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The Adiabatic Thermal Explosion in a Small System: Comparison of the Stochastic Approach with the Molecular Dynamics Simulation

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A new model of the adiabatic thermal explosion with biomolecular reaction $X + X \rightleftarrows A + A$ is proposed. The parameters of reaction are chosen such that the stochastic description predicts a transient bimodality of behavior. For the same system the nondeterministic character of the time evolution is confirmed by a molecular dynamics simulation.

KEY WORDS: Fluctuations; computer simulations; combustion; ignition.

1. INTRODUCTION

The adiabatic thermal explosion seems to be an example of a realistic process which exhibits a transient bimodality of behavior. In the first paper on this subject,(1) a very simple model of the adiabatic thermal explosion based on the unimolecular reaction $A \to X$ was discussed. The stochastic description of this process (pure master equation approach) predicts the high dispersion of $P(X, t)$ (probability distribution of finding a given number of molecules of X for fixed time t). For a special choice of the parameters of explosion $P(X, t)$ has a double maximum for a period of time, which means that different ways of evolution are possible.

However, the model of Baras *et al.*(1) contains some important simplifications. It is assumed that the system is homogeneous and the tem-

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perature is uniform in space. This means that the relaxation of the system is instantaneous and then it is possible to neglect all the transport processes (mass and energy) within it. The question of whether such an assumption is possible has not been discussed yet.

The aim of this paper is to include the transport processes in the description of the adiabatic thermal explosion. This is done by a molecular dynamics computer simulation. Now the unimolecular reaction $X \rightarrow A$ seems to be too simple to be studied by molecular dynamics. In this paper we are therefore concerned with a slightly more realistic reaction, $\mathrm{X}+\mathrm{X} \rightleftharpoons \mathrm{A}+\mathrm{A}$. We assume that the molecules are hard spheres without any internal structure and we adopt a three-level model for the chemical reaction. In the framework of our model the change of kinetic energy is the only kind of excitation of molecules after the reaction.

The paper is divided into two parts. Section 2 we introduce a new model of adiabatic thermal explosion and we present the results of the stochastic analysis. The methods used there are closely connected to these of Refs. 1 and 2. The results of the molecular dynamics simulation of the time evolution for the same system are presented in Section 3.

2. THE STOCHASTIC MODEL OF THE ADIABATIC THERMAL EXPLOSION WITH BIMOLECULAR REACTION

In this paper we are concerned with the bimolecular exothermic reaction $\mathrm{X}+\mathrm{X} \rightleftharpoons \mathrm{A}+\mathrm{A}$. The relative energies of $\mathrm{X}+\mathrm{X}$ and $\mathrm{A}+\mathrm{A}$ states are displayed in Fig. 1 (the so-called three-level model for chemical reaction). Here U_A and U_R denote, respectively, the activation energy and the heat of reaction for the direct reaction $\mathrm{X}+\mathrm{X} \rightarrow \mathrm{A}+\mathrm{A}$. Of course the activation energy for the inverse reaction $\mathrm{A}+\mathrm{A} \rightarrow \mathrm{X}+\mathrm{X}$ is $U_A + U_R$ and the heat is equal to $-U_R$. Now let us consider a system of N_0 molecules of X at the temperature T_0 at time $t=0$. The temperature of the system is a function of time, since the reaction is exothermic. If we assume that the process is adiabatic (no exchange of energy with surroundings) and that the system is homogeneous, with the temperature uniform at every point of space, then the conservation of energy gives the following relationship between N_{X}, the number of molecules of X, and the temperature $T(N_{\mathrm{X}})$:

$$N_0 U_R + 3k_{\mathrm{B}} T_0 N_0 = 3k_{\mathrm{B}} T(N_{\mathrm{X}}) N_0 + N_{\mathrm{X}} U_R \tag{1}$$

where k_{B} is Boltzmann's constant. In the above equation the assumption that our system is composed of hard spheres has been used ($C_V = \frac{3}{2} k_{\mathrm{B}} N_0$). The assumption about uniform temperature has been the basis of many recent papers on the adiabatic thermal explosion (for example, Refs. 1–3). The method presented in the nexxt section does not require it.

