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Molecular-dynamics study on the influence of nonequilibrium effects on the rate of chemical reaction

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A molecular-dynamics model of chemically reacting hard spheres is applied to study the influence of nonequilibrium effects on the rate constant of a thermally activated chemical reaction. It is demonstrated that these effects can be important if the activation energy of a chemical reaction is in the range between 0.5-$k_B T$ and $6k_B T$. The decrease in reaction-rate constant observed in simulations is larger than that predicted by models of a chemical reaction based on Boltzmann or Enskog equations.

I. INTRODUCTION

The standard formulation of chemical kinetics is based on the assumption of local thermal equilibrium for reactants and products. There are, however, cases (for example thermally activated reactions) in which one may expect that this equilibrium breaks down and consideration of the nonequilibrium character of a chemical reaction is necessary. The influence of such nonequilibrium effects on the rate of a model chemical reaction is studied in this paper.

Let us consider a very simple model of a chemical reaction:

$$A+A\xrightarrow{k}B+C \tag{1}$$

where k denotes the rate constant. In the standard formulation of the rate theory all the nonequilibrium effects are neglected and the rate constant k is described by the Arrhenius law [$k \approx T^{1/2} \exp(-E/k_B T)$, where T, E, and k_B denote the temperature of the system, the activation energy, and Boltzmann constant] and it does not depend on concentrations of products. However, for fast chemical processes we may expect that the Arrhenius form of the rate constant is not valid. A bimolecular chemical reaction (1) may be represented by a simple molecular model, which seems to be useful for computer simulations using the hard spheres technique [1]. This model (the line-of-centers model) is based on the assumption that the reactive collisions are those for which the value of kinetic energy of colliding molecules (spheres), associated with their motion along the line of centers, calculated in the center-of-mass reference system, exceeds the activation energy E [2]. The origin of nonequilibrium effects caused by a thermally activated chemical reaction is simple. Fast molecules of A can react and they are constantly transformed into product. Therefore, if we start from a system which is in thermal equilibrium at the beginning, then after a few reactive collisions the reactant may become "cooler." So the reaction slows down. The thermal equilibrium in the system is restored by the nonreactive collisions (including these between reactant and products). For a large activation energy reactive collisions are separated by many nonreactive collisions and the system has enough time to return to thermal equilibrium. But when there are only a few elastic collisions for every reactive one then the rate of equilibration is too low and we should observe that reaction (1) progresses slower than may be expected for the system in thermal equilibrium.

The pioneering study in this field was done by Prigogine and Xhrouet [3], who solved the Boltzmann equation suitably generalized to take reaction (1) into account and obtained the first-order correction to the reaction rate. Then, their method was generalized for a dense gas [4] (the Enskog equation has been applied). The different aspects of the influence of nonequilibrium effects on properties of systems with a chemical reaction in the dilute gas were discussed in the works of Present [2], Shizgal and Karplus [5], and others (see, for example, [6]). These papers lead to a general conclusion that for a typical situation (similar masses of reacting molecules and a reaction cross section smaller then the cross section for elastic collisions) the decrease in k due to nonequilibrium effects is small ($<10\%$) and it does not depend on density [7]. This conclusion, however, has never been (within our knowledge) verified experimentally due to the fact that it seems hardly possible to approximate a real reaction mechanism using the concepts appropriate to describe collisions of hard spheres. Studying Refs. [2–6] one may feel disappointed with many strong assumptions, which are necessary to achieve the final result (for example, one of the most popular is the neglecting of products; this problem was discussed in [8]). Furthermore, it is very difficult to see how these assumptions affect the final result. In this situation computer simulations of nonequilibrium effects caused by a chemical reaction seem to be interesting because they can provide us with the results which can play the role of missing experimental data and these results can be used for testing different theoretical approaches. Here we present the results of simulations which show how the rate constant of a chemical reaction in the system of hard spheres is changed by nonequilibrium effects. We hope this information answers some of the points recently raised by Baras and Malek Mansour [9] in their paper on simulations (the Bird method) of the influence of nonequilibrium effects on temperature profiles.

