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ANALYSIS OF NONEQUILIBRIUM EFFECTS IN A BIMOLECULAR CHEMICAL REACTION IN A DILUTE GAS*

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We analyze a thermally activated bimolecular reaction in a dilute gas proceeding with introduction of the Prigogine–Xhrouet model (PX) for the reactive cross section. We use the Shizgal–Karplus perturbation method of solution of the Boltzmann equation for reactions $A + A \to B + B$ and $A + A \rightleftarrows B + B$ to obtain the analytical expressions for the nonequilibrium temperatures of reagents and for the rate of chemical reaction. We present the results obtained within one and two Sonine polynomials approximations. The rate constant of chemical reaction depends on concentration of products for the first reaction only and for the second reaction is constant. The analytical results for the temperature of the reagent A and its value in the beginning of reaction for the product B are compared with those obtained from the Monte Carlo computer simulations with use of the Bird method. It is shown that the nonequilibrium effects in Shizgal–Karplus temperatures and in decrease of the chemical constant rate are more pronounced than for the lines-of-centers model. For the PX model the rate constant can be decreased even 4 times.

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1. Introduction

The nonequilibrium effects connected with proceeding of a bimolecular chemical reaction in a dilute gas were first analyzed by Prigogine and Xhrouet [1]. These authors [1] using the perturbation method [2] solved the Boltzmann equation for the early stages of reaction in which the role of products could be neglected. The early stages of chemical reaction were also analyzed by Present [3, 4] who introduced the line-of-centers model for this purpose. In all those papers [1, 3, 4] one temperature of reacting system was introduced because the products were neglected. As shown by Shizgal and Karplus [5, 6], in an analysis of further stages of chemical reaction the role of products becomes important. In this case the reagents can have different nonequilibrium temperatures. Recently, Shizgal and Napier [7] have analyzed carefully the possibilities of solutions of the Boltzmann equation for reactions proceeding in various conditions and described the differences between nonequilibrium effects in the early and further stages of chemical reaction. In Refs. [3–7], as well as in many other papers [8–22] the line-of-centers model was introduced because this model is simple and gives reasonable results. However, another model introduced in the first paper [1] has not been used for the description of the further stages of chemical reaction yet.

It is important that for the stages of reaction in which the reaction proceeds slow enough interesting analytical results can be obtained. Namely, the relative decrease of the forward chemical reaction rate depends on the molar fraction of the product and, on the contrary, for the overall reaction rate such a decrease is constant. This problem was analyzed in some recent papers for the line-of-centers model [23–26] and also for the reverse line-of-centers model [26] for which the Arrhenius activation energy can be very small and even negative [27–30].

The aim of this paper is to derive some analytical equations for the model originally used by Pigogine and Xhrouet [1], *i.e.* the expressions for the nonequilibrium Shizgal–Karplus temperatures and for the relative decrease of the rate constant of chemical reaction. We derive these results in the same way as used previously [23] for the line-of-centers model. We verify the new analytical results by the Monte Carlo simulations in a similar way as that presented in Ref. [23].

Our paper is organized as a follows: in Sec. 2 we describe definitions of quantities used to characterize the nonequilibrium effects; in Sec. 3 we formulate the Boltzmann equation for the chemical reactions considered; in Sec. 4 we present the perturbation solution of the Boltzmann equation obtained within the Shizgal–Karplus method; in Sec. 5 we show the analytical expressions describing nonequilibrium effects on temperature of components and in Sec. 6 such expressions for the rate of chemical reaction; in Sec. 7

we characterize the reacting system used for Monte Carlo simulations and compare the numerical results obtained from these simulations with the analytical results. In Sec. 8 we discuss the results obtained.

2. Definitions of quantities describing nonequilibrium effects of reaction

We analyze the bimolecular chemical reactions

$$A + A \to B + B\,, \tag{2.1}$$

$$A + A \rightleftarrows B + B\,. \tag{2.2}$$

In Eq. (2.1) we take into consideration only the forward reaction, whereas in Eq. (2.2) we also include the reverse reaction. We introduce the nonequilibrium value of the rate of forward chemical reaction in the usual way

$$v_{A\mathrm{f}} = -\left(\frac{dn_A}{dt}\right)_{\mathrm{f}} = \iiint f_{A1} f_{A2} \sigma_0 \, g \, d\Omega \, d\boldsymbol{c}_{A1} \, d\boldsymbol{c}_{A2}\,, \tag{2.3}$$

where the index f is introduced to distinguish the forward reaction from the reverse one for which the index r will be introduced; n_A is the number density, f_{A1} and f_{A2} are the velocity distribution functions of two colliding molecules A, σ_0 is the differential reactive cross section, Ω is the solid angle, $\boldsymbol{c}_{A1}$, $\boldsymbol{c}_{A2}$ and g denote the velocities and relative velocity, respectively. The equilibrium value of $v_{A\mathrm{f}}$ is

$$v_{A\mathrm{f}}^{(0)} = \iiint f_{A1}^{(0)} f_{A2}^{(0)} \sigma_0 \, g \, d\Omega \, d\boldsymbol{c}_{A1} \, d\boldsymbol{c}_{A2}\,, \tag{2.4}$$

where $f^{(0)}$ is the Maxwell–Boltzmann velocity distribution function at temperature T

$$f_A^{(0)} = n_A \left(\frac{m_A}{2\pi kT}\right)^{3/2} \exp\left(-\frac{m_A c_A^2}{2kT}\right), \tag{2.5}$$

where m_A denotes the molecular mass and k is the Boltzmann constant. These equations can be also used for the component B if the indices A are replaced by indices B. However, it is important to take into consideration that the total rate of chemical reaction is v_A which can be expressed as

$$v_A = v_{A\mathrm{f}} + v_{A\mathrm{r}} = v_{A\mathrm{f}} - v_{B\mathrm{f}}\,, \tag{2.6}$$

$$v_A^{(0)} = v_{A\mathrm{f}}^{(0)} + v_{A\mathrm{r}}^{(0)} = v_{A\mathrm{f}}^{(0)} - v_{B\mathrm{f}}^{(0)}\,. \tag{2.7}$$

We define also the following useful quantities

$$\eta_{R\mathrm{f}} = 1 - \frac{v_{R\mathrm{f}}}{v_{R\mathrm{f}}^{(0)}} \qquad (R = A, B)\,, \tag{2.8}$$

$$\eta_R = 1 - \frac{v_R}{v_R^{(0)}} \qquad (R = A, B)\,, \tag{2.9}$$

which are very convenient for a description of nonequilibrium corrections to the rate of chemical reaction.

