Chemical Reactions on Small Interstellar Dust Grains

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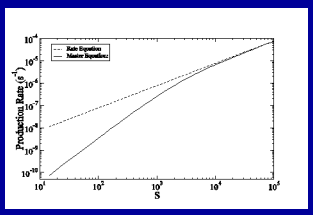
Abstract

Chemical reactions on dust grains are of crucial importance in interstellar chemistry. The computational modeling of chemical reaction networks is typically done using rate equations. However, for reactions taking place on the surfaces of small dust grains, rate equations are not always valid. This is because they ignore fluctuations as well as the discrete nature of the atomic and molecular species.
Recently, a master equation approach was proposed, that is suitable for the simulation of chemical reactions on microscopic grains. We present here some applications and computational aspects of this approach.



Molecular production rate vs. grain size, as calculated by the rate equation (dashed line) and by the master equation (solid). Significant deviations appear in cases of small grains.

Rate equation:

$$\frac{dn}{dt} = F - Wn - 2An^2$$

atoms on grain

flux (atoms s^{-1})

desorption coefficient $W=\nu \exp(-E_1/kT)$

sweeping rate $A=(\nu/S)\exp(-E_0/kT)$

Problem: In case of small grains, where n is of order of 1, there are large fluctuations and the rate equation is not valid.
The **solution** is the master equation.

Master equation:

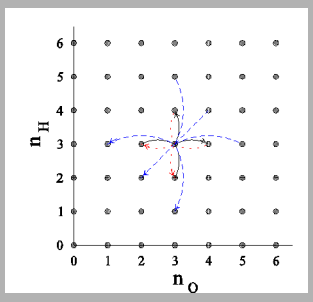
$$\frac{dP(n)}{dt} = F\left[P(n-1)-P(n)\right] + W\left[(n+1)P(n+1)-nP(n)\right] + A\left[(n+2)(n+1)P(n+2)-n(n-1)P(n)\right]$$

Master equation for more than a single specie:

$$\begin{aligned} \frac{dP(n_H,n_O)}{dt} = {} & F_H\left[P(n_H-1,n_O)-P(n_H,n_O)\right] \\ & + F_O\left[P(n_H,n_O-1)-P(n_H,n_O)\right] \quad \} \text{ flux} \\ & + W_H\left[(n_H+1)P(n_H+1,n_O)-n_H P(n_H,n_O)\right] \\ & + W_O\left[(n_O+1)P(n_H,n_O+1)-n_O P(n_H,n_O)\right] \quad \} \text{ desorption} \\ \text{H+H}\rightarrow\text{H}_2: & \; A_H\left[(n_H+2)(n_H+1)P(n_H+2,n_O)-n_H(n_H-1)P(n_H,n_O)\right] \\ \text{O+O}\rightarrow\text{O}_2: & \; A_O\left[(n_O+2)(n_O+1)P(n_H,n_O+2)-n_O(n_O-1)P(n_H,n_O)\right] \\ \text{H+O}\rightarrow\text{OH}: & \; (A_H+A_O)\left[(n_H+1)(n_O+1)P(n_H+1,n_O+1)-n_O n_H P(n_H,n_O)\right] \end{aligned}$$

Problem: The number of equations grows **exponentially** in the number of species.
The **solution** is using the multi-plane approximation.

Monte Carlo simulations:



Instead of direct integration of the master equation, one can perform a Monte Carlo simulation. Each state is defined by the populations of the different species, and the transfer probabilities can be determined by the rates of the fundamental physical process. Here we demonstrate the possible transfers for a 2-species system. A state is a pair of populations (n_H,n_O). The state can be changed due to incoming flux (solid black arrows) desorption (dotted red) and reactions (dashed blue). The advantage of MC simulation is that there is no need to have the whole space in memory. However, this simulation can give only the steady state solution of the master equation, but not to follow the time dependence of the average populations.

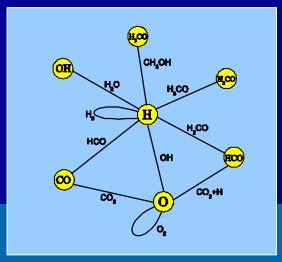
Moment equations:

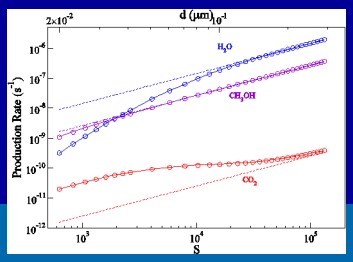
By summing the set of master equations, one can achieve a simple set of dynamic equations for the moments of the distribution. The time derivative of each moment is expressed by a linear combination of other moments.

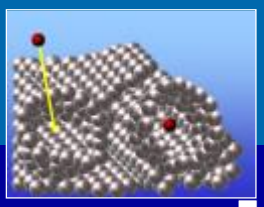
$$\frac{d\langle n\rangle}{dt} = F + (2A-W)\langle n\rangle - 2A\langle n^2\rangle$$
$$\frac{d\langle n^2\rangle}{dt} = F + (2F+W-4A)\langle n\rangle + (8A-2W)\langle n^2\rangle - 4A\langle n^3\rangle$$
$$\vdots$$
$$\frac{d\langle n^k\rangle}{dt} = F\left\langle (1+n)^k - n^k\right\rangle + W\left\langle n\left[(n-1)^k - n^k\right]\right\rangle + A\left\langle n(n-1)\left[(n-2)^k - n^k\right]\right\rangle$$

Example: Reaction network of 7 species and 10 reactions:

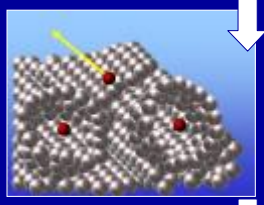
In the standard master equation approach, simulating a 7 species network requires the derivatives of 7-bodies probabilities $P(N_1,N_2,\ldots N_7)$. Even if the number of atoms of each specie is limited by some cutoff, the total number of equations is huge. In the multi-plane approximation, the complete set of equations is being separated into small set of two or three bodies probabilities, where the other species are traced over. In this way, only fluctuations of correlated species are being calculated in detail, and the average populations of the non-correlated species are taken into account. In the figure we show some results of simulating the drawn reaction network. The rate equations results (dashed lines) deviate significantly from the master equation results (solid). The multi-plane method results (circles) are in perfect agreement with the exact results of the master equations, although achieved by much fewer equations.



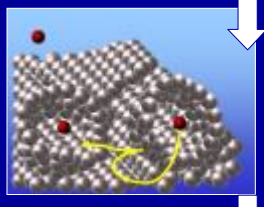




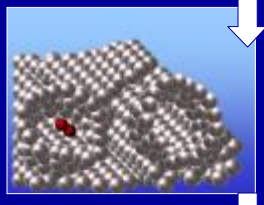
1. incoming atomic flux



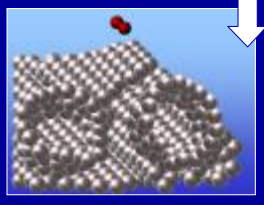
2. thermal desorption of atoms



3. diffusion



4. molecule formation



5. desorption

References:

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