II. RESULTS OF MOLECULAR-DYNAMICS SIMULATIONS

The molecular-dynamics technique for hard spheres in a system with the periodic boundary conditions is well known [10]. Using this technique we have generated a number of long trajectories ($\approx 10^5$ collisions each) recording collision times, the identities of colliding spheres, and their kinetic energy. The eight data sets have been generated for a system of 500 hard spheres with the packing density v equal to 0.0824 (v is defined as the ratio between the volume of spheres and the total volume of the system). Another three sets of data have been recorded for a system of 200 spheres, for which the packing density is equal to 0.26. Each system has been thermalized for more then 20 collisions per molecule before recording the data. If no energetic effects are associated with reaction (1) then the reaction rate can be easily calculated using recorded data. Let us fix the activation energy and let us assume that at the beginning the system is composed of the reactant A only. Now it is easy to watch the progress of a reaction path, which starts from an arbitrary point at the recorded trajectory, by "coloring" all the spheres as A and then checking if successive collisions are reactive (i.e., both the colliding spheres represent reactant and the energetic condition is satisfied). Of course after a reactive collision the parameter marking the chemical identity of spheres has to be changed. Such a procedure may be repeated by choosing different starting points at the recorded trajectory and we obtain different reaction paths. For the statistics presented below we have generated trajectories by assuming that they start immediately after any collision for which the energetic condition is satisfied. This method gives us the largest number of different reaction paths from the data available. Their number, for a fixed amount of recorded data, scales as $\exp(-E/k_BT)$. In this paper 2.5×10^5 of trajectories have been generated for $E=1k_BT$ in the system of 500 spheres. We have also tested the approach in which the generated reaction paths are separated by a few collisions in which the collision energy exceeds E. The results are the same but the statistical error larger, because of a reduced amount of data.

Every single reaction paths gives us a sequence of times $\{t_n\}_{n=1,N/2}$ corresponding to the moments when the nth reactive collision occurs. To obtain more objective information about the system the mean value is calculated using the data coming from all generated reaction paths (this kind of average is denoted by $\langle\ \rangle$). Such an approach assigns the same statistical weight to all reaction paths. We have also applied another method of averaging, in which the weight is proportional to the interval of time between the beginning of simulation and the first reactive collision. The second method seems to be better because it describes more precisely the average over a molecular-dynamics trajectory, but in practice both methods lead to similar results. The rate constant, which corresponds to the concentration of products c ($c=2n/N_0$) is calculated as

$$k(c)=\frac{2}{N_A(N_A-1)(\langle t_{n+1}-t_n\rangle)} \qquad (2)$$

where N_0 is the total number of molecules and N_A denotes the number of molecules of A ($N_A=N_0-2n$). The error in $\langle t_n\rangle$ can be estimated using the central limit theorem

$$\delta t_n=[\langle(t_n-\langle t_n\rangle)^2\rangle/N_p]^{1/2} \qquad (3)$$

where N_p is the number of reaction paths created in simulations. Finally the relative error of $k(c)$ should be of the order of

$$\delta k(c)/k(c)\cong\frac{[(\delta t_n)^2+(\delta t_{n+1})^2]^{1/2}}{(\langle t_{n+1}-t_n\rangle)} . \qquad (4)$$

The reaction rate as a function of c, normalized to its equilibrium value $k(0)=k(c=0)$ is presented in Fig. 1. The dashed curves show $[k(c)-\delta k(c)]/k(0)$ and $[k(c)+\delta k(c)]/k(0)$ and they help us to estimate the statistical error. Of course $k(0)$ represents the rate constant for a well thermalized system. It may be calculated from Eq. (2) if we substitute the beginning of simulation as t_0 or from the frequency of reactive collisions all along the trajectory [1]; in our case both numbers have agreed very well.

The nonequilibrium rate constant can also be calculated from the phenomenological rate equation, which for reaction (1) reads

$$\frac{dc(t)}{dt}=k(c(t))[1-c(t)]^2 . \qquad (5)$$

The concentration of products as a function of time $c(t)$ can be calculated from molecular-dynamics data as the average of $(N_0-N_A)/N_0$ over all the reaction path; $c(t)=1-\langle N_a(t)\rangle/N_0$. Then it is easy to extract $k(c)$ from Eq. (5) by numerical differentiation. In our case both methods [Eqs. (2) and (5)] lead to almost the same function $k(c)$. The comparison for $E/k_BT=1$ and 2 is shown in Fig. 2.

