Modelling heterogeneous molecule formation

Vasco Guerra

Instituto de Plasmas e Fusão Nuclear, Instituto Superior Técnico, Universidade de Lisboa,
1049-001 Lisboa, Portugal
vguerra@tecnico.ulisboa.pt

This work reports a study of molecule formation on surfaces using a mesoscopic description. In particular, two different variants of a stochastic dynamical Monte Carlo approach are developed and compared with the deterministic approach based on reaction-rate equations. NO_2 formation by NO oxidation on Pyrex surfaces is taken as a case study. The model accounts for Eley-Rideal NO_2 formation and NO_2 adsoprtion, on a surface exhibiting a distribution of reactivity among the adsorption sites. The influence of the grid size on the CPU calculation time and the accuracy of the results are analysed. It is shown that the dynamical Monte Carlo scheme can run very efficiently for the system under analysis and provide highly reliable results. Moreover, the present formulation of this method provides a relatively simple procedure to describe fully coupled surface and gas phase chemistries.

1. Introduction

Surface recombination of atoms and molecule formation on surfaces is a prevalent subject in various areas of plasma science and technology, such as deposition and etching [1], volatile organic compound (VOC) oxidation [2] or space-vehicle re-entry studies [3].

This work addresses the question of modelling heterogeneous molecule formation on silica or Pyrex surfaces. Despite the impressive evolution of semi-classical molecular dynamics calculations in recent years [4,5], its application to realistic conditions of molecule formation on silica surfaces is still difficult. Moreover, the direct coupling with complex gas-phase chemistry models remains unpractical. In this context, "coarse-gained" mesoscopic models describing the surface in terms of fractional coverages of different adsorption sites, albeit the lack of a true predictive capacity, continue to form powerful tools to describe and interpret surface phenomena.

The most common mesoscopic approach to investigate surface kinetics is to adopt a *deterministic* description where the time-evolution of the adsorbed species and adsorption sites is ruled by a system of reaction-rate differential equations associated with the different elementary processes taken into account [6,7]. A different approach is to use a *stochastic* dynamical Monte Carlo scheme [8,9]. These methods, which *simulate the time evolution* of the system without dealing with the *master equation* directly, follow the evolution of one element of the statistical ensemble. They are exact, relatively simple to implement regardless the complexity of the kinetics, handle easily probabilities that depend on the local configuration of the system, provide the study of averages,

deviations and correlations, and help bridging the gap between molecular dynamics and the macroscopic or less sophisticated mesoscopic approaches. In addition, Monte Carlo (MC) methods are particularly suited to study systems where surface diffusion of physisorbed atoms and/or molecules plays an important role. Indeed, while in a MC algorithm the rates for surface diffusion are simple to interpret and their general expressions are known, in the reaction-rate deterministic description the calculation of the associated rate coefficients, such as, *e.g.*, those for Langmuir-Hinshelwood recombination involving one chemisorbed atom and a diffusing physisorbed atom, always involve additional assumptions and lose some microscopic detail.

In this work the validity and efficiency of dynamical MC methods in the study of molecule formation on surfaces is investigated. NO oxidation on Pyrex pre-treated with an oxygen discharge is chosen as a case study. This system has been studied both experimentally [10] and theoretically [11], providing a reliable benchmark for the new calculations.

2. Theoretical formulation

The system under analysis is the formation of NO_2 molecules on a Pyrex tube of inner radius 1 cm, as a result of NO oxidation by previously adsorbed O atoms on the wall [10,11]. In short, an oxygen discharge is used to graft O atoms on the wall; the discharge tube is then pumped for about 10 minutes to remove gas phase species and let the temperature cool down to room temperature; finally, a controlled amount of NO diluted in argon is introduced, corresponding to pressures between 0.1 and 4 Torr, and the time-dependent gas phase NO and NO_2

concentrations are measured using a diode laser spectrometer. The reader should refer to [10,11] for further details.

