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MOLECULAR DYNAMICS SIMULATION OF A CHEMICAL REACTION *

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Molecular dynamics is used to study of the chemical reaction $A + A \rightarrow B + B$. It is shown that the reaction rate constant follows the Arrhenius law both for Lennard-Jones and hard sphere interaction potentials between substrate particles A . For the denser systems the reaction rate is proportional to the value of the radial distribution function at the contact point of two hard spheres.

A preliminary data of the computer simulation of the rate of the chemical reaction $A + A \rightarrow B + B$ are presented. The rate of the reaction have been studied for two interaction potentials between substrate particles A , namely hard sphere (HS) potential and Lennard - Jones potential (LJ). The reaction is at very initial stage, when the concentration of the reaction products can be completely neglected. For this case a theoretical description based on the Boltzmann [1] and Enskog [2] equations is well known. In terms of a parameter G [3] ($G = 1 - \frac{n_A}{n_A^0}$, where n_A , n_B are concentrations of reacting species and K_p is the reaction equilibrium constant) our results correspond to $G = 1$. Theoretical description based on the kinetic equations assumes that the Maxwellian distribution of velocities of the substrate atoms is only slightly perturbed by the chemical reaction. This means that the substrate particles are practically in the thermal equilibrium. Obviously this assumption is valid for slow reactions with high activation barrier. In this case substrate particles can thermalise their velocities after each reactive collision.

The computer simulations reported here use a standard molecular dynamics with periodic boundary conditions [4]. In the case of HS interaction potential the collision is reactive if the kinetic energy of the relative motion in the direction along the line of centers of colliding particles is greater than activation energy E_a . This model of the reactive collision is consistent with the collision integral of the Boltzmann and Enskog equations. An alternative choice where a collision is reactive if the relative energy of colliding particles is greater than E_a seems to overestimate a frequency of the reactive collisions [5]. This is due to fact that in this case the collisions occurring nearly at the grazing angle may be also reactive. In the case LJ potential the collision is reactive if the distance between two particles is r_0 , where: $V_{LJ}(r_0) = E_a$.

During computer run the time at which the reactive collision occurs and the separation between colliding particles is stored. In the case of HS interaction the time of the first reactive collision corresponding to the activation energy E_a is stored. In these simulation we assume that the heat of reaction is zero and that the interaction potential between products is the same as between substrates. This implies that the temperature of the system is constant during simulation (except small fluctuations

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in the case of LJ interaction). The rate constant of the chemical reaction has been determined by computing an average of the time elapsing between successive reactive collision at a given activation energy E_a .

The numerical results reported here are for the system of $N_o = 200$ hard spheres and $N_s = 300$ LJ particles. The particles were thermalised initially (2000 collisions for HS and 2000 time steps for LJ) before simulation run has started. Typical probability distribution $P_{\Delta t}$ of the time intervals Δt between successive reactive collisions is shown in Fig. 1. The dispersion δt of the time interval average, $\langle \Delta t \rangle = \frac{1}{n} \sum_i \Delta t_i$; is given by [6]:

$$\delta t = \sqrt{(\Delta t - \langle \Delta t \rangle)^2} = \frac{\langle \Delta t \rangle}{\sqrt{n}} \quad (1)$$

where: n is the number of reactive collisions. This dispersion is used to estimate the accuracy of the rate constant.

In the stochastic approach the chemical reaction is treated as a jump process [7]. The master equation for the probability of finding of N_o particles of the substrate after time t , $P(N_o, t)$ is:

$$\frac{dP(N_o, t)}{dt} = -\alpha \frac{N_o(N_o - 1)}{2} P(N_o, t). \quad (2)$$

The average time interval elapsing up to the first reactive collision is:

$$\langle \Delta t \rangle = - \int_0^{\infty} t \frac{dP(N_o, t)}{dt} dt = \frac{2}{\alpha N_o(N_o - 1)}. \quad (3)$$

On average, after time $\langle \Delta t \rangle$ the number of substrate particles changes from N_o to $N_o - 2$. Taking into account the phenomenological equation for the time evolution of the substrate density, $n(t)$:

$$\frac{dn(t)}{dt} = -kn^2(t), \quad (4)$$

where k is the reaction rate constant, we see that:

$$k \sim \Omega \alpha \sim \frac{1}{t} \frac{\Omega}{N_o} = \frac{1}{\langle \Delta t \rangle n_o}, \quad (5)$$

where: Ω is the volume of the system and n_o is the number density. Eq.(5) does not determine the absolute value of the rate constant, but it is sufficient to study the dependence of k on the density of the reacting system.