In the studied range of activation energies (from $0.5k_BT$ to $6k_BT$) the data of molecular-dynamics simulations show that the reaction rate is significantly reduced if compared with its value for a well thermalized system. The character of changes in k depends on the value of activation energy. For low activation energies [$\leq 1k_BT$, Figs. 1(a) and 2(a)] the reactive collisions only slightly disturb the velocity distribution of the reactant. Nevertheless, due to the high frequency of such collisions the effect cumulates and becomes the most important for $c\approx 0.4$. For activation energies larger than $3.0k_BT$ [Figs. 1(d), and 3(b)] the change in rate constant is very fast and occurs for $c<0.1$. Then the progress of reaction is governed by a steady nonequilibrium value of k. The largest influence of the nonequilibrium effects on the reaction rate is observed around $E/k_BT=2$. Let us also notice that the reaction rate starts to increase towards its equilibrium value for a large concentration of products [Fig. 1(b)]. It can be easily understood because for a high concentration of product the nonreactive collisions which thermalize the system become more frequent than the reactive ones.

The results obtained from the Boltzmann equation formalism are compared with the molecular-dynamics simulations in Table I. However, this formalism neglects the presence of the reaction products and describes the influence of the nonequilibrium effects on the rate constant by a single number, whereas as one can see [Figs. 1(a), 1(b), and 2(a)], for low values of the activation energy the nonequilibrium rate constant strongly depends on c. Therefore the direct comparison is meaningful only if the nonequilibrium value of the rate constant is achieved at small concentration of product and then remains constant ($E/k_BT \geq 3.0$). For lower activation energies the results of the Boltzmann formalism are compared with the maximum observed change in the rate constant.

For low activation energies the change in the rate constant obtained in simulations is larger than the one predicted by the theory. For larger activation energies the agreement is better because the assumptions of the Boltzmann equation approach (small deviation of the velocity distribution function for reactant from the Maxwell distribution) are satisfied. Unfortunately, the calculations for activation energy larger then $6k_NT$ are strongly affected by the statistical error (too small an amount of data) and we are unable to judge how fast the nonequilibrium effects decrease with increasing E (theory