As discussed in [10,11], the surface exhibits a distribution of reactivity among the adsorption sites. A very good simulation of the experimental results was achieved in [11], by considering 7 types of chemisorption sites, with different activation energies for recombination, and a relatively simple kinetics described by the following reactions: Eley-Rideal NO oxidation,

$$NO+O_S(i) \rightarrow NO_2+S_V(i),$$
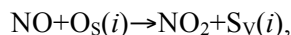
where $O_S(i)$ and $S_V(i)$ represent an adsorbed oxygen atom on a chemisorption site of type i and a vacant chemisorption site of type i, respectively; slow NO_2 chemisorption on vacant sites,

$$NO_2+S_V(i) \rightarrow (NO_2)_S(i).$$
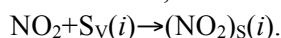
This system of equations was solved in [11] using an implicit Runge-Kutta (RK) method. Taking into account the excellent agreement between the deterministic model calculations and the experimental results reported in [11], the former results are used as a benchmark for the present study. Notice as well that this system does not pressupose reactions with physisorbed atoms, so that the RK calculations do not involve any additional assumptions as compared to the ones required to develop a MC simulation.

Two different dynamical MC algorithms were implemented. The first one is a null collision method, similar to the ones proposed in [8,9]. It can be described from the sequence: *i)* pick randomly a surface site; *ii)* check which processes may occur on that site, depending on its occupancy; *iii)* use a random number to verify if any process does happen; *iv)* if something happens, calculate the time increment, and update the *surface and gas phase concentrations* and the different reaction rates; *v)* repeat the procedure until the desired time. The second one is closer to the formulation of a dynamical Monte Carlo for gas phase chemical reactions proposed by D. Gillespie [12], with local update and lists (DMCL) [13]. In this scheme, for each potential reaction a list is kept with the surface sites where it can possibly occur. In this case the algorithm can be informally described as: *i)* chose the next event (reaction) type, by drawing a random number according to the appropriate probability density function [12]; *ii)* chose randomly, *from the list* of possible sites for this event to happen, the site where it will take place; *iii)* calculate the time increment, and *update the surface and gas concentrations* and the different reaction rates; *iv)* repeat the procedure until the desired time.

As it should be clear from the above descriptions, the dynamical Monte Carlo methods provide an accurate treatment of time, with a proper correspondence between Monte Carlo time and real time. What is more, in the present calculations the time-evolution of both gas phase and surface densities are simulated in a coupled way.

3. Results and discussion

Figures 1a) and 1b) show the calculated time evolution of NO and NO_2 species for the 1 Torr case (see [11] for details) in one run, obtained from the dynamical Monte Carlo with lists (DMCL), when 500 and 7500 surface sites are considered in the simulations, respectively. Take note that in this system there are only 10% of the surface sites corresponding to the highest reactivity (see [11]), so that there are only 5 sites of this type in the simulation when 500 surface sites are used. For comparison, the results obtained from the Runge-Kutta solution to the reaction-rate model (RK) from [11] are also represented on these figures. As it can be seen, the DMCL furnishes a consistent simulation of the system. Not surprisingly, the simulation made using 500 sites exhibits significant "noise" around the expected values, while the one made with 7500 sites already provides results barely distinguishable from the exact ones. The absolute error, defined here as the average of

$$\Delta = \sqrt{\sum_{i=1}^{N} \left([NO]_{MC}(i) - [NO]_{RK}(i)\right)^2}$$

over 10 realisations of the system, where the RK and MC solutions are compared over $N=100$ points, decreases from 6.4×10^{13} to 2.2×10^{13} cm^{-3} when the number of surface sites in the simulation increases from 500 to 7500.
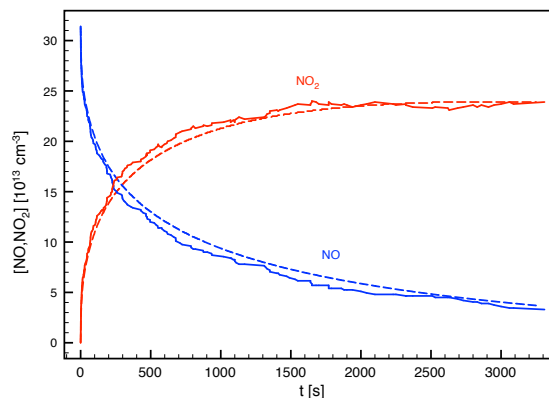

Figure 1a): comparison of the RK and DMCL simulations for 1 Torr (see [11]) when the 500 surface sites are considered.