We introduce as Shizgal and Karplus [5] the temperature of components

$$T_R = T_R^{\mathrm{SK}} = \frac{2}{3n_R k} \int f_R \frac{1}{2} m_R\, c_R^2\, d\boldsymbol{c}_R \qquad (R = A, B) \tag{2.10}$$

and the temperature of the system is related to these temperatures by

$$T = \frac{n_A T_A + n_B T_B}{n_A + n_B}\,. \tag{2.11}$$

The change of temperature T_R due to nonequilibrium effects can be calculated as

$$\Delta T_R = T - T_R^{\mathrm{SK}} \qquad (R = A, B)\,, \tag{2.12}$$

where T_R^{SK} is the nonequilibrium temperature (see Eq. (2.10)). As in our previous papers we introduce the indices SK to emphasize that this is the Shizgal–Karplus temperature. The quantities η (see Eqs. (2.8) and (2.9)) and ΔT_R (see Eq. (2.12)) can be used to describe simple analytical expressions obtained from the perturbation theory. In order to get these expressions we need to solve the Boltzmann equation.

3. The Boltzmann equation

We assume that the reagents are hard spheres and that their masses and diameters do not change when the reaction proceeds

$$m_A = m_B = m \qquad d_A = d_B = d\,, \tag{3.1}$$

where d denotes the diameter. After taking into consideration Eq. (3.1) we write down the Boltzmann equation [22, 23] for reaction (2.2) for the component A in the following form

$$\frac{\partial f_A}{\partial t} = I_{\mathrm{el}} + I_{\mathrm{re}} \tag{3.2}$$

where t is the time and

$$\begin{aligned} I_{\text{el}} &= \int\!\!\int (f'_{A1} f'_{A2} - f_{A1} f_{A2})\, \sigma_{AA} g\, d\Omega dc_2 \\ &+ \int\!\!\int (f'_A f'_B - f_A f_B)\, \sigma_{AB} g\, d\Omega dc_2 \,, \end{aligned} \tag{3.3}$$

$$I_{\text{re}} = \int\!\!\int (f_{B1} f_{B2} - f'_{A1} f'_{A2})\, \sigma_0\, g\, d\Omega\, d\boldsymbol{c}_2 \,, \tag{3.4}$$

where f'_i are the velocity distribution functions for i-th component after collisions, respectively, σ_{ij} are the differential elastic cross sections for collisions between spheres i and j, $\boldsymbol{c}_2$ is shortly written to denote the velocity of second colliding molecule. It is worthwhile to observe that in Eq. (3.2) the post-collisional values of f'_i appear because of the reasons discussed in Refs. [1, 2]. The Boltzmann equation for the change of f_B in time may be written in the same way after changing the appropriate indices only.

We neglect all heat effects of this reaction, *i.e.* we assume that this reaction is neither exothermal nor endothermal one and also neglect the heat effects connected with internal degrees of freedom. However, we take into consideration that, even in the simplest models of reactive collisions, the particles of reagents need not have the same average kinetic energies.

For the elastic differential cross sections σ_{AA} and σ_{AB} we use the expression

$$\sigma_{AA} = \sigma_{AB} = \frac{1}{4}\, d^2. \tag{3.5}$$

We introduce the Prigogine–Xhrouet model [1] for the differential reactive cross section for collisions between the molecules A as well as for collisions between the molecules B

$$\sigma_0 = \begin{cases} 0 & g \le g_0 \\ \frac{1}{4} s_F d^2 & g > g_0 \,, \end{cases} \tag{3.6}$$

where s_F is the steric factor and g denotes the threshold relative velocity of colliding spheres. This velocity is simply related to the threshold energy E_0

$$E_0 = \frac{m g_0^2}{4}\,. \tag{3.7}$$

We introduce the dimensionless reduced threshold energy ε_0 as

$$\varepsilon_0 = \frac{E_0}{kT}\,. \tag{3.8}$$

This quantity similarly as s_F will appear in our final equations.

4. Solution of the Boltzmann equation

We solve the Boltzmann equation by the perturbation method described by Shizgal and Karplus [5, 6] and developed by Shizgal and Napier [7]. We replace f_A by $f_A^{(0)}$ in the left hand side of Eq. (3.2) and in Eq. (3.4) by $f_A^{(0)}$. We introduce in Eq. (3.3) the nonequilibrium velocity distribution function as

$$f_A = f_A^{(0)} + f_A^{(1)} = f_A^{(0)}(1 + \psi_A)\,. \tag{4.1}$$

The quantity ψ_A is expanded in the Sonine polynomials [5, 15]

$$\psi_A = \sum_i a_A^{(i)} S_{1/2}^{(i)}(\mathcal{C}_A^2)\,, \tag{4.2}$$

where

$$\mathcal{C}_A^2 = \frac{m_A c_A^2}{2kT}\,. \tag{4.3}$$

After taking into account that the temperature T of the system does not change when the reaction proceeds and $dT/dt = 0$ we can write

$$\frac{\partial f_A^{(0)}}{\partial t} = \frac{\partial f_A^{(0)}}{\partial n_A}\left(\frac{dn_A}{dt}\right)^{(0)} = \frac{f_A^{(0)}}{n_A}\left(\frac{dn_A}{dt}\right)^{(0)}, \tag{4.4}$$

where

$$\begin{aligned}\left(\frac{dn_A}{dt}\right)^{(0)} = &- \iiint f_{A1}^{(0)} f_{A2}^{(0)} \sigma_0 g\, d\Omega\, d\boldsymbol{c}_2\, d\boldsymbol{c}_1 \\ &+ \iiint f_{B1}^{(0)} f_{B2}^{(0)} \sigma_0 g\, d\Omega\, d\boldsymbol{c}_2\, d\boldsymbol{c}_1\,.\end{aligned} \tag{4.5}$$