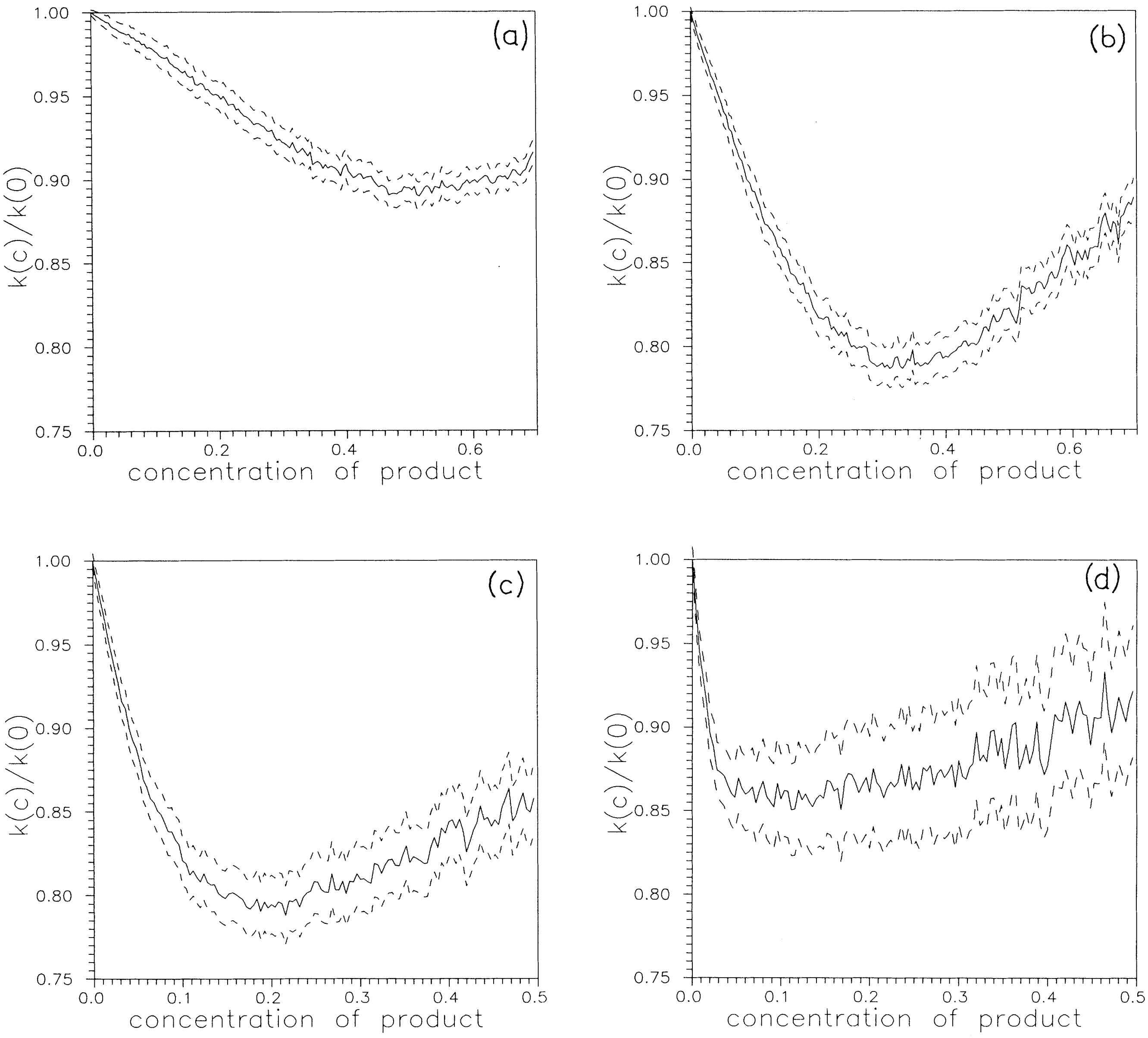

FIG. 1. The solid line shows the rate constant normalized to its equilibrium value as a function of the total concentration of products c. The activation energy $E^* = E/k_BT$ equals (a) 0.5, (b) 1.5, (c) 2.5, (d) 4.0. The simulations have been performed for a system of 500 spheres with the packing density equal to 0.0824. The dashed lines estimate the statistical error [Eq. (4)].

