

## Molecular Dynamics Simulations of Nonequilibrium Effects Associated with Thermally Activated Exothermic Reactions

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**Abstract.** In this paper we discuss the influence of nonequilibrium effects on the rate of a thermally activated, exothermic reaction. The system with a binary process  $A + A \rightleftharpoons B + B + \{\text{energy}\}$  is considered as an example, on which we compare molecular dynamics simulations with a simple phenomenology based on the assumption that a nonequilibrium state can be characterized by many time dependent temperatures. A good agreement between results of both methods is observed. We have found that the rate constants are changed significantly by the nonequilibrium effects, which affects system's evolution.

### 1. Introduction

In order to predict the time evolution of a chemical system we usually apply the standard chemical kinetics based on the mass action law. In such approach the rate constant is just a number, which links the concentrations of reactants with the reaction rate.

At the microscopic level of description the rate constant for an elementary reaction is related to two factors: the reaction cross section  $\sigma^*(E_i)$  for a reactive "encounter" between reactants at a particular quantum state  $E_i$  and the rate such state appears in the system  $p(E_i)$ . In this notation the rate constant  $k$  is the average of  $\sigma^*$  over all states:

$$k = \sum_{E_i} \sigma^*(E_i) p(E_i). \quad (1)$$

Let us assume that at the beginning all reactants are equilibrated. In the case of an activated process the energetic barrier has to be crossed and the reaction cross section increases with the energy of interacting molecules (STILLER, 1989). Therefore the high energy part of reactant's distribution function  $p$  will be strongly disturbed by the reaction, because the corresponding states can be easily transformed into products, and the rate constant calculated from (1) shall differ from its initial, equilibrium value. As the result, the time evolution of the system will differ from the one calculated using the equilibrium rate (cf. Fig. 1).

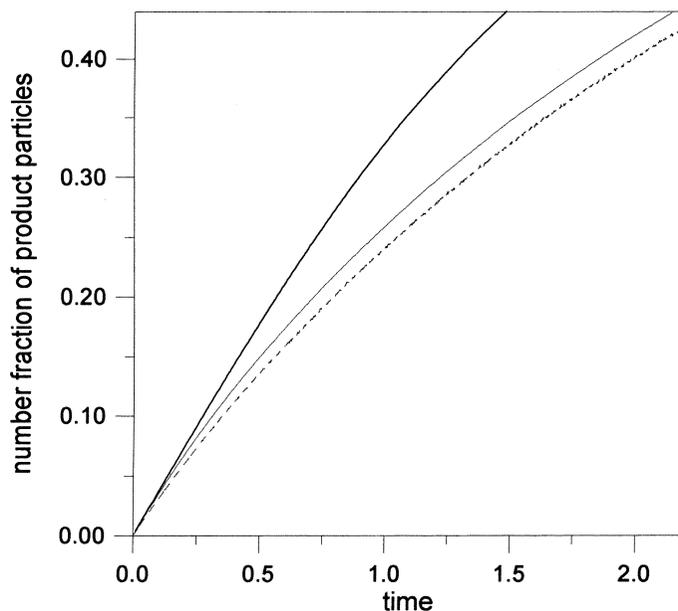


Fig. 1. The concentration of product B as a function of time for the system characterized by  $\varepsilon_{A1} = 1$  and  $u = 4$  ( $\varepsilon_{A2} = 5$ ). The dashed line—MD simulations, the thick solid line—“classical” phenomenology (Eqs. (4) and (5)); the thin solid line—Eqs. (6)–(8).

The influence of nonequilibrium effects on the rate constant has been investigated for more than 50 years. Most of the theoretical considerations were concerned with the thermally activated, thermoneutral chemical processes (PRIGOGINE and XHOUET, 1949; PYUN and ROSS, 1964; SHIZGAL and NAPIER, 1996; NOWAKOWSKI, 1998). The number of results for thermally activated exothermic reactions is limited (see for example PRIGOGINE and MAHIEU, 1950; XYSTRIS and DAHLER, 1978; BARAS and MALEK MANSOUR, 1989, 1997; GORECKI and GORECKA, 2000). In this paper we study the nonequilibrium effects for the reaction:



using molecular dynamics (MD) simulations. We also show that a very simple phenomenology gives a good agreement with simulations. We think that it may be easily applied to estimate the strength of nonequilibrium effects in other systems with exothermic reactions.

