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## A computational method to optimize the distribution of a catalytically active material inside a nano-scale pore

Henrik Ström<sup>a,b,\*</sup>

<sup>a</sup>Department of Applied Mechanics, Chalmers University of Technology, Gothenburg SE-412 96, Sweden

<sup>b</sup>Department of Energy & Environment, Chalmers University of Technology, Gothenburg SE-412 96, Sweden

### Abstract

Catalysis is a key phenomenon in a great number of energy processes, including feedstock conversion, tar cracking, emission abatement and optimizations of energy use. Within heterogeneous, catalytic nano-scale systems, the chemical reactions typically proceed at very high rates at a gas-solid interface. The present work investigates the performance of a Direct Simulation Monte Carlo (DSMC) code with a stochastic optimization heuristic for optimizations of such nano-scale systems. The DSMC code is able to treat molecular motion with homogeneous and heterogeneous chemical reactions in wall-bounded systems with a prescribed pressure difference between an inlet and an outlet. An algorithm has been devised and implemented that allows optimization of the distribution of a catalytically active material within a three-dimensional pore where the flow field is described by the code. The objective function is the outlet concentration of computational molecules that have interacted with the catalytically active surface, and the optimization method used is simulated annealing. The application of a stochastic optimization heuristic is shown to be more efficient within the present DSMC framework than using a macroscopic overlay method. Furthermore, it is shown that the performance of the developed method is superior to that of a gradient search method for the current class of problems.

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*Keywords:* Optimization; DSMC; Catalysis; Stochastic optimization; Nanoscale

### 1. Introduction

The most viable route to a reduction of the environmental costs of modern societies is an increase in the efficiencies of processes used in the manufacturing and transportation of products and in the production of energy [1]. Catalysis is a key phenomenon in a great number of relevant industrial processes, including feedstock conversion [2], tar cracking [3], emission abatement [4] and optimizations

\* Corresponding author. Tel.: +46-31-7721360; fax: +46-31-180976.

E-mail address: [henrik.strom@chalmers.se](mailto:henrik.strom@chalmers.se).

of energy use [5]. A particularly promising field of catalysis is now being developed on very small spatial scales – often referred to as nanotechnology. Within heterogeneous, catalytic nano-scale systems, the chemical reactions are allowed to proceed at very high rates at a gas-solid interface (often the surface of a precious metal). The process efficiency is limited by the acceptable cost of the particular material in combination with the surface-to-bulk atom ratio obtainable, since the chemical reaction only occurs at the surface and the interior atoms remain unused. As the gas containing the reactants is typically brought into contact with the catalyst while being forced to flow past it, optimization of the efficiencies of such systems require numerical tools that take into account both the chemistry and the fluid dynamics of the system. The governing processes in applications where the bounding geometry is of micro- or nanometer size typically spans several orders of magnitude in spatial and temporal scales [6, 7]. Consequently, there are many inherent difficulties involved in performing non-intrusive, non-destructive experimental investigations of the processes occurring on the smallest scales in such systems. Comprehensive numerical models therefore form an indispensable basis in the research into their behaviour. The purpose of the present work is to develop a numerical tool for investigations of reacting, molecular flows that can be applied in optimizations of catalytic systems on the micro- and nano-scales.

## 2. Modeling

### 2.1. The Direct Simulation Monte Carlo (DSMC) framework

The route to accurate descriptions of molecular flows with chemical reactions is via molecular methods, e.g. by obtaining the solution to the Boltzmann equation rather than the Navier-Stokes equations [8-11]. One well-established molecular method is Direct Simulation Monte Carlo (DSMC) [12], which is a probabilistic simulation approach. The fluid flow is modelled using particles that represent a large number of real molecules. The particle motion is updated deterministically using a time step that is smaller than the mean collision time, so that the intermolecular collisions can be decoupled from the molecular motion. The code developed in this work is based on Bird's DSMC method [12] and is able to handle chemistry in the gas phase and surface chemistry at gas-solid interfaces [cf. 13, 14]. More specifically, the code is designed for performing optimizations of the distribution of an active material over the bounding surfaces of the system. The aim is to make possible a complete optimization during the course of one single simulation run. The code is written in the programming language C.

