Numerical analysis of chemical reactions by Monte Carlo simulation and numerical resolve of the Boltzmann equation

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Abstract
The nonequilibrium velocity distributions and reaction rates are studied with numerical resolve of the semiclassical Boltzmann equation and Direct Monte Carlo Simulation. The order of differences in the temperatures and the concentrations are studied by these ways. When the chemical reaction activity decreases, the differences between the concentrations and the temperatures obtained by the different ways decrease.

Keywords: DSMC, chemical reaction, Boltzmann equation

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 present a lot of 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) have investigated 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 the collisions. The second error is deterministic. García 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.

Model chemical reactions are used in this paper. Our aim is to estimate the differences between these two ways for modeling the chemical reaction probability.

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 $\varepsilon_f$ and $\varepsilon_b$ 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 Boltzmann equations [7]:

\[ \frac{\partial}{\partial t} f_i = J_{i}^{el} + J_{i}^{r}, \quad i=A, B, C, D \]

when

\[ J_{i}^{el} = \sum_{j=1}^{4} J_{ij}^{el} = \sum_{j=1}^{4} \int \left( f_{i}^{*} f_{j}^{*} - f_{i} f_{j} \right) P_{ij}^{el} g_{ij} \sigma(g_{ij}, \Omega) d\Omega d\vec{v}_{j} \]

\[ J_{i}^{r} = \sum_{r} J_{ij}^{r} = \sum_{r} \int \left( f_{i}^{*} f_{j}^{*} - f_{i} f_{j} \right) P_{ij}^{el} g_{ij} \sigma(g_{ij}, \Omega) d\Omega d\vec{v}_{j} \]

where $f_{i}^{*} = f_{i}^{*}(t, \vec{v}_{i}^{*})$, $\vec{v}_{i}^{*}$ is the post collision molecular velocity, $g_{ij} = \left| \vec{v}_{i} - \vec{v}_{j} \right|$ is the relative velocity, and $\sigma(g_{ij}, \Omega) d\Omega$ is differential cross-section of the particle scatter within the solid angle $d\Omega$.

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

\[ P_{ij}^{el} = \begin{cases} 1, \mu_y g_{ij}^2 / 2 \geq \varepsilon_f \\ 0, \mu_y g_{ij}^2 / 2 < \varepsilon_f \end{cases} \]

\[ P_{ij}^{r} = \begin{cases} 1, \mu_y (\vec{g}_{ij}, \vec{k}_{ij})^2 / 2 \geq \varepsilon_f \\ 0, \mu_y (\vec{g}_{ij}, \vec{k}_{ij})^2 / 2 < \varepsilon_f \end{cases} \]

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

### 2.1 Numerical resolve of the semiclassical Boltzmann equation

If $m_A = m_C$ and $m_B = m_D$ and the model of the reaction is (2.4), the post-collision velocities can be written in the form: $\vec{v}_{i}^{*} = \vec{v}_{i} - 2 M_j (\vec{k}_{ij}, \vec{g}_{ij}) \vec{k}_{ij}$, $\vec{v}_{j}^{*} = \vec{v}_{j} + 2 M_i (\vec{k}_{ij}, \vec{g}_{ij}) \vec{k}_{ij}$ at elastic collisions; $\vec{v}_{i}^{*} = \vec{v}_{i} - M_j (q_{ij} + q_{ij}^\prime) \vec{k}_{ij}$, $\vec{v}_{j}^{*} = \vec{v}_{j} + M_i (q_{ij} + q_{ij}^\prime) \vec{k}_{ij}$ at chemical reaction. The five-dimensional integrals (2.2) and (2.3) can be reduced to three-dimensional and one-dimensional integrals [7]. Then, the integral (2.3) has the following form:

\[ J_{ij}^{r} = 2 \pi^2 \sigma_{ij}^{el} \int_{-1}^{1} \int_{-1}^{1} \int_{0}^{2\pi} \left[ f_{i}^{*} f_{j}^{*} - f_{i} f_{j} \right] P_{ij}^{el} v_{ij}^{2} g_{ij} d\vec{v}_{j} dxdy \]

\[ v_{ij}^{2} = v_{ij}^{2} + 2 M_j v_x (q_{ij} + q_{ij}^\prime) + M_j^2 (q_{ij} + q_{ij}^\prime)^2 \]

\[ v_{ij}^{2} = v_{ij}^{2} - 2 M_i v_x (q_{ij} + q_{ij}^\prime) + M_i^2 (q_{ij} + q_{ij}^\prime)^2 \]
\[ q_{ij} = v_j y - v_i x \]

\[ P_{ij}^{kl} = \begin{cases} 
1, & \mu_y q_{ij}^2 / 2 \geq \epsilon_s, s = f, b \\
0, & \mu_y q_{ij}^2 / 2 < \epsilon_s, s = f, b 
\end{cases} \]