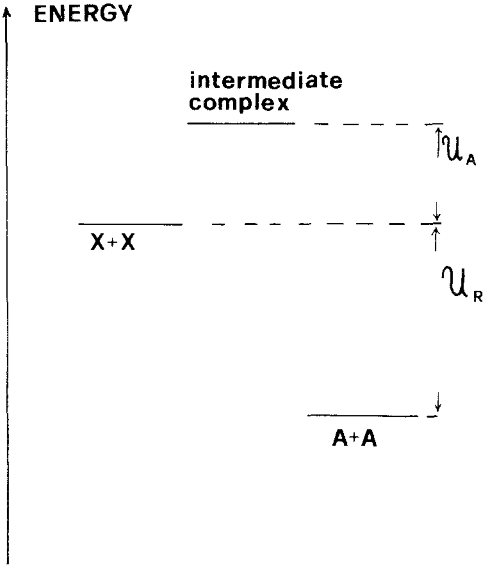


Fig. 1. The three-level model of chemical reaction.

The temperature dependence on the reaction rate $k(T)$ may be described by the Arrhenius law:

$$k(T) \sim \exp[-(\text{activation energy})/k_B T] \tag{2}$$

The transition probabilities for the direct reaction μ and for the inverse reaction λ are given by the following formulas[4]

$$\begin{aligned}\mu(N_X) &= \mu(\{N_X, N_A\} \to \{N_X - 2, N_A + 2\}) \\ &= k_{D_0} \frac{N_X(N_X-1)}{2} \exp - \frac{U_A}{k_B T(N_X)} \\ &= \frac{N_X(N_X-1)}{2} k_D T(N_X) \end{aligned} \tag{3a}$$

$$\begin{aligned}\lambda(N_X) &= \lambda(\{N_X, N_A\} \to \{N_X + 2, N_A - 2\}) \\ &= k_{I_0} \frac{N_A(N_A-1)}{2} \exp - \frac{U_A + U_R}{k_B T(N_X)} \\ &= k_{I_0} \frac{(N_0 - N_X)(N_0 - N_X - 1)}{2} \exp - \frac{U_A + U_R}{k_B T(N_X)} \\ &= \frac{N_A(N_A-1)}{2} k_I T(N_X) \end{aligned} \tag{3b}$$

For the set of parameters for adiabatic thermal explosion used in this paper ($N_0 = 100$, $T_0 = 200$ K, $U_A = 1200k_B * \text{deg}$, $U_R = 6000k_B * \text{deg}$) the functions $\mu(N_X/2)$ and $\lambda(N_X/2)$ are displayed in Fig. 2. The values of k_{I_0} and k_{D_0} [Eqs. (3a) and (3b)] have been set to unity.

Having the values of μ and λ, we are able to solve the master equation for $P(Y, t)$. In the discussed case it reads

$$\frac{dP(Y,t)}{dt} = -[\mu(Y) + \lambda(Y)] * P(Y,t) + \mu(Y+2) * P(Y+2,t) + \lambda(Y-2) * P(Y-2,t) \tag{4a}$$