The analysis of the average error in the MC simulations is presented in figure 2, where the absolute error Δ averaged over 10 runs is shown for both NO and NO$_2$ concentrations (with the obvious modification on the definition), as a function of the number of surface sites considered. There is a strong reduction of the average error as the dimension of the lattice grows up to 5000 points to describe the surface. An increase of the number of points considered beyond this point continues to improve the accuracy of the results, but on a relatively small scale.
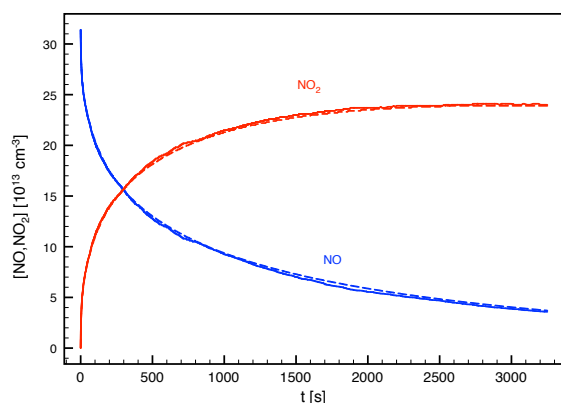

Figure 1b): comparison of the RK and DMCL simulations for 1 Torr (see [11]) when the 7500 surface sites are considered.
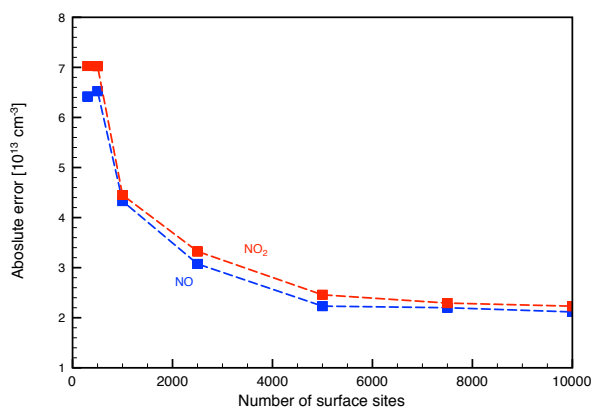

Figure 2: Evolution of the absolute error of the MC simulations as defined in the text, averaged over 10 realisations of the system, as a function of the number of surface sites considered in the simulation.

Finally, the results and performance of both dynamical Monte Carlos algorithms were compared. It has been verified that the two procedures lead to similar results. Therefore, the choice of one or another has to be made in terms of simplicity of use and computational efficiency. However, the former criterion does not play a significant role in the choice, as both algorithms are relatively easy to implement. Hence, figure 3 shows the average CPU

time used by each of the methods, as a function of the number of surface sites considered in the simulations. It is immediate to verify that the dynamical Monte Carlos with lists is much more efficient than the null event scheme, with CPU calculation times about two orders of magnitude shorter than the null event algorithm, in accordance with the results from [13]. In addition, the CPU computation time scales linearly with the number of surface sites used.
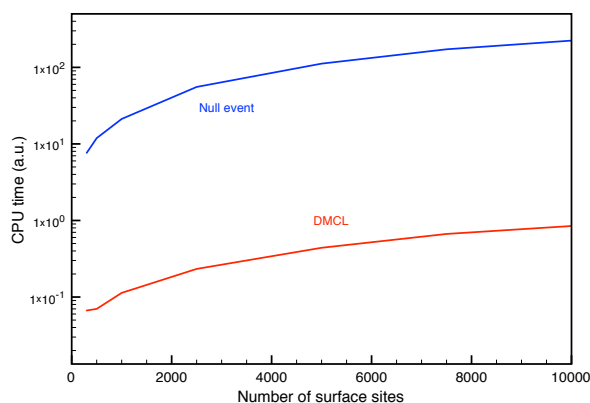

Figure 3: CPU time used in the null event dynamical Monte Carlo algorithm and the dynamical Monte Carlo with lists, as a function of the number of surface sites considered in the simulations.

4. Conclusions

Dynamical Monte Carlo methods, in particular with an algorithm based on local update with lists, can be effectively used to simulate surface kinetics and coupled gas phase and surface chemistries. Their validity has been assessed in a relatively "simple" system, but which involves very different timescales, associated with recombination in surface sites with a distribution of reactivity.

Future work shall concentrate on the application of the method to systems where physisorbed atoms play a relevant role and to situations where gas phase chemistry may be coupled to surface kinetics in a more complex way. In addition, other procedures to increase the already impressive computational efficiency of the method can be explored, namely the use of a relatively small number of adsorption sites together with an averaging procedure over different realisations of the system.

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