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NUMERICAL ANALYSIS OF CHEMICAL REACTIONS BY
MONTE CARLO SIMULATION*

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This paper presents numerical results for chemical reaction simulation with Direct Simulation Monte Carlo method using two different reaction probability models. The order of differences in the temperatures and the concentrations are studied by these ways. When the chemical reaction activity decreases, then the differences between the concentrations and the temperatures obtained by the two ways decrease.

1. Introduction. The effects of nonequilibrium physical chemistry processes are important for many applied problems. A chemical reaction produces the nonequilibrium velocity distributions. These distributions in bimolecular reactions are described by semiclassical Boltzmann equation. The first stage in modeling such a process is creating reliable mathematical models. At this time many approaches exist for the chemical reaction modeling. The Chapman-Enskog (CE) method of solution has been extensively used for a slow reaction [1], and for the fast reaction Shizgal [2] has used the moment method. The effect of the heat of reaction on the velocity distribution has been studied by Prigogine and Mahieu using the CE method [3]. Karleman [4] shows that for some collision models in a homogenous chemical reaction 5 dimensional integral can be reduced to 3 dimensional integral. Koura [5] and Nurlabaev [6] using Direct Simulation Monte Carlo method investigate the fast chemical reaction.

Two ways are used for modeling the probability for chemical reaction occurrence. The first uses the relative velocity while the second uses the relative velocity projection on the line of the center of the molecules. The purpose of this paper is to make comparison between two probabilities for the bimolecular chemical reaction modeling in rarefied gas by Direct Simulation Monte Carlo (DSMC) method.

There are two components of the error when DSMC is used – statistical error (due to the statistical nature of the method) and systematic (due to the truncation). Chen and Boyd [8] estimate that this error can decrease by increasing of the collisions. The second error is deterministic. Garcia and Wagner [10] show that the time-step truncation error is proportional to the square of the time-step. Truncation error due to discretization in space is proportional to the square of the cell size.

We use model chemical reactions in this paper. Our aim is to estimate the differences between these two ways for modeling of the chemical reaction probability.

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2. Formulation of the problem and methods of solution. Let us consider homogenous bimolecular reversible chemical reaction $A + B \leftrightarrow C + D$ with activation energy ε_f and ε_b for the forward and the backward chemical reaction, Let $\varepsilon = \varepsilon_b - \varepsilon_f$. The mass and the diameters of the components are noted by $m_A, m_B, m_C, m_D, d_A, d_B, d_C, d_D$. The molecules are modeled by hard spheres. In accordance with the kinetic approach, this chemical reaction is described by a system of four semiclassical Boltzmann equations [7]:

$$(2.1) \quad \frac{\partial}{\partial t} f_i = J_i^{el} + J_i^r \quad i = A, B, C, D$$

where

$$(2.2) \quad J_i^{el} = \sum_{j=1}^4 J_{ij}^{ij} = \sum_{j=1}^4 \int (f_i^* f_j^* - f_i f_j) P_{ij}^{ij} g_{ij} \sigma(g_{ij}, \Omega) d\Omega d\vec{v}_j$$

$$(2.3) \quad J_i^r = \sum_r J_{ij}^{kl} = \sum_r \int (f_k^* f_l^* - f_i f_j) P_{ij}^{kl} g_{ij} \sigma(g_{ij}, \Omega) d\Omega d\vec{v}_j$$

$$f_i^* = f_i^*(t, \vec{v}_i^*)$$

\vec{v}_i^* – the post collision molecular velocity
 $g_{ij} = |\vec{v}_i - \vec{v}_j|$ – the relative velocity
 $\sigma(g_{ij}, \Omega) d\Omega$ – differential cross-section of the particle scatter within the solid angle $d\Omega$.

The two ways for modeling the probability for chemical reaction are:

$$(2.4) \quad \text{Call "A" method } P_{ij}^{kl} = \begin{cases} 1, \mu_{ij} g_{ij}^2 / 2 \geq \varepsilon_f \\ 0, \mu_{ij} g_{ij}^2 / 2 < \varepsilon_f \end{cases}$$

$$(2.5) \quad \text{Call "B" method } P_{ij}^{kl} = \begin{cases} 1, \mu_{ij} (\vec{g}_{ij}, \vec{k}_{ij})^2 / 2 \geq \varepsilon_f \\ 0, \mu_{ij} (\vec{g}_{ij}, \vec{k}_{ij})^2 / 2 < \varepsilon_f \end{cases}$$

where \vec{k}_{ij} is a unit vector along the line of the center of the molecules.

3. Direct Simulation Monte Carlo (DSMC) Method. (a) The time interval $[0, T]$, over which the solution has been found out, is subdivided into subintervals with step Δt ;

(b) The space domain is subdivided into cells with sides $\Delta x, \Delta y$;

(c) The gas molecules are simulated in the gap G using a stochastic system of N points (particles) having positions $\underline{x}_i(t) = (x_i(t), y_i(t))$ and velocities $\underline{\xi}_i(t) = (\xi_1(t), \xi_2(t), \xi_3(t))$;

(d) At any given time there are $N_m(i)$ particles from i -th component in the m -th cell; this number varies by computing its evolution in the following two stages:

Stage 1. The binary collisions in each cell are calculated without moving the particles.

