$ sets of equations for $P(N_1, N_j), j = 2, \ldots, J$. Each of these sets is obtained by tracing over all the populations $N_i$ except for $N_1$ and $N_j$. The number of equations is reduced from the exponential form of Eq. (2) to

$$N_E = (N_1^{\text{max}} + 1) \sum_{j=2}^{J} (N_j^{\text{max}} + 1),$$

namely to a linear dependence on the number of reactive species. In case that there is also a reaction between two different species $X_j + X_k \rightarrow X_p$, where $j, k \neq 1$, the three dimensional set of equations for $P(N_1, N_j, N_k)$ should be included in order to keep track of the correlations between these species. The reaction network can be described by a graph in which the nodes represent the reactive species, and any two species that react are connected by an edge. In general, each set of multi-plane equations is associated with a maximal fully-connected subgraph, namely with a maximal set of nodes which are all connected to each other. Chemical networks tend to be sparse, namely most pairs of species do not react. Therefore, the multi-plane equations mostly consist of sets that involve pairs of species and only few sets with three species or more.

As an example, consider the case in which CO molecules are added to the H, O, OH system considered above [16]. This gives rise to the following sequence of hydrogen addition reactions: $H + CO \rightarrow HCO \ (X_1 + X_7 \rightarrow X_8)$, $H + HCO \rightarrow H_2CO \ (X_1 + X_8 \rightarrow X_9)$, $H + H_2CO \rightarrow H_3CO \ (X_1 + X_9 \rightarrow X_{10})$ and $H + H_3CO \rightarrow CH_3OH \ (X_1 + X_{10} \rightarrow X_{11})$. Two other reactions that involve oxygen atoms also take place: $O + CO \rightarrow CO_2 \ (X_2 + X_7 \rightarrow X_{12})$ and
O + HCO → CO₂ + H (X₂ + X₈ → X₁₂ + X₁). This reaction network is described by the graph shown in Fig. 2. To account for the correlations between the populations of all pairs of species that react with each other, the multi-plane approach yields five sets of equations that account for \( P(N₁, N₃) \), \( P(N₁, N₉) \), \( P(N₁, N₁₀) \), \( P(N₁, N₂, N₇) \) and \( P(N₁, N₂, N₈) \). The first three sets reside on planes while the last two sets are three dimensional sets that are needed in order to account for the correlations between the species that form CO₂. Since the production of CO₂ is low compared to other products, one may consider an approximation in which these correlations are neglected, reducing the equations into only planar sets. In this case the set of equations will include: \( P(N₁, N₂) \), \( P(N₁, N₃) \), \( P(N₁, N₇) \), \( P(N₁, N₈) \), \( P(N₁, N₉) \) and \( P(N₁, N₁₀) \).

In the simulations presented here the activation energies for diffusion and desorption of CO, HCO, H₂CO and H₃CO were taken as \( E₀(7) = 30 \), \( E₁(7) = 36 \), \( E₀(8) = 30 \), \( E₁(8) = 38 \), \( E₀(9) = 33 \), \( E₁(9) = 39 \) and \( E₀(10) = 35 \), \( E₁(10) = 41 \) meV, respectively. The flux of CO molecules was taken as \( F₇ = 0.001F₁ \). In Fig. 3 we present the production rates per grain of H₂O, CO₂ and CH₃OH vs. grain size. An excellent agreement is found between the multi-plane approach (circles) and the complete master equation set (solid line). For small grains the approximated multi-plane set (+) shows significant deviations in the production rate of CO₂ but still provides good results for the other species. The rate equation results are also shown (dashed line). For this reaction network the number of equations required in the complete master equation is between tens of thousands to several millions, depending on the grain size. Numerical integration of the complete master equation is impractical. The steady-state results presented here for the complete master equation set were obtained using Newton’s method. Unlike the complete set, the multi-plane set consists of up to about a thousand equations, and can be simulated efficiently by numerical integration both under steady state and time dependent conditions using standard steppers such as Runge-Kutta.