In this way taking into account Eqs. (2.5), (4.1) and (4.4) we write Eq. (3.2) in the following form

$$\begin{aligned}&\frac{f_A^{(0)}}{n_A}\left(\frac{dn_A}{dt}\right)^{(0)} + \iint f_{A1}^{(0)} f_{A2}^{(0)} \sigma_0 g d\Omega d\boldsymbol{c}_2 - \iint f_{B1}^{(0)} f_{B2}^{(0)} \sigma_0 g\, d\Omega\, d\boldsymbol{c}_2 \\ &= \iint f_{A1}^{(0)} f_{A2}^{(0)} (\psi'_{A1} - \psi'_{A2} - \psi_{A1} - \psi_{A2}) \sigma_{AA} g\, d\Omega\, d\boldsymbol{c}_2 \\ &+ \iint f_{A1}^{(0)} f_{A2}^{(0)} (\psi'_{A1} - \psi_{A1}) \sigma_{AB} g\, d\Omega\, d\boldsymbol{c}_2 \\ &+ \iint f_{A1}^{(0)} f_{B2}^{(0)} (\psi'_{B1} - \psi_{B1}) \sigma_{AB} g\, d\Omega\, d\boldsymbol{c}_2\,,\end{aligned} \tag{4.6}$$

where the terms $\psi_1\psi_2$ as smaller than ψ_1 or ψ_2 are neglected. We solve Eq. (4.6) within one and two Sonine polynomials expansion for the velocity distribution function. We begin with the one Sonine polynomials approximation

$$\psi_{A1} = a_1^{(A)}(1) S_{1/2}^{(1)}(\mathcal{C}_A^2) = a_1^{(A)}(1) S_A^{(1)}\,, \tag{4.7}$$

where we introduce $S_A^{(1)}$ to write the first Sonine polynomial in a shorter way.

We define very convenient quantities A in a following way

$$A_{Ri} = \iiint f_{R1}^{(0)} f_{R2}^{(0)} S_R^{(i)} \sigma_0 g \, d\Omega \, d\boldsymbol{c}_2 \, d\boldsymbol{c}_1\,, \qquad (R = A, B)\,, \quad (i = 0, 1, 2)\,. \tag{4.8}$$

For the Prigogine–Xhrouet model (see Eqs. (3.6)–(3.8)) it can be easily calculated that

$$\begin{aligned} A_{R0} &= 4 s_F n_R^2 d^2 \left(\frac{\pi k T}{m}\right)^{1/2} (\varepsilon_0 + 1) \exp(-\varepsilon_0)\,, \\ A_{R1} &= -2 s_F n_R^2 d^2 \left(\frac{\pi k T}{m}\right)^{1/2} \varepsilon_1 \exp(-\varepsilon_0)\,, \\ A_{R2} &= -\frac{1}{2} s_F n_R^2 d^2 \left(\frac{\pi k T}{m}\right)^{1/2} \varepsilon_2 \exp(-\varepsilon_0)\,, \qquad (R = A, B)\,, \end{aligned} \tag{4.9}$$

where

$$\begin{aligned} \varepsilon_1 &= \varepsilon_0^2 + \frac{1}{2}\varepsilon_0 + \frac{1}{2}\,, \\ \varepsilon_2 &= -\varepsilon_0^3 + 2\varepsilon_0^2 + \frac{1}{4}\varepsilon_0 + \frac{1}{4}\,. \end{aligned} \tag{4.10}$$

From Eqs. (4.6) and (4.7) after using the definition (4.8) in a typical way (see Refs. [16] and [21]) we obtain

$$A_{A1} - \delta_{\rm cr} A_{B1} = a_1^{(A)}(1) n_A^2 \left\{ S_A^{(1)}, S_A^{(1)} \right\} + a_1^{(B)}(1) n_A n_B \left\{ S_A^{(1)}, S_B^{(1)} \right\}\,, \tag{4.11}$$

where $\delta_{\rm cr}$ equals 1 if the reverse reaction is taken into account and 0 if not, $\{,\}$ are the brace symbols introduced by Chapman and Cowling [2] and particularly analyzed by Shizgal and Karplus [5]. As shown in Ref. [5]

$$n_A a_1^{(A)}(1) + n_B a_1^{(B)}(1) = 0\,, \tag{4.12}$$

$$\left\{ S_A^{(1)}, S_A^{(1)} \right\} + \left\{ S_A^{(1)}, S_B^{(1)} \right\} = 0\,. \tag{4.13}$$

From Eqs. (4.11)–(4.13) we get

$$A_{A1} - \delta_{\rm cr} A_{B1} = a_1^{(A)}(1) \left(n_A n_B + n_A^2 \right) \left\{ S_A^{(1)}, S_A^{(1)} \right\}\,. \tag{4.14}$$

As follows from Tables I and II of Ref. [5]

$$\{S_A^{(1)}, S_A^{(1)}\} = -4d^2 \left(\frac{\pi kT}{m}\right)^{1/2} . \tag{4.15}$$

After taking into account Eqs. (4.9), (4.14) and (4.15) we can write

$$a_1^{(A)}(1) = \frac{1}{2} s_F x_A \left(1 - \delta_{\rm cr} \frac{x_B^2}{x_A^2}\right) \varepsilon_1(-\varepsilon_0) , \tag{4.16}$$

where x_A and x_B are the molar fractions. In order not to write such expressions as Eq. (4.16) separately for reactions (2.1) and (2.2) we treat them as two cases-c:
1. c = n corresponds to neglecting (n) of the reverse reaction, whereas
2. c = r to taking into consideration the reverse (r) reaction. It means that for reactions (2.1) and (2.2) $\delta_{\rm cr}$ is $\delta_{\rm nr}=0$ and $\delta_{\rm rr}=1$, respectively. In order to solve Eq. (4.6) within two Sonine polynomials approximation we introduce instead of Eq. (4.7) the following approximation for ψ

$$\begin{aligned} \psi_{A1}(2) &= a_1^{(A)}(2) S_{1/2}^{(1)}(\mathcal{C}_A^2) + a_2^{(A)}(2) S_{1/2}^{(2)}(\mathcal{C}_A^2) \\ &= a_1^{(A)}(2) S_A^{(1)} + a_2^{(A)}(2) S_A^{(2)} . \end{aligned} \tag{4.17}$$

Then using the typical method of solution mentioned above we obtain instead of Eq. (4.11) a set of two linear equations

$$\begin{aligned} A_{A1} - \delta_{\rm cr} A_{B1} &= n_A n_B \Bigg[a_1^{(A)}(2) \left(\left\{ S_A^{(1)}, S_A^{(1)} \right\} - \left\{ S_A^{(1)}, S_B^{(1)} \right\} \frac{n_A}{n_B} \right) \\ &\qquad + a_2^{(A)}(2) \left(\left\{ S_A^{(1)}, S_A^{(1)} \right\} - \left\{ S_A^{(1)}, S_B^{(1)} \right\} \frac{n_A}{n_B} \right) \Bigg] , \\ A_{A2} - \delta_{\rm cr} A_{B2} &= n_A n_B \Bigg[a_1^{(A)}(2) \left(\left\{ S_A^{(2)}, S_A^{(1)} \right\} - \left\{ S_A^{(2)}, S_B^{(1)} \right\} \frac{n_A}{n_B} \right) \\ &\qquad + a_2^{(A)}(2) \left(\left\{ S_A^{(2)}, S_A^{(2)} \right\} - \left\{ S_A^{(2)}, S_B^{(2)} \right\} \frac{n_A}{n_B} \right) \Bigg] . \end{aligned} \tag{4.18}$$