## 2. Results

Let us assume that the activation energy for the direct process of (2) ( $A + A \rightarrow B + B$ ) is  $E_{A1}$  and the reaction heat  $U > 0$ . Therefore the activation energy of the reverse reaction

( $B + B \rightarrow A + A$ ) is  $E_{A2} = E_{A1} + U$  and the reaction heat  $-U$ . Our MD simulations are performed for the simplest case in which the molecules of both  $A$  and  $B$  are represented by identical hard spheres (the same masses and diameters). Now the only form of molecule's energy is the kinetic one. One can define  $\sigma^*$  for a thermally activated process using the line-of-centers model for reactive collisions (PRESENT, 1959). According to this model a collision between reactant's molecules in which the energy of the relative motion along the line of centers calculated in the center of mass reference system exceeds  $E_A$  may lead to reaction. The probability that reaction occurs for a collision satisfying the energetic condition is called a steric factor ( $s_F \leq 1$ ).

The line-of-center model for reactive collisions can be naturally adopted in simulations of exothermal processes. When a reactive collision of two  $A$  particles occurs the reaction heat is released as the additional kinetic energy of outgoing  $B$  particles. In case of reactive collision of two  $B$  particles the energy of products is decreased by the value of reaction heat in the same way. For a Maxwellian distribution of velocities at the temperature  $T$  the reaction rate  $k$  for line-of-centers model equals (GORECKI, 1993):

$$k = s_F \eta(T) \exp\left(-\frac{E_A}{k_B T}\right) \quad (3)$$

where  $\eta(T)$  is the frequency of collision between spheres.

Our simulation starts with all spheres marked as the reactant  $A$  and randomly distributed in the system with velocities chosen from the Maxwellian distribution corresponding to the initial temperature  $T_0(t = 0)$ . We follow system's evolution by checking which collisions are reactive and if so changing the chemical identity of spheres and their kinetic energy. The periodic boundary conditions are applied so the total number of particles is conserved and the system is adiabatic. In a single simulation run one obtains the number fraction of  $A$  particles ( $\alpha$ ) and the average energies per particle for  $A(E_a)$  and  $B(E_b)$  and for the system as a whole ( $E_0$ ) as functions of time. The outcome of a single simulation program strongly depends on the initial conditions, therefore we present the data, which are averaged over more than 10000 of individual runs. They have been obtained for 512 spheres and the packing fraction of the system was 0.21. We have restricted the simulations to the initial stages of reaction because in this region the nonequilibrium effects are the most pronounced.

Assuming that reaction (2) proceeds in a closed system, the standard kinetic equations describing system's temperature and concentration of  $A$  are:

$$\frac{\partial \alpha}{\partial \tau} = -s_{F1} \alpha^2 \xi_0^{1/2} \exp\left(-\frac{\varepsilon_{A1}}{\xi_0}\right) + s_{F2} (1 - \alpha)^2 \xi_0^{1/2} \exp\left(-\frac{\varepsilon_{A2}}{\xi_0}\right), \quad (4)$$

$$\frac{\partial \xi_0}{\partial \tau} = \frac{2}{3} u \left[ s_{F1} \alpha^2 \xi_0^{1/2} \exp\left(-\frac{\varepsilon_{A1}}{\xi_0}\right) - s_{F2} (1 - \alpha)^2 \xi_0^{1/2} \exp\left(-\frac{\varepsilon_{A2}}{\xi_0}\right) \right] \quad (5)$$

where  $\alpha$  is the number fraction of  $A$  molecules and  $\xi_0$ ,  $u$ ,  $\varepsilon_{A1}$ ,  $\varepsilon_{A2}$  are the system temperature  $T_0$ , reaction heat and the activation energies scaled to the initial temperature of the system respectively ( $\xi_0 = T_0(t)/T_0(t=0)$ ,  $u = U/k_B T_0(t=0)$ ,  $\varepsilon_{Ai} = E_{Ai}/k_B T_0(t=0)$ ). Equations (4) and (5) are written in the time scale in which  $\eta(T_0(t=0)) = 1$ . The accuracy of such description for reaction (2) can be easily tested if one compares it with the results of molecular dynamics simulations and for example for  $\varepsilon_{A1} = 1$  and  $u = 4$  the outcome is rather disappointing (compare the thick solid and the dashed lines in Fig. 1). What is the origin of the discrepancy?