### 2.2. The stochastic optimization heuristic

Macroscopic fields in a DSMC procedure typically contain statistical scatter, as the information has to be deduced by sampling over the computational molecules and the presence of a statistically significant number of molecules in all sampling cells at all times cannot be guaranteed. In addition, the objective function in the optimization process may very well exhibit both global and local optima. Furthermore, it is not possible to test every conceivable design due to the large computational cost of such an investigation. A suitable compromise is then to use a stochastic optimization method, such as simulated annealing [15, 16]. In the current work, the following simulated annealing heuristic is used: 1) Sample the objective function for one initial (randomly chosen) design case. 2) Pick another design case (using an algorithm that has to be specified separately). 3) If the new case is better, move to it. If it is worse, accept it anyway with a certain probability,  $P$ . This probability is to be a function of the time elapsed in the

optimization process and it too has to be specified separately. 4) Repeat steps 2-3 a pre-determined number of rounds or until the objective function reaches a pre-defined threshold value.

At the heart of the simulated annealing algorithm lies the determination of the probability  $P$ . The original probability function of Kirkpatrick et al. [15] is here modified slightly, so that  $P = \exp\{-\{f' - f\}/f\} / T(t)$ . In this notation,  $f$  is the value of the objective function, a prime denotes the value for the newer design case, and  $T(t)$  is the analogue of temperature in a physical annealing process. In this work, the function  $T(t)$  is defined as  $T(t) = 2e^{-3} - 1.9e^{-3} t/t_{max}$ , where  $t$  is the total time elapsed in the simulation and  $t_{max}$  is the time at which the optimization process is stopped. Hence, the tendency to accept a design case that is worse decreases with time.

The final component in the optimization routine is the algorithm for picking another design. In the present work, the following algorithm has been found to produce satisfactory results: 1) The new design is obtained by moving the catalytically active region a random distance in the interval  $[\Delta x/20, \Delta x/10]$ , where  $\Delta x$  is the extent of the domain in coordinate direction  $x$ . 2) The direction in which to move is by default the direction of increasing value of the objective function, but in 25% of the cases the direction is reversed to introduce a pseudo-random behavior also to the design picking algorithm.

It is clear that this stochastic method cannot be guaranteed to find the global optimum of an objective function. However, it can avoid becoming trapped in a local optimum (when there is a better global optimum somewhere else), it prevents premature termination due to scatter in the objective function and it can help avoid the tedious task of investigating every possible design case.

### 3. Results and Discussion

#### 3.1. Validation of the DSMC code

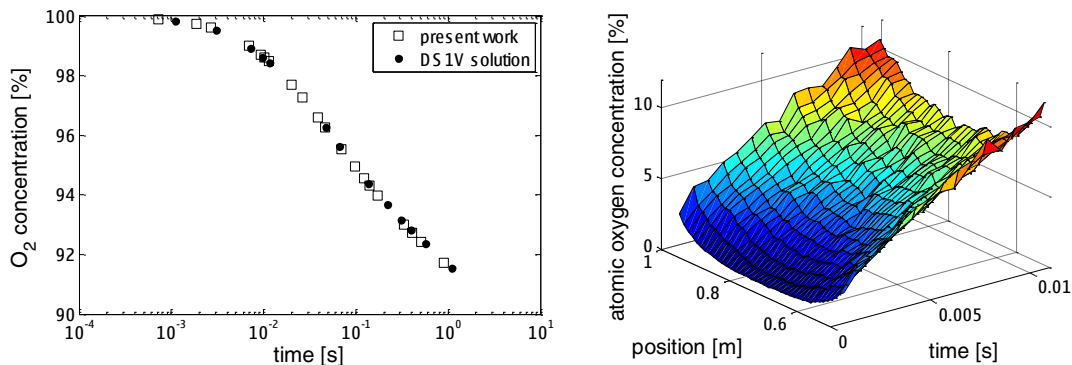


Fig. 1. To the left: Volume-averaged concentration of diatomic oxygen as a function of time in the homogeneous chemistry test case. To the right: 3D surface plot showing the time-and-space resolved atomic oxygen concentration in the heterogeneous chemistry test case. The code predicts that the concentration of atomic oxygen increases with time and penetrates into the domain.