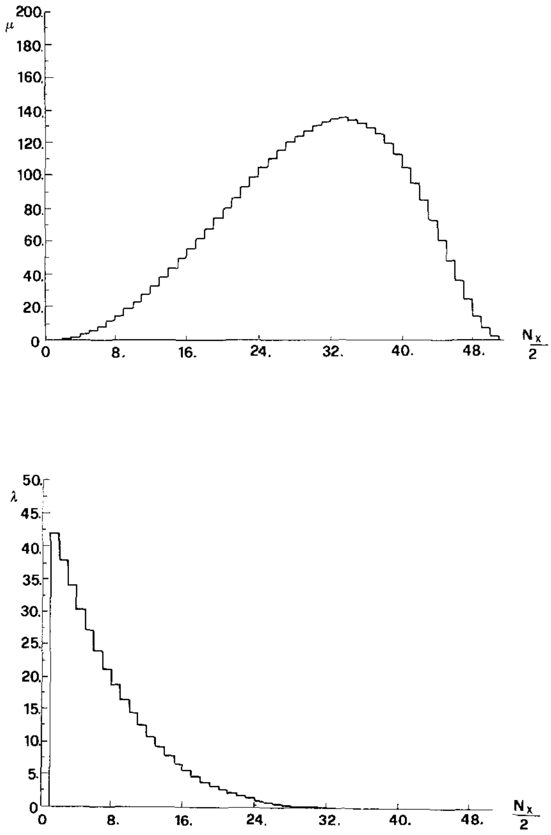


Fig. 2. The transition probabilities for the direct (μ) and the inverse (λ) reactions.