Figure 2 shows results of MD simulations (dashed lines) for average energies of  $A$  and molecules of the system treated as a whole scaled by  $3/2k_B T_0(t=0)$  as a function of the number fraction of  $A$  molecules for  $\varepsilon_{A1} = 2$  and two values of  $u$  ( $u = 1.5$  and  $u = 2.5$ ). It is convenient to use  $\alpha(t)$  instead of time as the measure of reaction progress. One can notice that the differences between the average energy of  $A$  particle and the average energy per particle of the system are significant, what indicates that the energy distribution of  $A$  particles differs from the energy distribution of the whole system. At the initial stage of the reaction  $E_a$  decreases because the most energetic  $A$  particles are consumed by the direct reaction. Next it starts to increase as the result of the energy exchange in non-reactive collisions with  $B$  particles and because highly energetic particles of  $B$  are transformed into  $A$  in the reverse reaction.

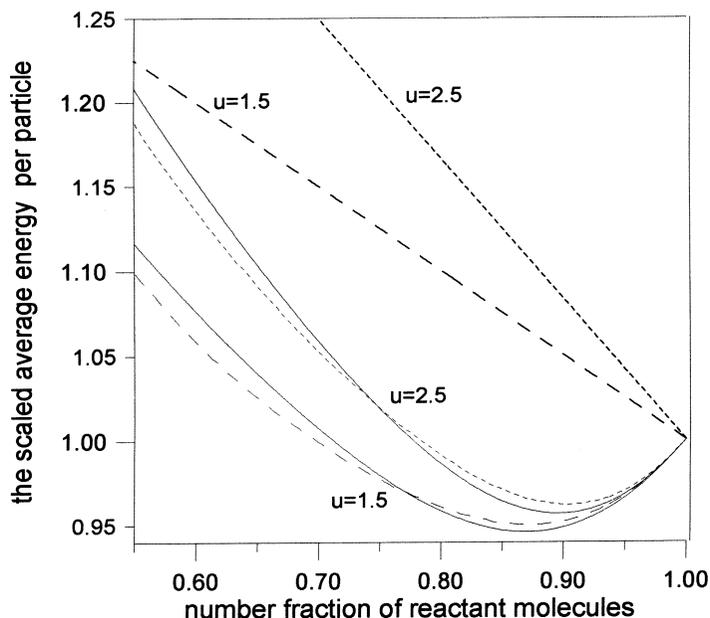


Fig. 2. The average energy per a particle of reagent  $A$  (the thin lines) and per an average particle of the system (the thick lines) scaled to  $3/2k_B T_{00}$  as a function of  $\alpha$ . The results are presented for  $\varepsilon_{A1} = 2$  and two values of  $u$ . The dashed lines show results of MD simulations (long dashed— $u = 1.5$ , short dashed— $u = 2.5$ ), the thin solids lines are solutions of Eqs. (6)–(8).

Figure 3 shows the average energy per particle of  $B$  and per a particle of the system treated as a whole for the same sets of parameters as in Fig. 2. At the initial stage of process the average energy of  $B$  particles is much higher than  $E_0$  because only the most energetic  $A$  particles are transformed into  $B$ . The difference between  $E_b$  and  $E_0$  is more important than this between  $E_a$  and  $E_0$ . Now it is easy to explain the difference between MD simulations and Eqs. (4) and (5) shown in Fig. 1. The studied reaction is very fast so the energy exchange between reagents is not sufficient to keep the same energy distribution for all of them. The rate constant for the direct process should be smaller than considered in Eqs. (4) and (5) because  $E_a(\alpha) < E_0(\alpha)$ . On the other hand  $E_b(\alpha) > E_0(\alpha)$  so the reverse reaction is faster. Both effects “work” in the same direction, so finally the actual rate of product’s creation is much lower than predicted by the standard kinetics. Let us notice that the effect is qualitatively similar to the one observed for coupled reactions (GORENSEK and KOSTIN, 1984, 1985; CUKROWSKI *et al.*, 1992; GORECKI and HANAZAKI, 1994): a fast reaction with low activation energy ( $\varepsilon_{A1}$ ) prepares a nonequilibrium distribution of reactant which significantly changes the rate of another process with a higher activation energy.