The DSMC code is validated in an extensive series of tests, of which only a few are reported here. As the most challenging aspect of the DSMC procedure in relation to molecular motion lies in the modelling of molecular collisions, one fundamental validation test carried out is that of a homogeneous gas at rest in a one-dimensional domain. This test case proves that the code is able to predict the correct solution for a one-dimensional homogeneous gas and that the performance of the random number generator used is acceptable. The number of collisions predicted is very close to the theoretical value [12], and the mean

collision separation is less than 5% of the cell-width, meaning that collision partners are located within the same subcell. These observations support the conclusion that the code can be used in its present form for the optimization processes described in Section 3.2.

The ability of the code to handle different molecular species and chemical reactions is validated in a homogeneous chemistry test case. Two stationary walls are separated by a distance of 0.5 m. Both walls have surface properties such that there is 100% specular reflection. The gap between the walls is initially occupied by oxygen ( $O_2$ ) at a number density of  $10^{20} \text{ m}^{-3}$  and a temperature of 5,000K. In this test case, two chemical reactions may occur, namely the dissociation and recombination, respectively, of diatomic oxygen and atomic oxygen:  $O_2 \leftrightarrow 2O$ . For this problem, the performance of the current code is validated by comparing its predictions to benchmark results from one of Graeme Bird's program in the DS suite (DSIV) [17]. The total duration of the simulation is approximately one second of real time, and the result is shown to the left in Fig. 1. The current code is in excellent agreement with the DSIV solution.

Surface reactions are implemented as occurring at a wall with a certain probability [14]. As a test case, the wall-catalysed dissociation of oxygen is simulated at a temperature of 300K in the same geometry as the homogeneous validation case. Dissociation is prescribed to occur at the walls with a reaction probability of 1%. The temporal evolution of the atomic oxygen concentration profile is depicted to the right in Fig. 1. The results presented here agree with what is qualitatively expected for the system under investigation.

### 3.2. Optimization of the position of a catalytically active region

A nano-scale “pore” is constructed where two boundaries are specified as an inlet and an outlet, and a procedure is implemented by which the pressure difference between these boundaries is maintained throughout the simulation [18]. The aim is to design a numerical framework that can be used to determine the optimal distribution of a limited amount of catalytically active material over the pore surface. To simplify the problem setup, the catalytically active material is limited to a single surface location, but generalization to an arbitrary number of active sites is straightforward. The chemical reaction is assumed not to influence the molecular flow field. In other words, no actual reaction (wherein molecules change nature) is carried out, but the molecules that have made contact with the catalytically active surface are marked, so that their concentration can be monitored by the code. This approach is equivalent to monitoring the impingement rate on the catalytically active sites, rather than the actual reaction rate [19]. Under the assumption that the flow field does not change significantly with the trace species conversion, this method may thus reduce the computational cost of obtaining converged statistics by several orders of magnitude. Additionally, it could be thought of as a means of probing the mass transfer rate towards the catalytically active sites (e.g., as in CO oxidation experiments over Pt/ $Al_2O_3$  catalysts).

It should be noted here that there are macroscopic overlay methods available for the DSCM framework [20, 21], but that such approaches are susceptible to numerical errors if the sampling of the macroscopic fields has not yet converged. This is a significant drawback in optimization, and it makes these methods less efficient than the sampling of marked molecules as proposed in the present work.