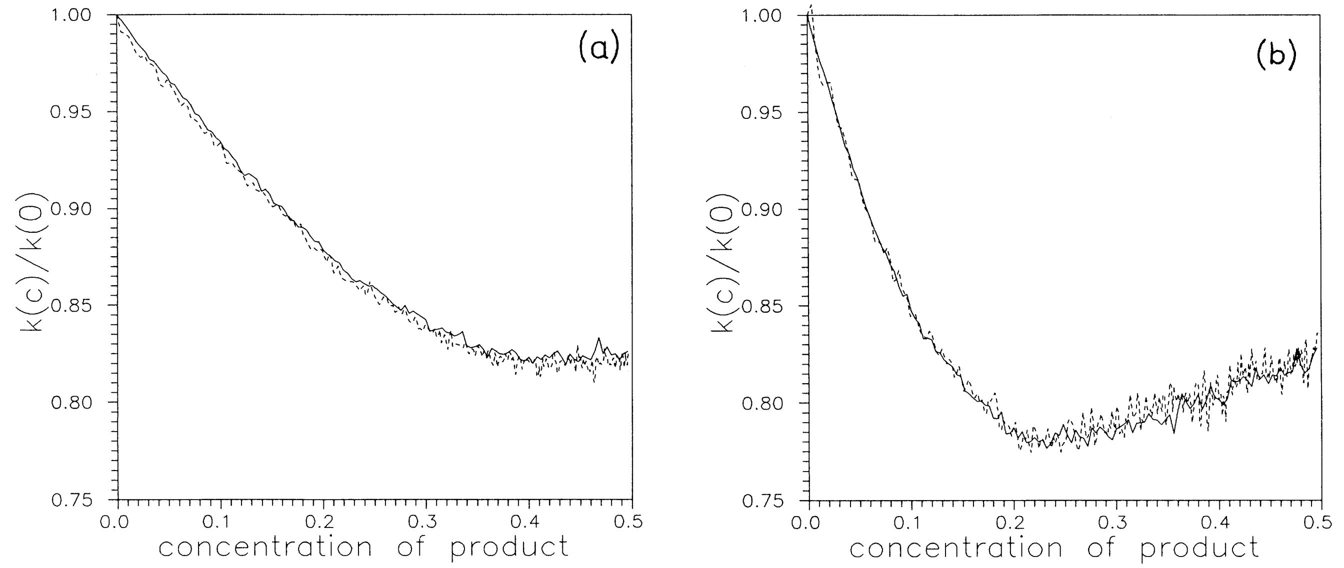

FIG. 2. The comparison of two methods for calculations of $k(c)$; the solid line, Eq. (2); the dashed line, Eq. (5). The results for a system of 500 hard spheres with the packing density $\nu=0.0824$; [(a) $E/k_BT=1$; (b) $E/k_BT=2$].

predicts that it is negligible for $E/k_BT>15$). Nevertheless we observe that the influence of nonequilibrium effects on the reaction rate starts to decrease above $E/k_BT=2$. The fact that the influence of nonequilibrium effects on the reaction rate reaches its maximum for $E/k_BT\cong 2$ has been recently confirmed by the novel analytical approach to the solution of the Boltzmann equation with the term describing a chemical reaction and by the numerical simulations of this equation using the Nambu-Babovsky method [11].

For large activation energies the fact that the results of simulations are compared with the theory based on the Boltzmann equation rather than with the one which uses the Enskog equation seems to be not very important. It was shown [12] that if the volumes of spheres representing reactant and products of (1) are the same then the rate constant for a dense fluid equals the rate for the diluted gas scaled by the value of the radial distribution function at the diameter of sphere. Therefore the ratio $k(c)/k(0)$ should not depend on density.

TABLE I. The change in rate constant $\eta(c)=1-k(c)/k(0)$ caused by nonequilibrium effects. Notation: $E^*=E/k_BT$, η_s the result obtained from the Boltzmann equation formalism by Shizgal and Karplus (formula (53) of [5(a)]), $\eta_{\max}$ and $c_{\max}$ the maximum change in the rate constant and corresponding concentration of product.

E^*	η_s	$\eta_{\max}$	$c_{\max}$
0.5	0.005	0.11	0.5
1.0	0.0008	0.18	0.4
1.5	0.003	0.21	0.3
2.0	0.017	0.22	0.25
2.5	0.037	0.20	0.2
3.0	0.057	0.19	0.15
3.5	0.072	0.16	≈ 0.1
4.0	0.081	0.14	<0.1
4.5	0.084	0.11	<0.1
5.0	0.082	0.09	<0.1
6.0	0.069	0.06	<0.1

This conclusion is confirmed by the results of molecular-dynamics simulations, in which different numbers of spheres and different densities of the system have been used. The comparison between the system of 500 spheres with $\nu=0.0824$ and the system of 200 with $\nu=0.26$ is shown in Fig. 3. The qualitative behavior of $k(c)/k(0)$ as a function of c remains unchanged. The quantitative results of different simulations for large activation energies ($E/k_BT\geq 3$) agree within the statistical error [Fig. 3(b)]. However, for low activation energies some differences may be observed [see Fig. 3(a)]. We believe that these differences are caused by nonequilibrium spatial correlations, which may depend on the system density. Nevertheless the contribution to the rate constant coming from such nonequilibrium spatial correlations, in the range of densities studied, seems to be only a small fraction of the observed nonequilibrium effect, which mainly comes from nonequilibrium velocity distribution function.