Stage 2. The particles are moved with the new initial velocities acquired after collision.

We allow no collisions in this stage.

(e) Stages 1 and 2 are repeated until $t = T$;

(f) The important moments of the distribution function are calculated by averaging.

Let us now describe the two stages of the calculation in some details:

Stage 1. We use Bird's "no time counter" scheme [11], which involves the following two steps:

1.1. To compute the maximum number of binary collisions, we use the formulas

$$(3.1) \quad N_{c \max} = \frac{N_m(p)N_m(p-1)}{2V_{cell}} \langle \pi \sigma^2 |\xi_i - \xi_j|_{\max} \rangle \Delta t,$$

$$(3.2) \quad N_{c \max} = \frac{N_m(p)N_m(q)}{2V_{cell}} \langle \pi \sigma^2 |\xi_i - \xi_j|_{\max} \rangle \Delta t,$$

where $1 \leq p < q \leq 4$ and $V_{cell} = \Delta x \Delta y$ is the volume of the cell. We use formula (3.1) when we calculate collisions between molecules from one component and (3.2) between molecules of different components.

1.2. The pairs (i, j) of particles are chosen randomly with probability $|\xi_i - \xi_j| / \left(|\xi_i - \xi_j|_{\max} \right)$. If the collision event occurs, then the condition (2.4) or (2.5) have been checked. If the reaction event occurs, then the velocities after collision are calculated in the following way:

$$(3.3) \quad \underline{\xi}_k^* = P - M_l \sqrt{\frac{2}{\mu_{kl}} \left(\frac{\mu_{ij} g_{ij}^2}{2} + \varepsilon \right)} \underline{k},$$

$$\underline{\xi}_l^* = P + M_k \sqrt{\frac{2}{\mu_{kl}} \left(\frac{\mu_{ij} g_{ij}^2}{2} + \varepsilon \right)} \underline{k},$$

where $P = M_i \underline{\xi}_i + M_j \underline{\xi}_j$ and \underline{k} is vector randomly distributed on the unit sphere. If the reaction doesn't occur, then the velocities are calculated by (3.3) as $\varepsilon=0$, $k = i$ and $l = j$. Otherwise the velocities remain unchanged.

Stage 2. We compute the new positions and velocities of the particles using the equations

$$(3.4) \quad \begin{aligned} x_i^* &= x_i + \underline{\xi}_i \Delta t \\ \underline{\xi}_i^* &= \underline{\xi}_i \end{aligned}$$

as the particles which interact with the boundary are reflected spectrally.

4. Numerical results. The main differences in numerical results obtained between methods "A" and "B" are due primarily to the effects of interactions between particles of the type shown in Figure 1. The possibility for the chemical interaction at method "A" is close to 0 while at method "B" is close to 1.

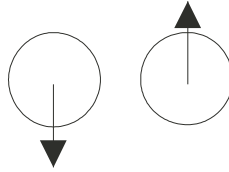


Fig. 1. Interaction particles

In our studies we fix the following parameters: $m_A = 1$, $m_B = 1$, $m_C = 1$, $m_D = 1$, $d_A = 1$, $d_B = 1$, $d_C = 1$, $d_D = 1$. These are model reactions. Our aim is to study the

influence of the probability for chemical reaction (2.4) and (2.5) on the process itself and to achieve this we use these model reactions.

Two main series of studies were made:

Cases I: $\varepsilon_f = 0.5$ while ε_b varies from 1 to 6.5 with step 0.5 (respectively ε varies from 0.5 to 6 with step 0.5).

Cases II: $\varepsilon = 0.5$ while ε_f varies from 0.5 to 5.0 with step 0.5 (respectively ε_b varies from 1.0 to 5.5 with step 0.5)

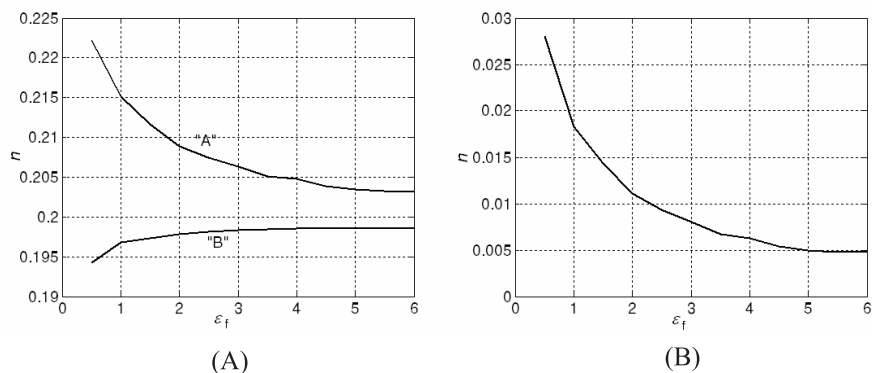


Fig. 2. Concentration n_A variation depending on the activation energy ε_f in cases I.
 (A) Concentration n_A values obtained by method "A" and "B".
 (B) Difference between concentrations n_A obtained by method "A" and "B"

