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NUMERICAL EFFECTS AT MONTE CARLO SIMULATION OF CHEMICAL REACTIONS*

Dobry Dankov, Vladimir Rousinov

The chemical reaction is investigated by two methods for modelling of chemical reaction probability using Direct Simulation Monte Carlo method. The order of differences in the temperatures and the concentrations are investigated by these methods when the number of molecules and the order of the reaction components change.

1. Introduction. The effects of nonequilibrium physical chemistry processes are important for many applied problems. A chemical reaction produces nonequilibrium velocity distributions. These distributions in bimolecular reactions are described by semi-classical Bolzman equation. The first stage in modelling such a process is creating reliable mathematical models. At this time many approaches exist for the chemical reaction modelling. 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] showed 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] investigate the fast chemical reaction using Direct Simulation Monte Carlo method.

Two ways are used for modelling 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 modelling in rarefied gas by Direct Simulation Monte Carlo (DSMC) method.

When DSMC method is used, two kinds of errors exist. The first one is the statistical error. Chen and Boyd [8] estimate that this error can decrease by increasing of the collisions. The second error is of deterministic nature. 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 methods.

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2. Formulation of the problem. 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 4 semiclassical Boltzman equations [7]:

$$\frac{\partial}{\partial t} f_i = J_i^{el} + J_i^r, \quad i = A, B, C, D \tag{1}$$

where

$$J_i^{el} = \sum_{j=1}^{4} J_{ij}^{ij} = \sum_{j=1}^{4} \int \left(f_i^* f_j^* - f_i f_j \right) P_{ij}^{ij} g_{ij} \sigma \left(g_{ij}, \Omega \right) d\Omega d\vec{v}_j, \tag{2}$$

$$J_i^r = \sum_r {}^r J_{ij}^{kl} = \sum_r \int \left(f_k^* f_l^* - f_i f_j \right) P_{ij}^{kl} g_{ij} \sigma \left(g_{ij}, \Omega \right) d\Omega d\vec{v}_j, \tag{3}$$

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

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

$$\overset{r\,kl}{P_{ij}} = \begin{cases} 1, \mu_{ij} \left(\vec{g}_{ij}, \vec{k}_{ij} \right)^2 / 2 \geq \varepsilon_f \\ 0, \mu_{ij} \left(\vec{g}_{ij}, \vec{k}_{ij} \right)^2 / 2 < \varepsilon_f \end{cases} \tag{4}$$

$$\overset{r\,kl}{P_{ij}} = \begin{cases} 1, \mu_{ij} g_{ij}^2 / 2 \geq \varepsilon_f \\ 0, \mu_{ij} g_{ij}^2 / 2 < \varepsilon_f \end{cases} \tag{5}$$

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

3. Methods of solution. (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, which involves the following two steps:

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

$$N_{c\max} = \frac{N_m(p) N_m(p-1)}{2 V_{cell}} \left\langle \pi \sigma^2 \left| \xi_i - \xi_j \right|_{\max} \right\rangle \Delta t, \tag{6}$$

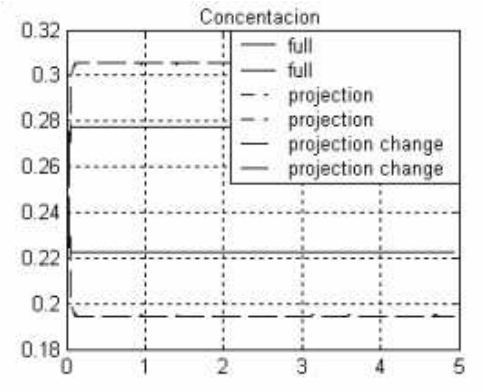

Fig. 1. Concentration variation along time

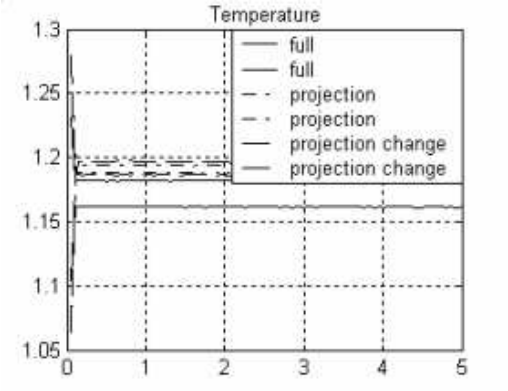

Fig. 2. Temperature variation along time

$$N_{c\max} = \frac{N_m(p)N_m(q)}{2V_{cell}} \left\langle \pi\sigma^2 \left|\xi_i - \xi_j\right|_{\max} \right\rangle \Delta t, \tag{7}$$

where $1 \le p < q \le 4$ and $V_{cell} = \Delta x \Delta y$ is the volume of the cell. We use formula (6) when we calculate collisions between molecules from one component and (7) between molecules of different components.