The simplest description of the nonequilibrium effects can be given if one assumes that the system is characterized by two different, time dependent temperatures: the reactant  $A$  has a temperature  $\xi_A(t)T_0(t=0)$  and the whole system is characterized by the temperature  $\xi_0(t)T_0(t=0)$ . NOWAKOWSKI and GORECKI (1996) demonstrated that similar phenomenology gives an accurate description of the time evolution for nonequilibrium systems with thermoneutral reactions. Considering all energy exchange processes between colliding particles one obtains the following equations:

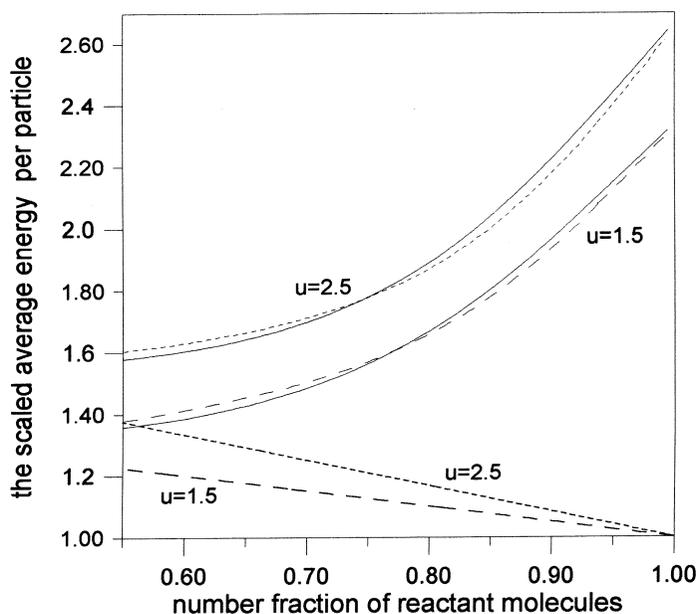


Fig. 3. The average energy per a particle of  $B$  and per an average particle of the system scaled to  $3/2k_B T_{00}$  as a function of  $\alpha$ . Notation as in Fig. 2.

$$\begin{aligned} \frac{\partial \alpha}{\partial \tau} = & -s_{F1} \alpha^2 \xi_A^{1/2} \exp\left(-\frac{\varepsilon_{A1}}{\xi_A}\right) + s_{F2} \xi_0^{1/2} \exp\left(-\frac{\varepsilon_{A2}}{\xi_0}\right) \\ & + s_{F2} \xi_A^{1/2} \alpha^2 \exp\left(-\frac{\varepsilon_{A2}}{\xi_A}\right) - 2\alpha s_{F2} \left(\frac{\xi_A + \xi_0}{2}\right)^{1/2} \exp\left(-\frac{2\varepsilon_{A2}}{\xi_A + \xi_0}\right), \end{aligned} \quad (6)$$

$$\begin{aligned} \frac{\partial \xi_A}{\partial \tau} = & \frac{2}{3} \left\{ -s_{F1} \alpha \xi_A^{1/2} \exp\left(-\frac{\varepsilon_{A1}}{\xi_A}\right) \xi_A \left(\frac{7}{4} + \frac{\varepsilon_{A1}}{2\xi_A}\right) + \left(\frac{\xi_0 + \xi_A}{2}\right)^{1/2} (\xi_0 - \xi_A) \right. \\ & + s_{F2} \xi_0^{1/2} \exp\left(-\frac{\varepsilon_{A2}}{\xi_0}\right) \xi_0 \left(\frac{7}{4} + \frac{\varepsilon_{A2}}{2\xi_0}\right) \frac{1}{\alpha} + s_{F2} \xi_A^{1/2} \exp\left(-\frac{\varepsilon_{A2}}{\xi_A}\right) \xi_A \left(\frac{7}{4} + \frac{\varepsilon_{A2}}{2\xi_A}\right) \alpha \\ & - s_{F2} \left(\frac{\xi_A + \xi_0}{2}\right)^{1/2} \exp\left(-\frac{\varepsilon_{A2}}{\xi_A + \xi_0}\right) \left[ \xi_A \left(\frac{3}{2} + \frac{\xi_A}{2(\xi_A + \xi_0)} + \frac{2\xi_A \varepsilon_{A2}}{(\xi_0 + \xi_A)^2}\right) \right. \\ & \left. \left. + \xi_0 \left(\frac{3}{2} + \frac{\xi_A}{2(\xi_0 + \xi_A)} + \frac{2\xi_0 \varepsilon_{A2}}{(\xi_A + \xi_0)^2}\right) \right] \right\} \\ & - \frac{1}{2} u s_{F2} \left[ \exp\left(-\frac{\varepsilon_{A2}}{\xi_0}\right) \xi_0^{1/2} \frac{1}{\alpha} + \xi_0^{1/2} \exp\left(-\frac{\varepsilon_{A2}}{\xi_A}\right) \alpha \right. \\ & \left. - 2 \left(\frac{\xi_A + \xi_0}{2}\right)^{1/2} \exp\left(-\frac{2\varepsilon_{A2}}{\xi_A + \xi_0}\right) \right] \\ & - \xi_A \left[ -s_{F1} \xi_A^{1/2} \exp\left(-\frac{\varepsilon_{A1}}{\xi_A}\right) \alpha + \frac{1}{\alpha} s_{F2} \xi_0^{1/2} \exp\left(-\frac{\varepsilon_{A2}}{\xi_0}\right) \right. \\ & \left. + s_{F2} \xi_A^{1/2} \exp\left(-\frac{\varepsilon_{A2}}{\xi_A}\right) \alpha - 2s_{F2} \left(\frac{\xi_A + \xi_0}{2}\right)^{1/2} \exp\left(-\frac{2\varepsilon_{A2}}{\xi_A + \xi_0}\right) \right], \end{aligned} \quad (7)$$