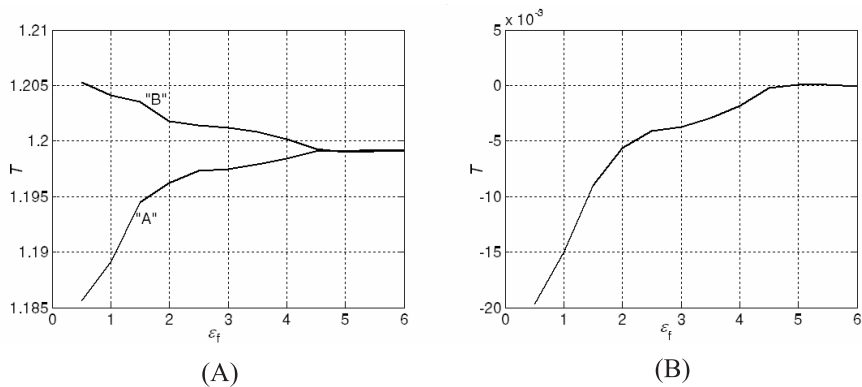


Fig. 3. Temperature variation depending on the activation energy ε_f in cases I.
 (A) Temperature values obtained by method "A" and "B".
 (B) Difference between temperature obtained by method "A" and "B"

By increasing the activity of the chemical reactions (Case I) the differences in temperature and concentration increases too, this confirms the adequacy of the two methods – Figure 2 and 3.

Methods A and B approximate the real process in cases II from "both sides" at activation energy increasing – Figure 4 and 5. When the chemical reaction activity

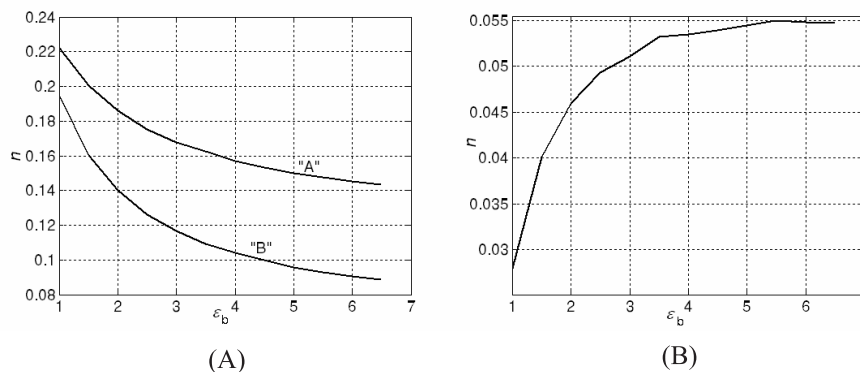


Fig. 4. Concentration n_A variation depending on the activation energy ε_f in cases II.
 (A) Concentration n_A values obtained by method "A" and "B".
 (B) Difference between concentrations n_A obtained by method "A" and "B"

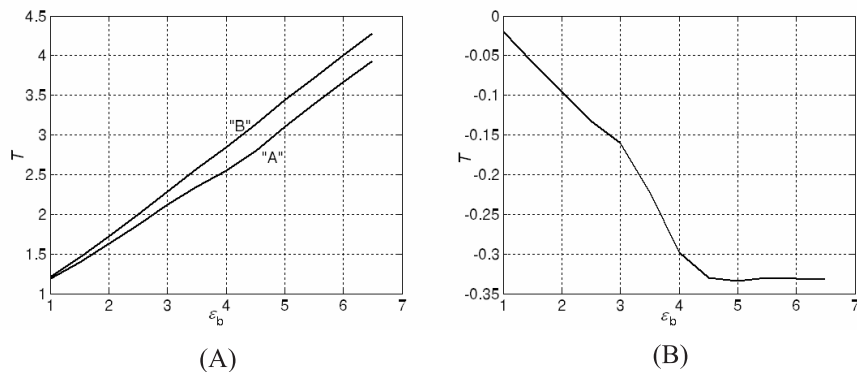


Fig. 5. Temperature variation depending on the activation energy ε_f in cases I.
 (A) Temperature values obtained by method "A" and "B".
 (B) Difference between temperature obtained by method "A" and "B"

decreases, the differences between the concentrations and the temperatures obtained by the two methods decrease.

An area of good coincidence of results obtained by method "A" and "B" is established. This can be used for a design of advanced MEMS – technology and equipment.

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ЧИСЛЕНО ИЗСЛЕДВАНЕ НА ХИМИЧЕСКИ РЕАКЦИИ ЧРЕЗ MONTE CARLO СИМУЛАЦИЯ

Добри Данков, Владимир Русинов, Мария Велинова, Жасмина Петрова

Изследвана е химическа реакция чрез два начина за моделиране на вероятността за химическа реакция използвайки Direct Simulation Monte Carlo метод. Изследван е порядък на разликите при температурите и концентрациите чрез тези начини. Когато активността на химическата реакция намалява, намаляват и разликите между концентрациите и температурите получени по двата начина.

Ключови думи: Механика на флуидите, Кинетична теория, Разреден газ, DSMC