From Eqs. (4.18) after making a similar derivation as that for obtaining Eq. (4.16) from Eq. (4.11) we get

$$\begin{aligned} a_1^{(A)}(2) &= \frac{1}{60} s_F x_A \left(1 - \delta_{\rm cr} \frac{x_B^2}{x_A^2}\right) \varepsilon_3 \exp(-\varepsilon_0) , \\ a_2^{(A)}(2) &= \frac{1}{15} s_F x_A \left(1 - \delta_{\rm cr} \frac{x_B^2}{x_A^2}\right) \varepsilon_4 \exp(-\varepsilon_0) , \end{aligned} \tag{4.19}$$

where

$$\begin{aligned}\varepsilon_3 &= -\varepsilon_0^3+33\varepsilon_0^2+\frac{63}{4}\varepsilon_0+\frac{63}{4}\,,\\ \varepsilon_4 &= -\varepsilon_0^3+3\varepsilon_0^2+\frac{3}{4}\varepsilon_0+\frac{3}{4}\,.\end{aligned} \tag{4.20}$$

Eqs. (4.16) and (4.19) are very useful in derivation of final analytical equations. For the component B we can use Eq. (4.12) in order to get $a_1^{(B)}(1)$.

5. Nonequilibrium effects in temperatures of components

We can use Eqs. (4.16) and (4.19) to calculate the nonequilibrium temperature T_A.

$$T_A^{\mathrm{SK}}(i)=T_A(i)=T\left[1-a_1^{(A)}(i)\right] \qquad (i=1,2)\,, \tag{5.1}$$

where i is introduced to distinguish the Shizgal–Karplus temperature $T^{\mathrm{SK}}(1)$ obtained within one Sonine polynomials approximation from that $T_A^{\mathrm{SK}}(2)$ obtained within two Sonine polynomials approximation. We also introduce

$$\Delta T_A(i)=T-T_A^{\mathrm{SK}}(i) \qquad (i=1,2)\,. \tag{5.2}$$

From Eqs. (5.1) and (5.2) after introduction of Eq. (4.16) we can write for the one Sonine polynomials approximation

$$\Delta T_A(1)=T-T_A^{\mathrm{SK}}(1)=\frac{1}{2}s_F T x_A\left(1-\delta_{\mathrm{cr}}\frac{x_B^2}{x_A^2}\right)\varepsilon_1\exp(-\varepsilon_0)\,. \tag{5.3}$$

Similarly, from Eqs. (5.1) and (5.2), after using Eq. (4.19) we get the following expression for two Sonine polynomials approximation

$$\Delta T_A(2)=\frac{1}{60}s_F T x_A\left(1-\delta_{\mathrm{cr}}\frac{x_B^2}{x_A^2}\right)\varepsilon_3\exp(-\varepsilon_0)\,. \tag{5.4}$$

It is important to take into consideration that if we neglect the reverse reaction $\delta_{\mathrm{cr}}=0$ we have relations for $\Delta T_A(i)$ in a simplified form (see Eqs. (5.3) and (5.4)), namely the effect of concentration would be proportional to x_A. In result the appropriate ratios $\Delta T_A/Ts_F x_A$ are functions of ε_0 only. In Fig. 1 we present these ratios in a form of two curves. Additionally, we introduce for a comparison two curves which represent such expressions for the line-of-centers model (LC) (see Eqs. (35) and (36) from Ref. [23]). For the LC model the appropriate reduced threshold energy is denoted ε^*.

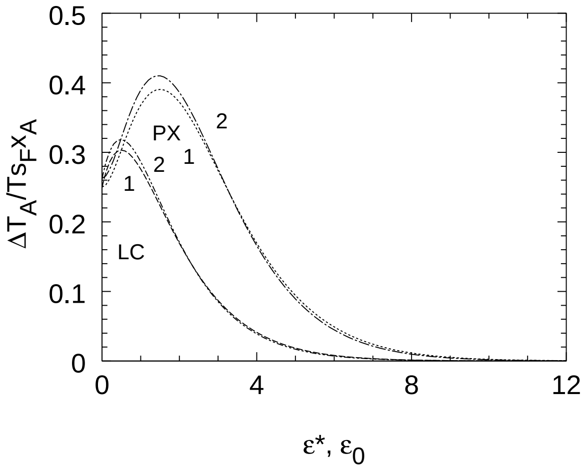

Fig. 1. Relative decrease of temperature T_A for the forward reaction (2.1) presented in a reduced form as $\Delta T_A/Ts_Fx_A$ calculated for the PX model from Eqs. (5.3) and (5.4) with $\delta_{\rm cr}=0$ as function of the reduced threshold energy ε_0 and such results for the LC model as a function of ε^*.

We see that we have four simple expressions for $\Delta T_A(i)$: Eqs. (5.3) and (5.4) with $\delta_{\rm cr}$ equal to 0 (if the reverse reaction is not considered) and to 1 otherwise. For these four cases comparisons of theoretical results for T_A and those obtained from the computer simulations will be presented.

Interesting effects can be observed if the early stages of chemical reaction are considered. As it follows from Refs. [15, 17] the largest value of T_B is in the very beginning of reaction when x_B is nearly equal to 0.