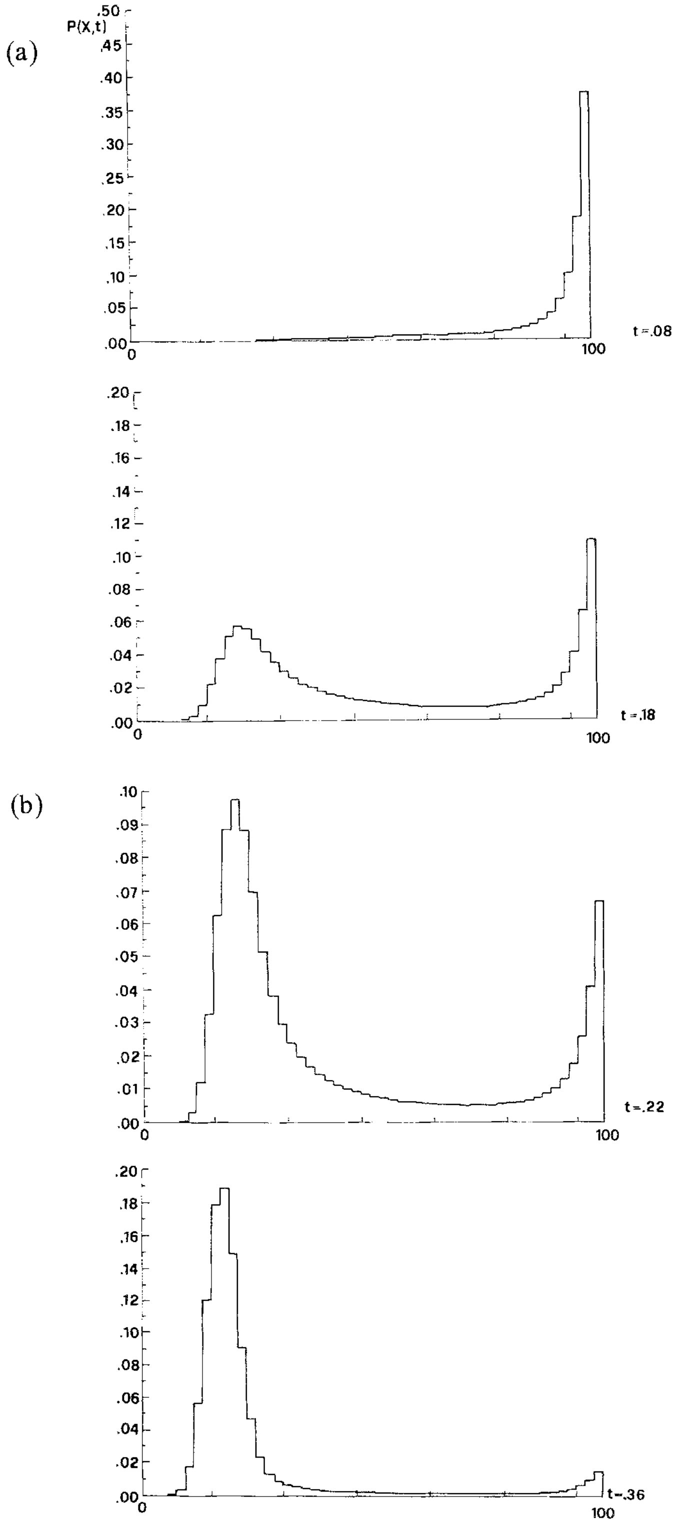


Fig. 3. The time evolution of the $P(X, t)$ according to the stochastic method.

where $(0 < Y < N_0)$

$$\frac{dP(N_0, t)}{dt} = -\mu(N_0) * P(N_0, t) + \lambda(N_0 - 2) * P(N_0 - 2) \tag{4b}$$

$$\frac{dP(0, t)}{dt} = -\lambda(0) * P(0, t) + \mu(2) * P(2, t) \tag{4c}$$

The initial condition is $P(Y, 0) = \delta_{Y,N_0}$. As the set of equations (4a)–(4c) has nonlinear coefficients (due to the nonlinear factor in the Arrhenius law), a numerical method has been applied. The time evolution of $P(Y, t)$ is presented in Fig. 3. As in the case of a unimolecular reaction,(1–3) a double maximum of the probability distribution, which corresponds to a transient bimodality, can be seen.

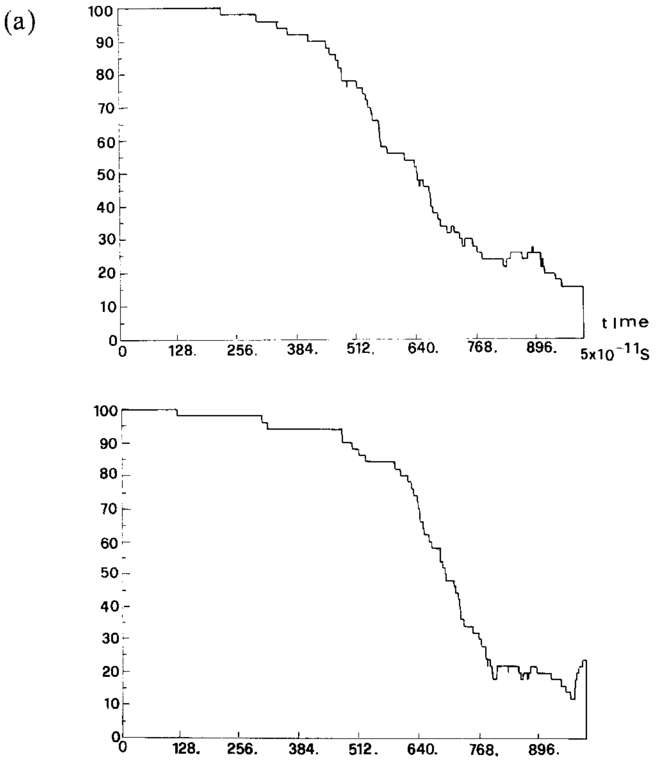
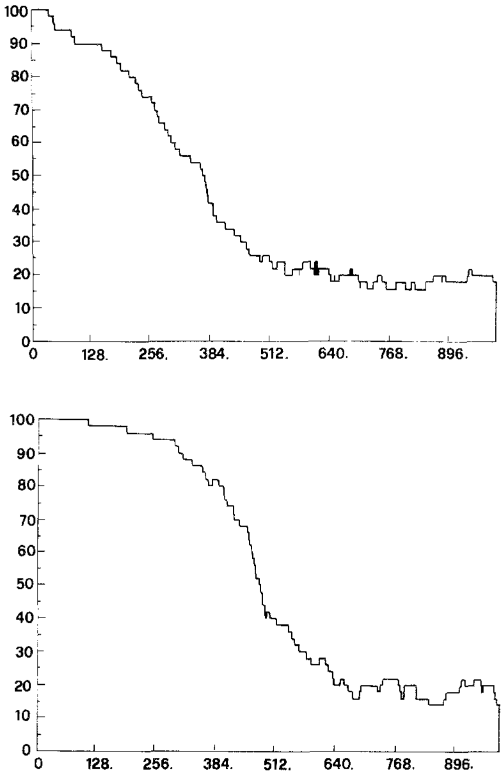