1.2. The pairs (i, j) of particles are chosen randomly with probability $\left|\underline{\xi_i} - \underline{\xi_j}\right| / \left(\left|\underline{\xi_i} - \underline{\xi_j}\right|\right)_{\max}$. If the collision event occurs, then the condition (4) or (5) has been checked. If the reaction event occurs, then the velocities after collision are calculated in the following way:

$$\underline{\xi_k^*} = P - M_l \sqrt{\frac{2}{\mu_{kl}} \left(\frac{\mu_{ij} g_{ij}^2}{2} + \varepsilon \right)} \underline{k}, \quad \underline{\xi_l^*} = P + M_k \sqrt{\frac{2}{\mu_{kl}} \left(\frac{\mu_{ij} g_{ij}^2}{2} + \varepsilon \right)} \underline{k}, \tag{8}$$

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

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

$$\underline{x_i^*} = \underline{x_i} + \underline{\xi_i} \Delta t, \quad \underline{\xi_i^*} = \underline{\xi_i} \tag{9}$$

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

4. Numerical results and discussion. In our studies we fix the following parameters: $m_A = 1$, $m_B = 1$, $m_C = 1$, $m_D = 1$, $d_A = 1$, $d_B = 1$, $4d_C = 1$, $d_D = 1$, $\varepsilon_b = 0.5$, $\varepsilon_f = 1$.

Numerical effects at the concentrations: Figure 1 shows the concentration values at different way of the probability calculation for the chemical reaction as the differences are due namely to the difference at the modelling. At the order change of the reaction component differences are of order 10^{-4}. When the molecular number changes (1 000 000 and 10 000 000), the differences are of the same order – Figure 3.

Numerical effects at the temperature: Figures 2 and 4 show the temperature values at different way of the probability calculation for the chemical reaction. Because

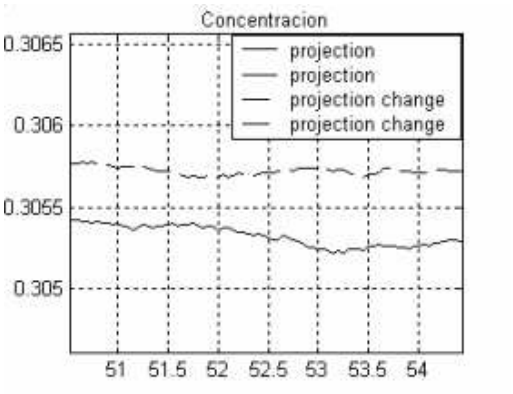

Fig. 3. Concentration variation along time at the stationary regime

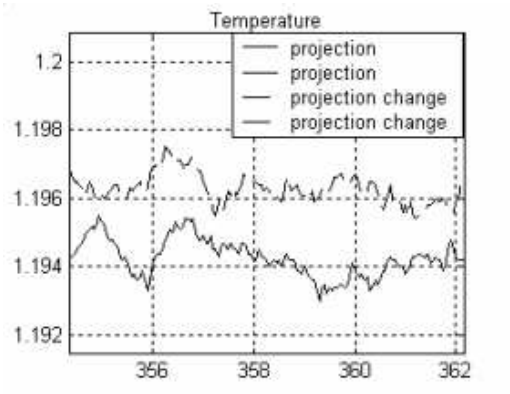

Fig. 4. Temperature variation along time at the stationary regime

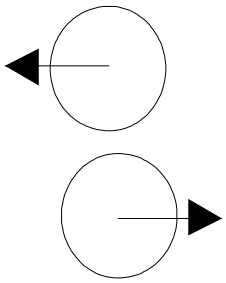

Fig. 5

of the commented difference in the concentration, different quantity of energy comes off at the transition regime which leads to differences at the stationary regime.

The main differences at the numerical modelling are due to the collision effect between particles of the type shown on Figure 5. At a modelling without projection, the chemical reaction probability for this collision is close to 1, while at collision with projection the probability is close to 0.

The aim of a further study is to estimate the cause for the differences at the increase of the reaction particle number.

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Dobri Dankov, Vladimir Rousinov
Institute of Mechanics
Acad. G. Bonchev Str., Bl. 4
Bulgarian Academy of Sciences
e-mail: dankov@imbm.bas.bg

ЧИСЛЕНИ ЕФЕКТИ ПРИ МОНТЕ КАРЛО СИМУЛАЦИЯ НА ХИМИЧЕСКА РЕАКЦИЯ

Добри Данков, Владимир Русинов

Изследвана е химическа реакция чрез два метода за моделиране на вероятността за химическа реакция, като се използва Direct Simulation Monte Carlo метод. Изследван е порядъкът на разликите при температурите и концентрациите чрез тези модели при промяна на броя на моделиращите частици и реда на взаимодействие на компонентите.