In order to derive the expression for the initial value of T_B we take into consideration that in the very beginning of reaction for $t=0$ and for a very small time $t=\tau$ we can write

$$n_A(0)=n\,, \qquad\qquad T_A(0)=T\,, \tag{5.5}$$

$$n_A(\tau)=n+\frac{dn_A}{dt}\tau\,, \qquad\qquad n_B(\tau)=-\frac{dn_A}{dt}\tau\,, \tag{5.6}$$

$$T_A(\tau)=T+\frac{dT_A}{dt}\tau\,. \tag{5.7}$$

After taking into account that $(n_A+n_B)T$ is constant and the square terms with τ are much smaller than those with τ from we can use Eqs. (5.5)–(5.7), (2.11), (2.3), (4.9) as well as the following Shizgal's [31] result

$$\frac{dT_A}{dt}=\frac{2}{3}\frac{T_A(0)}{n(0)}A_{A1} \tag{5.8}$$

and we can derive

$$T_B(0) = \lim_{x_B \to 0} T_B = T\left(1 - \frac{2}{3}\frac{A_{A1}}{A_{A0}}\right) . \tag{5.9}$$

From this result (discussed also in Sec. 8) for the PX model (see Eqs. (4.9)) it follows

$$\Delta T_B(0) = T - T_B(0) = \lim_{x_B \to 0} \Delta T_B = -\frac{1}{3} T \frac{\varepsilon_1}{\varepsilon_0 + 1} . \tag{5.10}$$

In the further stages of chemical reaction we can calculate T_B from the appropriate expression for T_A if we use Eq. (2.11). We can use Eqs. (5.3) and (5.4) for four cases mentioned above in order to have expressions for the nonequilibrium effects on temperature for the component B. We present these expressions in the following way:

(1) For one Sonine approximation with the reverse reaction neglected

$$\Delta T_B(1) = T - T_B^{\mathrm{SK}}(1) = -\frac{1}{2} s_F T \left(\frac{(1 - x_B)^2}{x_B}\right) \varepsilon_1 \exp(-\varepsilon_0) . \tag{5.11}$$

From Eq. (5.11) we see that for very small molar fraction of B this effect could be very large. It means that the results of the perturbation method cannot be analyzed in the ranges of very small x_B. We analyze this problem after showing the next 3 equations for ΔT_B.

(2) For two Sonine approximation with the reverse reaction neglected

$$\Delta T_B(2) = -\frac{1}{60} s_F T \left(\frac{(1 - x_B)^2}{x_B}\right) \varepsilon_3 \exp(-\varepsilon_0) . \tag{5.12}$$

(3) For one Sonine approximation with the reverse reaction taken into account

$$\Delta T_B(1) = -\frac{1}{2} s_F T \left(\frac{(1 - x_B)}{x_B} - 1\right) \varepsilon_1 \exp(-\varepsilon_0) . \tag{5.13}$$

(4) For two Sonine approximation with the reverse reaction taken into account

$$\Delta T_B(2) = -\frac{1}{60} s_F T \left(\frac{(1 - x_B)}{x_B} - 1\right) \varepsilon_3 \exp(-\varepsilon_0) . \tag{5.14}$$

It is possible that in some cases the chemical reaction proceeds so fast that the perturbation solution of the Boltzmann equation can not be used. In these cases it is very useful to observe that if the chemical reaction proceeds T_B decreases. Therefore, we can write

$$T_B^{\mathrm{SK}} < T_B(0) . \tag{5.15}$$

It is sufficient to compare the appropriate expression for ΔT_B to see the range of x_B in which the solutions obtained can be valid.

We analyze such a range of x_B for the case 3. in which the reverse reaction is taken into account for the solution within one Sonine polynomial approximation. From Eqs. (5.10), (5.13) and (5.15) it can be derived that

$$\left(2+\frac{2}{3}\frac{\exp(\varepsilon_0)}{s_F(\varepsilon_0+1)}\right)^{-1} < x_B < \frac{1}{2}\,. \tag{5.16}$$

Such inequalities for the ranges of x_B in which the results from the perturbation solution are valid, can be also simply derived for the cases 1, 2 and 4 if we use for a comparison of $T_B(0)$ with T_B calculated from Eqs. (5.11), (5.12) and (5.14), respectively.

6. Nonequilibrium effects in rate constants of chemical reaction

In order to distinguish separate results for the rates of forward reaction and the total one (in which the reverse reaction is also considered) we introduce

$$v_{A\mathrm{f}} = v_{A\mathrm{f}}^{(0)} + v_{A\mathrm{f}}^{(1)}\,, \tag{6.1}$$

$$\begin{aligned} v_A = v_A^{(0)} + v_A^{(1)} &= v_{A\mathrm{f}}^{(0)} + v_{A\mathrm{r}}^{(0)} + v_{A\mathrm{f}}^{(1)} + v_{A\mathrm{r}}^{(1)} \\ &= v_{A\mathrm{f}}^{(0)} - v_{B\mathrm{f}}^{(0)} + v_{A\mathrm{f}}^{(1)} - v_{B\mathrm{f}}^{(1)}\,, \end{aligned} \tag{6.2}$$

where the upper index (1) is connected with Eq. (4.1). After taking into account Eqs. (2.8) and (2.9) we introduce also

$$\eta_{R\mathrm{f}} = -\frac{v_{R\mathrm{f}}^{(1)}}{v_{R\mathrm{f}}^{(0)}}\,, \qquad (R = A, B)\,, \tag{6.3}$$

$$\eta_{R} = -\frac{v_{R}^{(1)}}{v_{R}^{(0)}}\,, \qquad (R = A, B)\,. \tag{6.4}$$

From Eqs. (2.4), (2.5) and (3.6) we obtain

$$v_{R\mathrm{f}}^{(0)} = k_{R\mathrm{f}}^{(0)} n_R^2 = 4 s_F n_R^2 \left(\frac{\pi k T}{m}\right)^{1/2} (\varepsilon_0+1)\exp(-\varepsilon_0)\,, \quad (R = A, B)\,, \tag{6.5}$$

where $k_{R\mathrm{f}}^{(0)}$ is the equilibrium forward reaction rate constant. After taking into consideration Eq. (6.1) and using, as in the previous section, the Shizgal–Karplus solution of the Boltzmann equation (see Eqs. (2.3)–(2.5), (4.1), (4.7)–(4.9), (4.16), (4.17) and (4.19)) we obtain the following nonequilibrium contributions to the rate of chemical reaction within one and two Sonine polynomial approximation, respectively

$$\begin{aligned} v_{\mathrm{Af}}^{(1)}(1) &= k_{\mathrm{Af}}^{(1)}(1)n_A^2 \\ &= -2s_F^2 n_A^2 x_A \left(1-\delta_{\mathrm{cr}}\frac{x_B^2}{x_A^2}\right) d^2 \left(\frac{\pi kT}{m}\right)^{1/2} \varepsilon_1^2 \exp(-2\varepsilon_0)\,, \qquad (6.6) \\ v_{\mathrm{Af}}^{(1)}(2) &= k_{\mathrm{Af}}^{(1)}(2)n_A^2 \\ &= -\frac{1}{15}s_F^2 n_A^2 x_A \left(1-\frac{\delta_{\mathrm{cr}}x_B^2}{x_A^2}\right) d^2 \left(\frac{\pi kT}{m}\right)^{1/2} (\varepsilon_1\varepsilon_3+\varepsilon_2\varepsilon_4)\exp(-2\varepsilon_0)\,. \\ & \qquad (6.7) \end{aligned}$$