In summary, we have introduced the multi-plane method for the simulation of the master equation of grain-surface chemistry. For complex reaction networks, this method achieves a great reduction in the number of equations. It thus enables the incorporation of the master equation in models of interstellar chemistry, providing accurate results for the production rates of molecules on interstellar dust grains. We expect that the multi-plane method will also be useful in other problems that exhibit a related mathematical structure, such as the modeling of stratospheric cloud chemistry and the analysis of genetic networks in cells.
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[1] T.W. Hartquist and D.A. Williams, The chemically controlled cosmos (Cambridge University Press, Cambridge, UK, 1995).
[2] R.J. Gould and E.E. Salpeter, Astrophys. J. 138, 393 (1963).
[3] D. Hollenbach and E.E. Salpeter, J. Chem. Phys. 53, 79 (1970); Astrophys. J. 163, 155 (1971); D. Hollenbach, M.W. Werner and E.E. Salpeter, Astrophys. J. 163, 165 (1971).
[4] J.B. Pickles and D.A. Williams, Astrophys. and Space Science 52, 433 (1977).
[5] L.B. d’Hendecourt, L.J. Allamandola and J.M. Greenberg, Astron. Astrophys. 152, 130 (1985).
[6] P.D. Brown and S.B. Charnley, Mon. Not. R. Astron. Soc. 244, 432 (1990).
[7] T.I. Hasegawa and E. Herbst and C.M. Leung, Astrophys. J. Supplement 82, 167 (1992).
[8] P. Caselli, T.I. Hasegawa and E. Herbst, Astrophys. J. 408, 548 (1993).
[9] A.G.G.M. Tielens and W. Hagen, Astron. Astrophys. 114, 245 (1982).
[10] S.B. Charnley, A.G.G.M. Tielens and S.D. Rodgers, Astrophys. J. 482, L203 (1997).
[11] P. Caselli, T.I. Hasegawa and E. Herbst, Astrophys. J. 495, 309 (1998).
[12] O.M. Shalabiea, P. Caselli and E. Herbst, Astrophys. J. 502, 652 (1998).
[13] T. Stantcheva, P. Caselli and E. Herbst, Astron. Astrophys. 375, 673 (2001).
[14] O. Biham, I. Furman, V. Pirronello and G. Vidali, Astrophys. J. 553, 595 (2001).
[15] N.J.B. Green, T. Toniazzo, M.J. Pilling, D.P. Ruffle, N. Bell and T.W. Hartquist, Astron. Astrophys. 375, 1111 (2001).
[16] T. Stantcheva, V.I. Shematovitch and E. Herbst, Astron. Astrophys. 391, 1069 (2002).
[17] T. Stantcheva and E. Herbst, Mon. Not. R. Astron. Soc. 340, 983 (2003); Astron. Astrophys., in press (2004).
[18] S.B. Charnley, Astrophys. J. 562, L99 (2001).
[19] N. Katz, I. Furman, O. Biham, V. Pirronello and G. Vidali, Astrophys. J. 522, 305 (1999); H.B. Perets, O. Biham, V. Pirronello, J. Roser, S. Swords and G. Vidali, in preparation (2004).
[20] J. Krug, Phys. Rev. E 67, 065102 (2003).
[21] H.H. McAdams and A. Arkin, Proc. Natl. Acad. Sci. USA 94, 814 (1997).

[22] J. Paulsson and M. Ehrenberg, Phys. Rev. Lett. 84, 5447 (2000).
FIG. 1: The production rates of H$_2$ (circles), O$_2$ (squares), H$_2$O (triangles) and the desorption rate of OH (×) per grain vs. grain size, given by the number of adsorption sites $S$ and the diameter $d$. Excellent agreement is found between the multi-plane method (symbols) and the complete master equation (solid lines). The results of the rate equations are also shown (dashed lines).

FIG. 2: A graph describing the reaction network that results from the adsorption of H and O atoms and CO molecules. The nodes represent the reactive species, while the edges connect pairs of species that react with each other. The reaction products are specified near the edges.

FIG. 3: The production rates of H$_2$O, CO$_2$ and CH$_3$OH vs. grain size as obtained from the multi-plane approach (circles) and the complete master equation (solid lines) are found to be in excellent agreement. The approximate multi-plane equations (+) deviate in the production rate of CO$_2$, but are still accurate for the other species. The rate equation results are also shown (dashed lines).
Fig. 1
Production Rate ($s^{-1}$)

$$2 \times 10^{-2}$$

$d$ ($\mu$m) $10^{-1}$

$$10^2$$

$$10^{-6}$$

$$10^{-7}$$

$$10^{-8}$$

$$10^{-9}$$

$$10^{-10}$$

$$10^{-11}$$

$$10^{-12}$$

$$10^3$$

$$10^4$$

$$10^5$$

$H_2O$

$CH_3OH$

$CO_2$

Fig. 3