$$\frac{\partial \xi_0}{\partial \tau} = \frac{2}{3} u \left[ s_{F1} \xi_A^{1/2} \exp\left(-\frac{\epsilon_A}{\xi_A}\right) \alpha^2 - s_{F2} \xi_0^{1/2} \exp\left(-\frac{\epsilon_{A2}}{\xi_0}\right) - s_{F2} \xi_A^{1/2} \alpha^2 \exp\left(-\frac{\epsilon_{A2}}{\xi_A}\right) + 2s_{F2} \alpha \left(\frac{\xi_A + \xi_0}{2}\right)^{1/2} \exp\left(-\frac{2\epsilon_{A2}}{\xi_A + \xi_0}\right) \right] \quad (8)$$

The results calculated on the basis of Eqs. (6)–(8) (thin solid lines on Figs. 1–5) are in a good agreement with simulations. Such agreement has been also obtained for the other studied values of  $\epsilon_{A1}$ ,  $\epsilon_{A2}$  and  $u$ .

In molecular dynamics simulations the nonequilibrium rate constants for the direct and reverse reactions ( $k_d$  and  $k_r$ , respectively) as functions of  $\alpha$  can be calculated from the average time  $\langle \delta t \rangle$  ( $\alpha$ ) the system spends in the state characterized by a given  $\alpha$ . In order to see clearly the nonequilibrium effect it is convenient to scale the rate constant for a given  $\alpha$  by the value calculated from the Arrhenius law using temperature  $\xi_0(\alpha)$ . Such scaled rate constant for the direct process obtained from simulations (the short dashed line) is presented in Fig. 4. The thin long dashed lines mark statistical errors of the simulation data ( $\epsilon_{A1} = 2$  and  $u = 2.5$ ). Figure 5 shows scaled rate constants of the reverse reaction  $k_{sr}$  as a function of  $\alpha$  for  $\epsilon_{A1} = 2$  and two values of reaction heat ( $u = 1.5$  (long dashed line) and  $u$