Fig. 4. The number of molecules of X as a function of time for different molecular dynamics simulations.

(b)



(c)

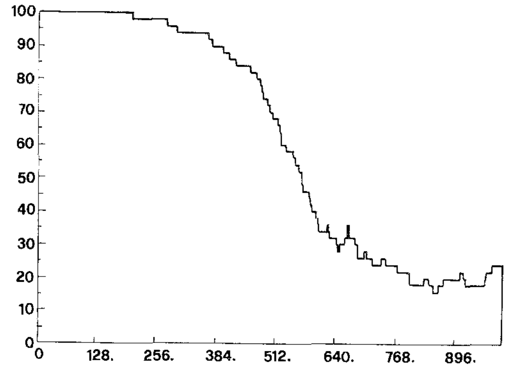


Fig. 4 (*continued*)

3. THE RESULTS OF MOLECULAR DYNAMICS SIMULATION OF AN ADIABATIC THERMAL EXPLOSION

As pointed out in the Introduction, the problem of energy transport in a system that exhibits an adiabatic thermal explosion was not discussed in previous papers.(1–3) To test if the transport processes have an important influence on the behavior of the system described in Section 2, we decided to study the time evolution with the use of molecular dynamics.

The standard molecular dynamics technique for hard spheres has been applied. The model for a reactive collision is the same as used by Xystris and Dahler.(6) Every collision of A with X is regarded as elastic, whereas the collisions of X with X and of A with A are reactive when the kinetic energy associated with the relative motion along the line of centers exceeds the activation energy. In such a case the reaction heat changes the component of velocity along the line of centers. A similar molecular dynamics technique was used by Chou and Yip(9) in their work on the temperature profile in a nonadiabatic, two-dimensional system with an exothermic reaction.

A system of 100 molecules has been studied. The molecular diameter (5 Å) has been chosen arbitrarily. As we are interested in the gas-phase reaction, the density should be very small. The results are presented for two different packing densities: $\eta = 0.052$, box length 50 Å (Fig. 4) and $\eta = 0.00042$, box length 250 Å (Fig. 5). The initial positions of molecules were randomly distributed in space and the initial velocities were chosen from the Maxwell distribution for the temperature $T_0 = 200$ K. The system was thermalized for more then 2000 collisions (only elastic collisions have been allowed). Such a method of thermalization seems to be sufficient to reach thermal equilibrium, because it is known that only a few collisions per molecule are needed to thermalize a system of hard disks.(7) To test if the velocity distribution describes the system in thermal equilibrium we have compared the number of molecules with energy greater then an assumed value with the value obtained assuming the Maxwell distribution. Good agreement (up to fluctuations) between these two numbers was obtained. Moreover, for thermalizations longer then 200 collisions no systematic approach toward the Maxwell distribution was observed. After the thermalization we allowed the reaction to start.