The integrals \( J_{ij}^{kl} \) and \( J_{ij}^{kl*} \) can be written as a sum of two integrals: \( J_{ij}^{kl} = J_{ij}^{kl} - J_{ij}^{kl*} \),

\[ J_{ij}^{kl} = J_{ij}^{kl} - J_{ij}^{kl*} \]

(2.7)

and

\[ I_{ij} = J_{ij}^{kl'} + J_{ij}^{kl} = \int \frac{2\pi^2 \sigma_y^2}{3v_i} \left( v_i + v_j \right)^3 + \frac{v_i - v_j}{3v_i} v_j f_i(v_j) f_j(v_i) dv_j, v_i \neq 0 \]

\[ 4\pi^2 \sigma_y^2 \int_0^\infty f_i(0) f_j(v_j) dv_j, v_i = 0 \]

The distribution function \( f = f(t,v) \) is calculated in velocity space in the interval \( v \in [0;V] \) with step \( \Delta v \) and at moment \( t + \Delta t \) by the Euler scheme. The one dimensional integral of the direct collisions is calculated by the trapezoidal rule and the tree-dimensional integral by Monte Carlo method.

2.2 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 \( \Delta t \);

(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 \( x_i(t) = (x_i(t), y_i(t)) \) and velocities \( \xi_i(t) = (\xi_1(t), \xi_2(t), \xi_3(t)) \);

(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. No collisions are allowed 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. Bird’s “no time counter” scheme is used [11], which involves the following two steps:

1.1 To compute the maximum number of binary collisions the following formula is used:

\[ N_{c,\text{max}} = \frac{N_m(p) N_m(p-1)}{2 V_{\text{cell}}} \left( \pi \sigma^2 \left| \bar{\xi}_i - \bar{\xi}_j \right|_{\text{max}} \right) \Delta t \]
\begin{equation}
N_{c_{\text{max}}} = \frac{N_m(p)N_m(q)}{2V_{cell}} \left\{ \pi \sigma^2 \left| \xi_i - \xi_j \right|_{\text{max}} \right\} \Delta t,
\end{equation}

where $1 \leq p < q \leq 4$ and $V_{cell} = \Delta x \Delta y$ is the volume of the cell. The formula (3.1) is used to 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 $\frac{\left| \xi_i - \xi_j \right|}{\left\{ \left| \xi_i - \xi_j \right| \right\}_{\text{max}}}$. If the collision event occurs, the condition (2.4) or (2.5) is checked. If the reaction event occurs, the velocities after collision are calculated in the following way:

\begin{equation}
\xi_{i_{\text{new}}}^* = P - M_i \sqrt{\frac{2}{\mu_{ii}} \left( \frac{\mu_y g_{ij}^2}{2} + \varepsilon \right) k},
\end{equation}

\begin{equation}
\xi_{j_{\text{new}}}^* = P + M_k \sqrt{\frac{2}{\mu_{kl}} \left( \frac{\mu_y g_{ij}^2}{2} + \varepsilon \right) k},
\end{equation}

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

Stage 2. The new positions and velocities of the particles are computed by using the equations:

\begin{equation}
x_{i_{\text{new}}}^* = x_i + \xi_{i_{\text{new}}}^* \Delta t,
\end{equation}

\begin{equation}\xi_{i_{\text{new}}}^* = \xi_{i_{\text{old}}}^* \end{equation}

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

3. 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 Fig. 1. The possibility for the chemical interaction at method “A” is close to 0 while at method “B” is close to 1.

![Fig1. Interaction particles.](image)

The following parameters have been fixed in our studies: $m_A=1$, $m_B=1$, $m_C=1$, $m_D=1$, $d_A=1$, $d_B=1$, $d_C=1$, $d_D=1$. 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, these model reactions have been used.

Two main series of studies have been made:
Cases I: $\varepsilon=0.5$ while $\varepsilon_f$ varies from 0.5 to 5.0 with step 0.5 (respectively $\varepsilon_b$ varies from 1.0 to 5.5 with step 0.5).

Cases II: $\varepsilon_f=0.5$ while $\varepsilon_b$ varies from 1 to 6.5 with step 0.5 (respectively $\varepsilon$ varies from 0.5 to 6 with step 0.5).

4. Conclusions

Methods A and B approximate the real process in cases I from "both sides" at activation energy increasing – Fig. 2 and Fig. 3. When the chemical reaction activity decreases, the differences between the concentrations and the temperatures obtained by the two methods decrease. By increasing the activity of the chemical reactions (Case II) the differences in temperature and concentration increases too. Thus the adequacy of the two methods is confirmed – Fig. 3 and Fig.4.

The results obtained by DSMC method and the numerical resolve of the semiclassical Boltzmann equation are in an excellent agreement for all studied cases for method “B”.

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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References