Similarly as in the discussion of nonequilibrium effects of chemical reaction on temperature we discuss four cases:

1. One Sonine polynomials approximation with the reverse reaction neglected (see Eq. (2.1)). From Eqs. (6.3), (6.5) and (6.6) after taking into account that $\delta_{\mathrm{cr}}=\delta_{\mathrm{nr}}=0$ we get

$$\eta_{\mathrm{Af}}(1) = \frac{1}{2}s_F x_A \frac{\varepsilon_1^2}{\varepsilon_0+1}(-\varepsilon_0)\,. \qquad (6.8)$$

2. Two Sonine polynomials approximation with the reverse reaction neglected. From Eqs. (6.3), (6.5) and (6.7) we get

$$\eta_{\mathrm{Af}}(2) = \frac{1}{60}s_F x_A \left(\frac{\varepsilon_1\varepsilon_3+\varepsilon_2\varepsilon_4}{\varepsilon_0+1}\right)\exp(-\varepsilon_0)\,. \qquad (6.9)$$

3. One Sonine polynomials approximation with the reverse reaction considered (see Eq. (2.2)). From Eqs. (6.4)–(6.6) after taking into account that $\delta_{\mathrm{cr}}=\delta_{\mathrm{rr}}=1$ we get

$$\eta_{A(\mathrm{f})}(1) = \frac{1}{2}s_F x_A \left(1-\frac{x_B^2}{x_A^2}\right)\frac{\varepsilon_1^2}{\varepsilon_0+1}(-\varepsilon_0)\,. \qquad (6.10)$$

As Eq. (6.10) concerns the forward reaction nonequilibrium contributions in reaction (2.2) we have introduced the index f as (f) to distinguish η in Eq. (6.10) from that in Eq. (6.8). For this case after a careful analysis of relations for the forward and reverse chemical reaction rates and rate constants (see, *e.g.* Ref. [23]) we can obtain.

$$\eta_A(1) = \frac{1}{2}s_F\frac{\left(\varepsilon_0^2+\frac{1}{2}\varepsilon_0+\frac{1}{2}\right)^2}{\varepsilon_0+1}\exp(-\varepsilon_0) = \eta_B(1)\,. \qquad (6.11)$$

This is a very important result which shows that if the reverse reaction is considered the nonequilibrium corrections to the rate of chemical reaction do not depend on concentrations and are the same for both the components.
4. Two Sonine approximation with the reverse reaction considered (see Eq. (2.2)). For this case we can perform derivations in the same way as in the case of one Sonine polynomial approximation described above. We use Eq. (6.7) instead of Eq. (6.6) and we get instead of Eq. (6.11)

$$\eta_{A(\mathrm{f})}(2) = \frac{1}{60} s_F x_A \left(1 - \frac{x_B^2}{x_A^2}\right) \left(\frac{\varepsilon_1\varepsilon_3 + \varepsilon_2\varepsilon_4}{\varepsilon_0 + 1}\right) \exp(-\varepsilon_0)\,. \tag{6.12}$$

For this case we can obtain

$$\eta_A(2) = \frac{1}{60} s_F \left(\frac{\varepsilon_1\varepsilon_3 + \varepsilon_2\varepsilon_4}{\varepsilon_0 + 1}\right) \exp(-\varepsilon_0) = \eta_B(2)\,. \tag{6.13}$$

It should be emphasized that, on the contrary to the case of neglecting of the reverse reaction in which in Eqs. (6.8) and (6.10) x_A appears, in Eqs. (6.11) and (6.13) the nonequilibrium corrections to the rate of chemical reaction are the same for both the components and do not depend on their concentrations. In Fig. 2 we present for the PX model the nonequilibrium decrease of the rate constant of chemical reaction as a function of the reduced threshold energy ε_0 (see Eqs. (6.11), (6.13)). For a comparison we present also such results for the LC model (see Eqs. (59) and (61) from Ref. [23]).

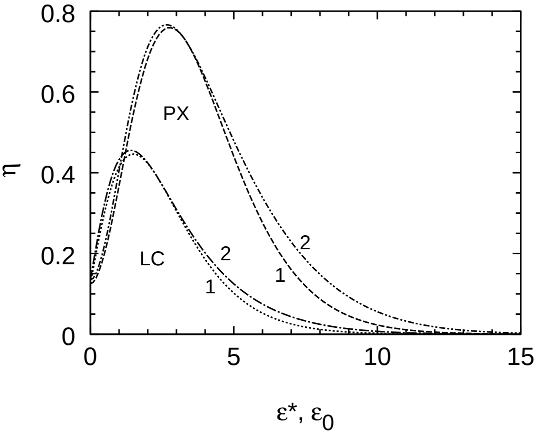

Fig. 2. Relative decrease of the rate constant of the overall reaction (2.2) for the PX model (Eqs. (6.11), (6.13)) as a function of ε_0 and such results for the LC model as a function of ε^*.

7. Comparison of results following from analytical results with those obtained from the Monte Carlo simulations

In order to perform computer simulations we use the Bird algorithm prepared by the second author of this paper. This algorithm is based on the earlier results Bird [32–35] discussed also in Ref. [36] and particularly described in Ref. [23].

We have used the following system for simulations. A volume $V = 2777.78\,\text{nm}^3$ contains in the beginning $N_A = 1000$ spheres A and $N_B = 0$ spheres B having the same diameter $d = 0.35$ nm and masses 16 g/mol. This corresponds to the packing factor 0.008082. The equilibrium temperature is 300 K. As the chemical reaction proceeds the spheres A change in reactive collisions to the spheres B and vice versa. Therefore, the number of spheres B increases and the number of spheres A decreases to $N_A = 1000 - N_B$. The average translational energy of the components A and B and also their temperatures change. The time is described by time steps $\Delta t = 0.6941 \times 10^{-13}$s. In order to obtain sufficient accuracy we have performed in each simulation a large number of runs $R \quad (R \geq 50000)$ and obtained average values of N_A, N_B, T_A and T_B as well as the number of elastic and reactive collisions as a function of the time steps. The results of such simulations are compared with the results following from the analytical expressions derived in preceding sections. In Fig. 3 we present the results for the initial temperature of component B as a function of the reduced threshold energy ε_0. The analytical curve for $T_B(0)$ is obtained from Eq. (5.10) and the small circles represent the average values of T_B obtained from the beginning time steps in the simulation.