The time evolution of the system after different thermalization times is shown in Fig. 4. Although all the initial states are equivalent from the thermodynamic point of view, we can see that the time evolution is not unique. The difference is caused by the coupling between fluctuations and the dynamics of the system. It can be noticed (see Fig. 2) that the characteristic time ($\sim\mu^{-1}$) in the initial period, where the reaction is very slow, is many

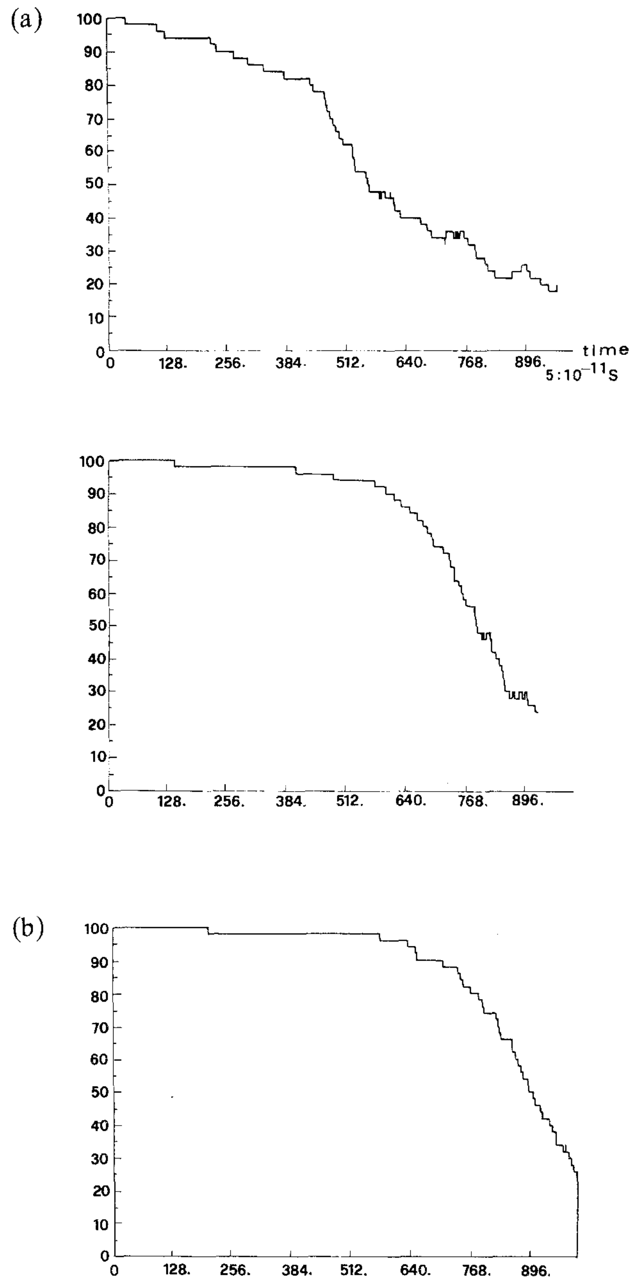


Fig. 5. The number of molecules of X as a function of time for different molecular dynamics simulations of a system with low density.

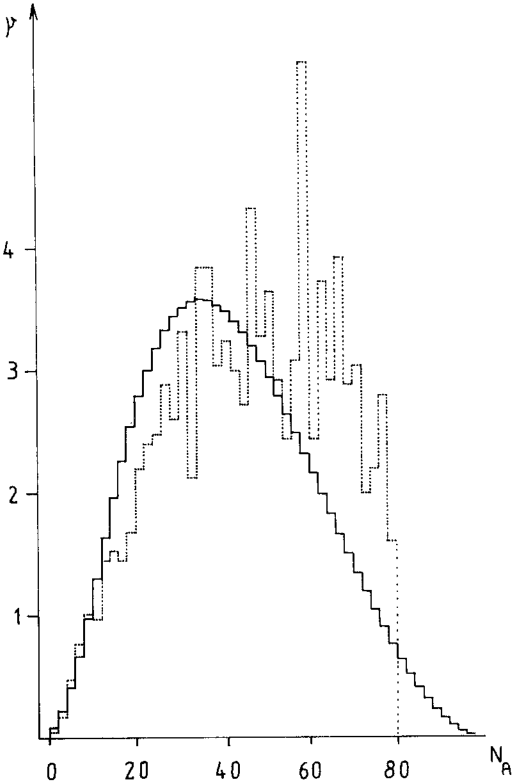


Fig. 6. Comparison of the transition probabilities for the direct reaction; (—) Eq. (3); (···) molecular dynamics simulation; (a) $k_{D_0} = \text{const}$, (b) $k_{D_0} \sim \sqrt{T}$.