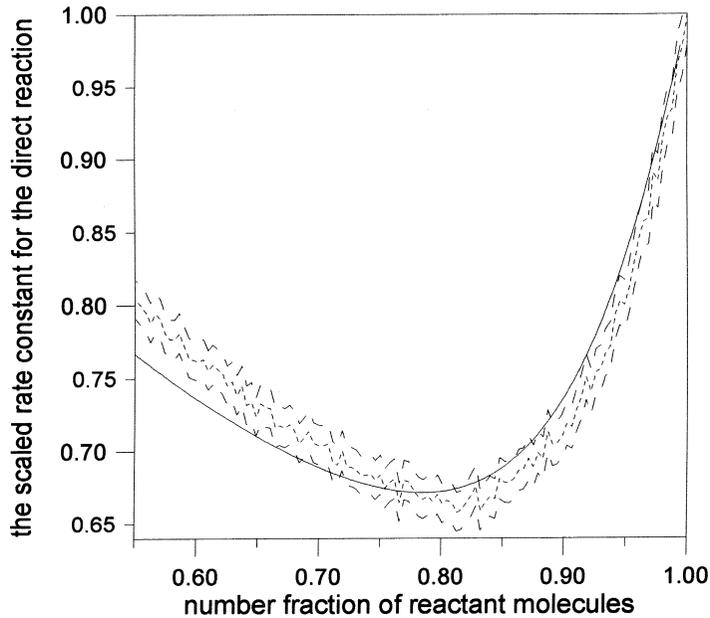


Fig. 4. The rate constant for the direct reaction as a function of  $\alpha$  for  $\epsilon_{A1} = 2$  and  $u = 2.5$  ( $\epsilon_{A2} = 4.5$ ) scaled to its equilibrium value. The short dashed line—MD simulation result; the long dashed lines estimate its statistical error; the solid line solution of Eqs. (6)–(8).

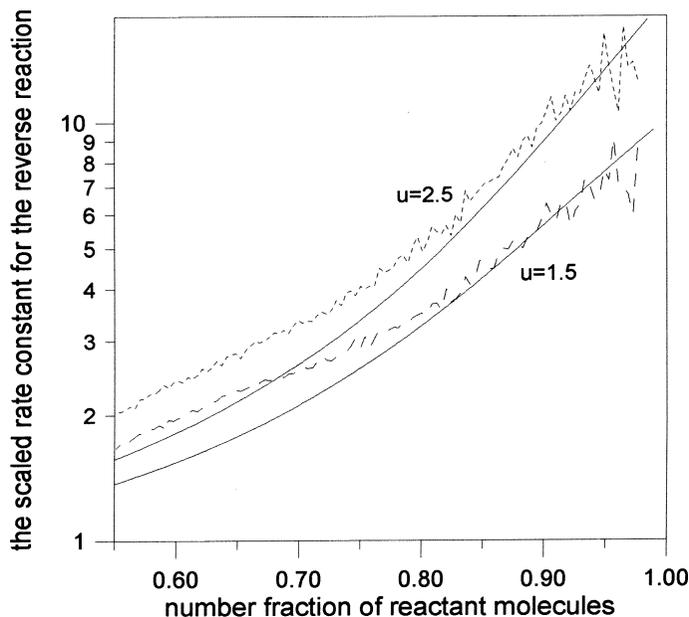


Fig. 5. The rate constant for the reverse reaction as a function of  $\alpha$  for  $\epsilon_{A1} = 2$  and two values of  $u$ :  $u = 1.5$  ( $\epsilon_{A2} = 3.5$ ) and  $u = 2.5$  ( $\epsilon_{A2} = 4.5$ ). The dashed lines are results of MD simulations, The solid lines come from solution of Eqs. (6)–(8).

$= 2.5$  (short dashed line)). As expected the influence of nonequilibrium effects on the reverse reaction is more pronounced.

In our opinion the small discrepancy between simulations and phenomenology is mainly caused by hot spots of product  $B$  which make the system inhomogeneous. Although the reverse process helps to restore system's homogeneity for a large reaction heat the activation energy of the reverse process is high and so the inverse reaction is slow and inefficient. The rate constant is calculated from MD results assuming that the system is homogeneous and it should be lower if one considers a higher effective concentration of  $B$  in the spots. Thus it is not surprising that it (see Fig. 5) overestimates theory.

### 3. Conclusions

In this paper we presented results of direct measurements of the nonequilibrium reaction rate constants in an adiabatic system with thermally activated reversible exothermic reaction (2). The measurements were performed on the basis of molecular dynamics simulations for the reactive hard spheres. We observe that the rate constant for the direct reaction is decreased with respect to the corresponding equilibrium value and the decrease is similar as for the thermoneutral process with the same activation energy. The rate constant for the reverse reaction is increased by nonequilibrium effects and its value may be orders of magnitude higher than the corresponding equilibrium value.

We compared the results of MD simulations with simple phenomenology which assumes that the system as a whole and reactant *A* are described by distribution functions with time dependent temperatures. The agreement between phenomenology and simulations is very good so such simple description of nonequilibrium effects may help to predict the time evolution of many reactive systems. For example the nonequilibrium effects can have a significant influence on systems exhibiting thermochemical oscillations (GRAY *et al.*, 1988).

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