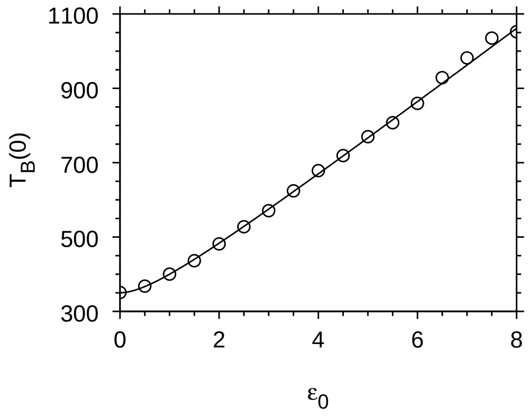

Fig. 3. The temperatures $T_B(0)$ as a function of ε_0. The solid curve represents the results calculated from Eq. (5.10) and the small circles those obtained from simulations.

In Fig. 4 we show the changes of temperature of component A for a system in which the forward reaction proceeds only and the number of spheres B can be even equal to 1000 which corresponds to the molar fraction of B $x_B = 1.0$. The reduced threshold energy is chosen $\varepsilon_0 = 3.0$ and the steric factor $s_F = 1.0$. The straight lines 1 and 2 are obtained from the analytical results within one and two Sonine polynomials approximation, respectively,

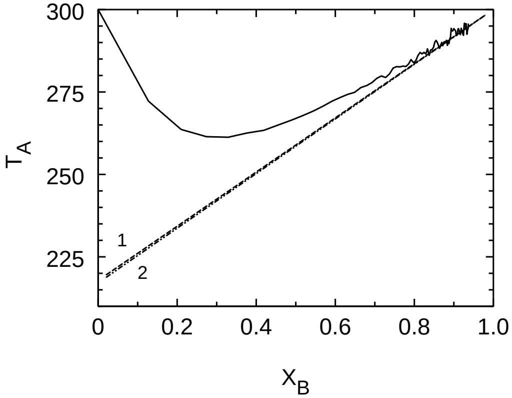

Fig. 4. Temperature T_A as a function of molar fraction x_B for the forward reaction (2.1) with $\varepsilon_0 = 3$ and $s_F = 1.0$. Results from the simulation are represented with irregular line and those from the perturbation solution within one and two Sonine polynomials approximation with straight lines denoted 1 and 2 (see Eqs. (5.3) and (5.4) with $\delta_{\mathrm{cr}} = 0$), respectively.

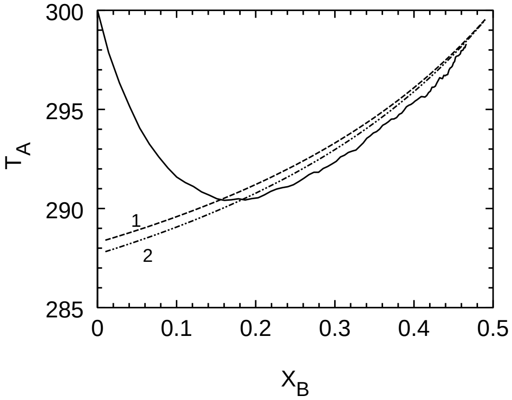

Fig. 5. Temperature T_A as a function of molar fraction x_B for the forward–reverse reaction (2.2) with $\varepsilon_0 = 1.5$ and $s_F = 0.1$. Results from the simulation are represented with irregular line and those from expressions obtained within appropriate Sonine polynomials approximations (see Eqs. (5.3) and (5.4) with $\delta_{\mathrm{cr}} = 1$) with curves denoted 1 and 2, respectively.

(see Eqs. (5.3) and (5.4) with $\delta_{\rm cr} = 0$). The irregular curve shows T_A obtained from simulations. In the next two figures we show such results as those presented in Fig. 4 but for the case in which also the reverse reaction proceeds. Therefore, the molar fraction x_B can not exceed 0.5. In this case we introduce $\delta_{\rm cr} = 1.0$ in Eqs. (5.3), (5.4). In Fig. 5 we introduce $\varepsilon_0 = 1.5$ and $s_F = 0.1$, whereas in Fig. 6 $\varepsilon_0 = 3.0$ and $s_F = 0.2$.

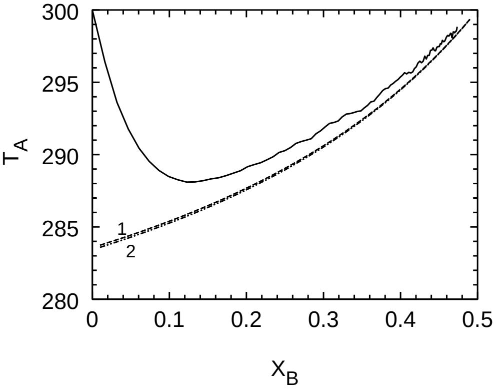

Fig. 6. Results for T_A represented in the same way as in Fig. 5 but for $\varepsilon_0 = 3.0$ and $s_F = 0.2$.

Additionally, in Fig. 7 we show the velocity distribution functions of the components A and B after a 1000 time steps in a typical simulation. We have chosen $\varepsilon_0 = 3.0$ and $s_F = 0.2$ for this purpose just to show the shapes of the curves only.

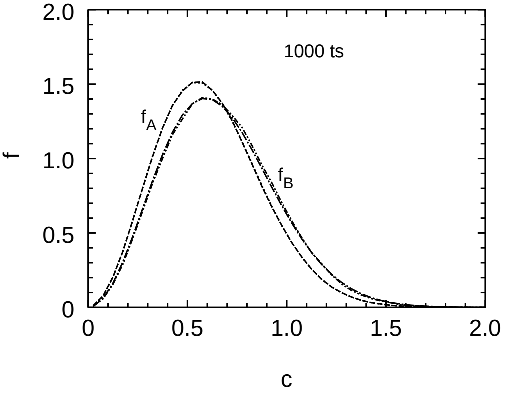

Fig. 7. The velocity distribution functions of reagents A and B as a function of c_A and c_B in 10^3 for the forward–reverse reaction (2.2) with $\varepsilon_0 = 3.0$ and $s_F = 0.2$ after 1000 time steps of simulation corresponding to $x_B = 0.23$. Results from simulations are represented with irregular lines and the Maxwell–Boltzmann distributions for the appropriate temperatures T_A and T_B with regular lines, respectively.