times longer then the characteristic time in the explosive regime. There is a strong correlation between fluctuations in the initial period and the time evolution. After a few reactive collisions the reaction speeds up and the evolution is almost deterministic. But the dispersion of the transition time in the initial period is large compared with the time of explosion. For 25 simulations we found that the transition time from the state $N_X = 100$ to the state $N_X = 90$ is $t_1 = 4.7$ E-11 sec and its dispersion is $\sigma_1 = 3.9$ E-11 sec. This high value of dispersion is a consequence of the fact that the probability of a single reaction is described by the Poissonian distribution, where the average is equal to the dispersion, and it is not reduced when a large statistical sample is considered. On the other hand, an average time of transition from $N_X = 90$ to $N_X = 30$ is $t_2 = 1.8$ E-11 sec with the dispersion $\sigma_2 = 3$ E-12 sec. The dispersion σ_1 is larger than t_2 and therefore the behavior of the system is nondeterministic. Our result means that the

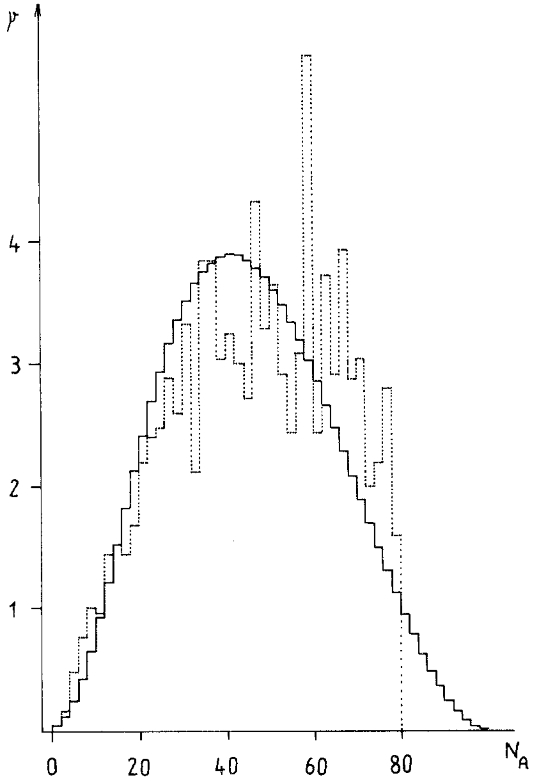


Fig. 6 (*continued*)

inclusion of a realistic mechanism for heat transport does not change the qualitative description of an adiabatic thermal explosion. This is not surprising, because both effects, heat transport and chemical reaction, are connected with collisions.

The transition probabilities for the direct reaction obtained from the molecular dynamics simulations are compared with that used in the stochastic model [Eq. (3)] in Fig. 6 (they are denoted by dotted and solid lines, respectively). In Fig. 6a one constant value of the parameter k_{D_0} [Eq. (3)] was adjusted to fit the simulation data. It corresponds to the assumption that the transition probability depends on the temperature by the Arrhenius factor only and k_{D_0} is constant. This assumption was used in previous papers on the thermal adiabatic explosion(1-3) and in the calculations presented in Section 2. However, the molecular dynamics approach suggests that the more realistic model should take into account the changes of k_{D_0} with temperature. This can be done according to the well-known formula for the number of collisions per unit time in a hard-sphere system,(10)

$$k_{D_0} = 4d^2(4\pi k_B T/m)^{1/2} \tag{5}$$

where m and d denote, respectively, the mass of a molecule and its diameter. Figure 6b shows a comparison between simulations and Eq. (3) when the factor $\sqrt{T}$ is included in k_{D_0}. The scale is chosen such that for $N_0 = 100$ the transition probability of both methods is equal to 1. The agreement is better then that presented in Fig. 6a. However, this additional factor has no significant influence on the qualitative description of the process in the stochastic method. It increases the difference of the time scales between the initial period and the explosive regime and if the transient bimodality is observed for the model with $k_{D_0} = \text{const}$, it also will be observed when $k_{D_0} = \tilde{k}_{D_0}\sqrt{T}$.