An algorithm is implemented that moves the catalytically active section around in the domain. This algorithm waits for a steady signal from the outlet sampling of marked molecules before changing the location of the catalytically active section. The objective function is judged to have converged when the relative change between two samples is less than  $10^{-3}$ . The catalytically active region is a 2 nm thin section around the perimeter of the rectangular 3D pore.

The optimization algorithm is then evaluated for an objective function that contains two local optima (and three extreme points), as depicted in Fig. 2. The global optimum is positioned around  $z = 0.2$  and is

~2.6%. There is also a local maximum (~1.5%) at around  $z = 0.7$ . There is a significant uncertainty in the sampling of the objective function, due to the presence of noise in the signal (not shown in Fig. 2). The extreme point that separates the curves leading to the two maxima is located at  $z = 0.5$ . Hence, for the current objective function – and in the absence of noise – a gradient search optimization process starting from a random location would find the global optimum in 50% of the cases and the other maximum in the remaining 50% of the cases. The aim here is to prove that the simulated annealing algorithm can exhibit superior performance to such an algorithm.

The statistics for the results of the simulated annealing algorithm when applied to a system that is described by the aforementioned objective function is shown to the right in Fig. 2. The optimization process has been repeated 1,000 times for every limit on the number of calls to obtain reliable statistics. The algorithm is typically able to find the correct optimum after 20 function calls. As the total number of calls allowed increases, the number of unsuccessful simulation runs decreases significantly. This behavior is superior to the performance of a gradient search method. A gradient search would only be able to find the local optimum closest to the initial position (if allowed a large enough number of calls), and would not in general be able to handle the fluctuations in the objective function. Consequently, a gradient search method could at best produce two ridges of equal height in Fig. 2.

#### 4. Conclusions

A Direct Simulation Monte Carlo (DSMC) code has been developed that treats molecular motion in wall-bounded systems with homogeneous and heterogeneous chemical reactions. A simulated annealing optimization algorithm is implemented to allow for optimization of the distribution of a catalytically active material within a 3D pore where the flow field is described by the present code. It is shown that the performance of the simulated annealing method for the current class of problems is superior to that of a gradient search method, and that a stochastic optimization heuristic can be more efficient than macroscopic overlay methods. The approach described in the present work represents a suitable starting-point for addressing a number of important research challenges involving reacting nano-scale flows and reacting heterogeneous flows with surface diffusion.

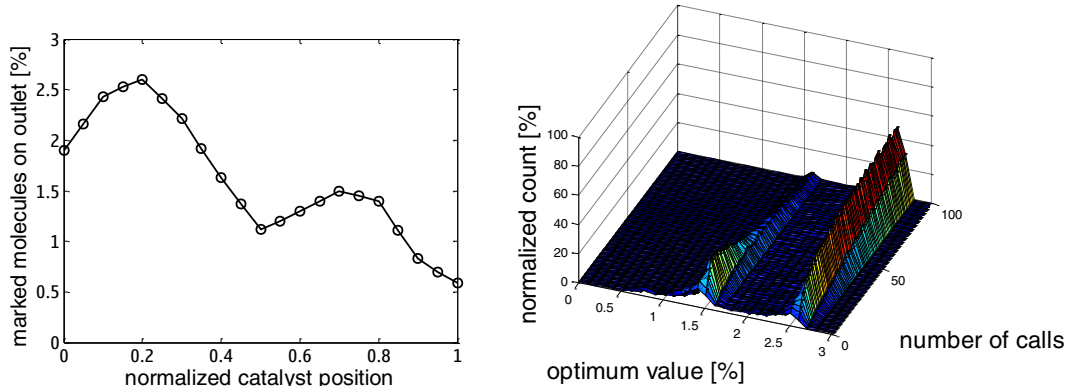


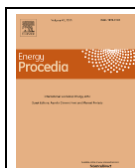
Fig. 2. To the left: Objective function with two local optima but only one global. To the right: Statistics for the simulated annealing algorithm developed in the present work for the objective function to the left.

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### Biography

Henrik Ström is an Assistant Professor in Multiphase Flow and Energy Technology at Chalmers University of Technology.