8. Discussion

We have solved the Boltzmann equation using the perturbation method for the case of bimolecular chemical reaction proceeding in a dilute gas. We have introduced the Prigogine–Xhrouet model (PX) for the reactive cross section and obtained the analytical expressions for the noneqilibrium Shizgal–Karplus temperatures and reaction rate constants as functions of the reduced threshold energy ε_0. We have analyzed such analytical results for two cases: 1. the reaction proceeds in forward direction only, 2. the forward and reverse reactions proceed.

For the case 1. we have obtained the results for temperatures T_A which can be calculated from appropriate ΔT_A for one and two Sonine polynomials approximations (see Eqs. (5.3) and (5.4) with $\delta_{\rm cr} = 0$). In Fig. 1 we have shown that for the PX model ΔT_A can be larger than it would be for the line-of-centers model (LC) for the appropriate reduced threshold energy ε^*. The temperature T_B can be calculated from Eqs. (2.12), (5.11) and (5.12). We have also derived expressions for the relative decrease of the rate constant of chemical reaction for both the approximations (see Eqs. (6.8) and (6.9)).

For the case 2. we have derived appropriate expressions for temperature T_A (see Eqs. (5.3) and (5.4) with $\delta_{\rm cr} = 1$). We have also obtained equations for the relative decrease of the rate constant of chemical reaction (see Eqs. (6.10)–(6.13)). It is interesting that in this case for the PX model the relative decrease of the rate constant of the overall reaction (see Eqs. (6.11) and (6.13) does not depend on x_B similarly as for the other models already analyzed (see Refs [23, 25, 26]). It even more interesting that for the PX model this decrease is more pronounced that for the other models. This can be seen from Fig. 2. Namely, for $\varepsilon_0 = 3$ the rate constant of reaction (2.1) can be even 4 times smaller than its equilibrium value which corresponds to $\eta = 0.75$. This result is very important because for the LC model the maximum value of η is about 0.45, *i.e.* the rate constant for that model could be about 1.8 times smaller than its equilibrium value.

From a comparison of Eqs. (6.8), (6.10) and (6.11) or Eqs. (6.9), (6.12) and (6.13) we can see that in general $\eta_{A({\rm f})}$ is smaller than $\eta_{A{\rm f}}$ which is smaller than η. It is important in the analysis for chemical reactions proceeding relatively far-from-equilibrium [15, 20]. Namely, only for reactions characterized by sufficiently large ε_0 and small s_F the results for $\eta_{A{\rm f}}$ and $\eta_{A({\rm f})}$ can be analyzed for small values of x_B. Only in this case the values of these quantities can approach to the value of η. We had this situation in the analysis of the LC model [20].

In order to verify the validity of results obtained within the perturbation method of solution we have additionally performed the Monte Carlo simulations. We have made comparisons between the results obtained from the analytical expressions and those obtained from simulations for the temperatures only, *i.e.* in the same way as we have done in Ref. [23] for the LC model. The reason is that the accuracy of results from simulations for temperatures is much better than for such results for the rate constants.

We have additionally derived the expression for $T_B(0)$, *i.e.* for the temperature of product B in early stages of reaction (see Eq. (5.10)). We think that the way of derivation is shown in Sec. 5 in more convincing way than earlier for the LC model in Ref. [17]. Namely, in Ref. [17] we assumed that, as the fastest molecules A change to B, the product B must have the maximum temperature in the beginning of reaction and the time derivative of T_B should be equal to zero, however, the last condition (although leads to good results) in general need not be fulfilled. In Fig. 3 we have shown the comparison for results for $T_B(0)$. We see that the agreement between the analytical results and those from simulations is very good. However, for large values of ε_0, *e.g.* $\varepsilon_0 > 7$ the accuracy is a little bit worse because we get very small amount of the product B. Naturally, the temperature T_B obtained from the analytical expressions should not be larger than $T_B(0)$ because T_B decreases as the reaction proceeds. For fast reactions, *e.g.* for those proceeding with $s_F = 1.0$, small values of ε_0 and in a stage of reaction with small x_B, the reaction can be too fast to use the perturbation method. A comparison of $T_B(0)$ with T_B , *i.e.* ($T_B < T_B(0)$), permits to find the range of x_B in which the perturbation solution can not work. Just to give one example, we have chosen one Sonine polynomial approximation for the forward–reverse reaction and obtained the inequality for x_B (see Eq. (5.16). In next figures, we have shown comparisons of analytical results for T_A with those obtained from simulations. From these figures it can be easily seen that, similarly as in the case of inequality discussed above, only for sufficiently large x_B such comparisons are reasonable. In Fig. 4 we have shown such a comparison for the case of neglecting of the reverse reaction with $\varepsilon_0 = 3.0$ and $s_F = 1.0$. We see that for large x_B the agreement is fairly good. In the next two figures we have presented such comparisons for the forward–reverse reactions introducing $\varepsilon_0 = 1.5$ and $s_F = 0.1$ (see Fig. 5) and $\varepsilon_0 = 3.0$ and $s_F = 0.2$ (see Fig. 6). These results are fairly good, however, the role of inequality (5.16) is important if x_B is not large enough. In Fig. 7 we have additionally shown the velocity distribution functions f_A and f_B for the simulation with $\varepsilon_0 = 3.0$ and $s_F = 0.2$ after 1000 time steps. From Fig. 7 it can be seen that the shapes of these distribution functions are nearly Maxwellian and they show that $T_A < T_B$, which is typical for the Shizgal–Kaplus temperatures for the reaction analyzed. The results presented in Figs. 4–7 confirm the fact that the perturbation method gives good results for slow chemical reactions. Naturally, for slow reactions the formulas for the relative decrease of the overall reaction rate constant are also valid (see Eqs. (6.11) and (6.13)).

It means that for $\varepsilon_0 = 3.0$, $s_F = 1.0$ and sufficiently large x_B the nonequilibrium rate constant could be even 4 times smaller than its equilibrium value. Therefore, the role of nonequilibrium effects for the PX model can be more visible than in the case of the LC model (Figs. 1 and 2). It is interesting that Nowakowski analyzing a bimolecular reaction with neglection of products in the Lorentz gas has obtained also larger nonequilibrium corrections to the reaction rate for the PX model than for the LC model [37].

Just to summarize, we have used the Shizgal–Karplus perturbation method of solution of the Boltzmann equation for the Prigogine–Xhrouet model in order to obtain the analytical results for the relative decrease of the rate constant of chemical reaction as well as for nonequilibrium temperatures. We have used the Bird method of Monte Carlo simulations to confirm the results obtained. We have shown that the noneqilibrium effects connected with proceeding of the chemical reaction can be more pronounced for the Prigogine–Xhrouet model than for the line-of-centers model.

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