Our molecular dynamics program uses periodic boundary conditions, which are justified for a system in equilibrium, but which in the nonequilibrium case can give additional stirring. To verify whether this additional energy transport is important for the results of the model, we have carried out simulations for a system characterized by a much lower density, where this stirring is much more important. If we compare the master equation (4a)–(4c) with the phenomenological equation for the reaction $X + X \rightleftharpoons A + A$,

$$dn_X/dt = -k_D(T) * n_X^2 + k_I(T) * (n_0 - n_X)^2 \tag{6}$$

where n_0 and n_X are the initial density of molecules and the density of molecules of X, respectively, we can find that k_{D_0} and k_{I_0} in the master equation scale like V^{-1}, where V is the volume of the system. Therefore, if the influence of the transport processes connected with the periodic boundary conditions on the behavior of our system is negligible, the results of molecular dynamics simulation for a different density m_0 should be the same when the time is rescaled by the factor n_0/m_0 (when we neglect the dependence of k_{D_0} on density,(8) which is not very important for low densities). We have done a molecular dynamics simulation of another system at a density 125 times lower. Figure 5 displays the time evolution in rescaled time. It may be noticed that these results are very similar to those of Fig. 4, which confirms the assumptions of the stochastic model.

4. CONCLUSIONS AND DISCUSSION

We have presented two different approaches for the description of an adiabatic thermal explosion: a stochastic method and a method based on molecular dynamics. The results of both methods are in qualitative agreement. The fluctuations in the initial period have a large influence on the time evolution, and the behavior of the system is nondeterministic because the dispersion of $P(X, t)$ is high. Our results show that the inclusion of transport does not change the qualitative description of the adiabatic thermal explosion and so the assumptions of the stochastic model are justified; however, more realistic stochastic models should take into account such effects as the change of k_{D_0} (in our case collision frequency) with temperature.

Some information on the qualitative agreement of both methods can be obtained by comparing the transient probabilities predicted by them (Fig. 6). Higher accuracy can be achieved, but the computer time required is very large.

The set of parameters of the adiabatic thermal explosion has been chosen rather arbitrarily, but there are some reasons justifying the choice. The number of molecules used in the simulation is strongly limited by the speed of the computer, since computing time increases at a rate greater then linearly with it. For the bimolecular reaction the factor connected with the number of molecules in the formula for transition rate μ [Eq. (3)] is more important than that for the unimolecular reaction. Therefore, a large thermal effect of reaction is necessary to increase μ when the number of molecules is decreasing. The ratio of the activation energy and the average thermal energy of the molecules in the system cannot be too large without causing the computer to waste a great deal of time waiting for the first reactive collision. Our the other hand, when the initial temperature is too high, the system does not exhibit transient bimodality. For the calculations presented here a quite low initial temperature ($T_0 = 200$) was chosen. This does not affect the properties of the hard-sphere system, since they depend on the density. A similar effect may be expected at higher temperature when the activation energy and the reaction heat are rescaled by a factor corresponding to the ratio of temperatures. The points listed above were taken into account when the set of parameters for the reaction was chosen.

The molecular dynamics technique seems to be a good tool for simulating processes far from equilibrium in small systems. Unlike the master equation approach, this method does not involve the concept of the temperature of a transient state, which can have no meaning. We intend to apply this technique to the description of more realistic reactions.

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