III. DISCUSSION

We believe that the effect calculated in this paper is the maximum one which may be expected for a system of "reacting" hard spheres. If only a fraction of collisions, for which the energetic condition is satisfied, is reactive (i.e., the steric factor is less than 1) then thermalization of

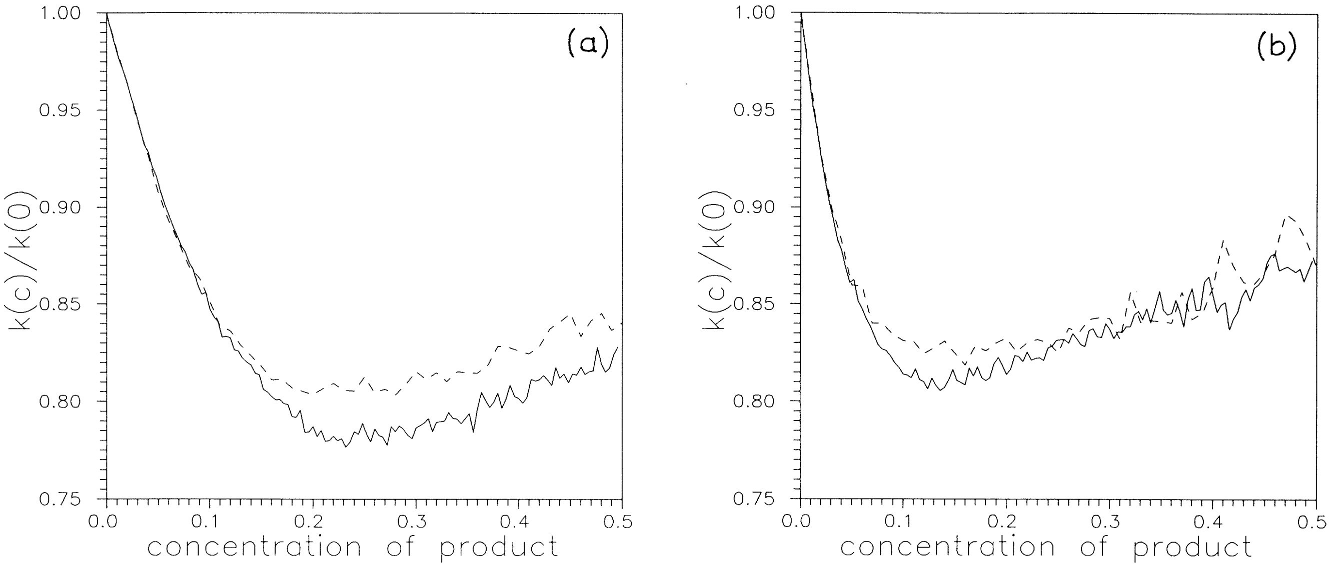

FIG. 3. The normalized rate constant as a function of c [(a) $E/K_BT=2$; (b) $E/k_BT=3$]. Parameters of simulations: solid curve, 500 spheres and $\nu=0.0824$; dashed curve, 200 spheres and $\nu=0.26$.

the reactant is more effective and so deviation from the equilibrium reaction rate is lower. Of course more effective thermalization can also be obtained by introducing nonreactive substances in our system.

Although the applied model of reacting hard spheres seems to be very crude, it reflects many aspects of real chemical processes. It is usually assumed that the distribution of all degrees of freedom relevant for the chemical reaction is the equilibrium one. In reality the chemical reaction destroys the equilibrium and the relaxation mechanisms act in the direction of restoring it. The actual state of the system results from balancing of these two opposite processes and the reaction rate may differ from its equilibrium value.

Of course, the numerical accuracy of simulations can be improved by increasing the number of molecules in the system and the amount of recorded data. Our calculations have been done on IBM PC-like microcomputers and we believe we have approached the technical limits of the machines available.

Ending this paper we would like to point out that the maximum decrease in the reaction rate obtained in molecular-dynamics simulations ($\approx 20\%$) is much larger than predicted by earlier methods ([2–6]). This means that it may be important in real chemical systems. A similar conclusion stressing the importance of nonequilibrium effects has been reached by Baras and Malek Mansour [9] in their study of exothermic chemical reactions.

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