As a first application of this simple model we study the dependence of the rate constant k on the activation energy E_a . The results displayed in Fig. 2 show that the rate constant depends exponentially on the activation energy in a wide density range. This is valid for both interaction potentials, HS and LJ. Therefore, the simple model of the chemical reaction presented here satisfies the Arrhenius law.

The dependence of k on the density of the system was studied for two values of the activation energy: $E_a = 0$ and $E_a = 13.31$ kJ/mol ($= 1600$ $k_B \cdot \text{deg}$). Although the larger values of E_a makes

our model more realistic, the time of simulation increases very fast with E_a . In other words for large E_a most collisions are elastic. For example, for HS potential and $E_a = 13.31$ kJ/mol on average only 21st collision is reactive. This means that the simulation time for this activation energy is 21 times longer than for $E_a = 0$ to get the same accuracy for the reaction rate from eq. (5).

The rate constant as a function of density for the temperature $T = 594.4^\circ\text{K}$ and two above values of the activation energy is presented in Fig. 3 and Fig. 4. As it was expected, a statistical uncertainty is much greater for $E_a = 13.31$ kJ/mol than for zero activation energy. Note that for the zero activation energy the reaction rate is essentially equivalent to the rate of elastic collisions.

The kinetic theory of chemical reactions, based on the Enskog equation [2] predicts that:

$$\frac{k}{k_o} \sim g(\sigma, n_o), \quad (6)$$

where k_o is the reaction rate for a dilute system and $g(\sigma, n_o)$ is the value of the radial distribution function at the density n_o at the contact point of two hard spheres. As it can be seen from Figs. 3 and 4, computer simulations confirm this result.

The results of computer simulations have been compared with the experimental data of Kistiakowsky [8] for the reaction $2HI \rightarrow H_2 + I_2$. The potential parameters selected for HI molecule were: hard sphere diameter $\sigma = 3.41$ Å (from viscosity data) and the depth of the LJ potential $\epsilon_{LJ} = 298.2^\circ\text{K}$ (from the value of critical temperature of HI). Due to large activation energy for this reaction (≈ 184.6 kJ/mol) [9] we can not determine absolute values of the rate constant by computer simulations. Therefore we have scaled the experimental results by the rate constant of dilute system, k_o and compare the slope of the experimental curve with computer simulations. The value of k_o has been found from reaction rates at low densities. The scaled experimental data are displayed in Figs. 3 and 4 together with the results obtained from computer runs. We see that for both activation energies computer simulations agree very well with the experimental data. This suggests that the relation $k \sim g(\sigma, n_o)$ does not depend on the details of the reaction model such as the activation energy and the interaction potential. This conclusion is supported by the theory based on the Enskog equation [2], and also by more elaborate theories of chemical reaction [10].

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1. I. Prigogine and E. Xhrouet, *Physica* **15** (1949) 913
2. A. S. Cukrowski and J. Popielawski, *J. Chem. Phys.* **78** (1983) 6584
3. N. Xystris and J. S. Dahler, *J. Chem. Phys.* **68** (1978) 387
4. B. J. Berne, *Statistical Mechanics* (Plenum Press, New York 1977)
5. R. Der and S. Fritache, *Chem. Phys. Lett.* **121** (1985) 177
6. W. Feller, *An Introduction to Probability Theory and its Applications*,
(Willey, New York 1966)
7. W. C. Gardiner, *Handbook of Stochastic Methods* (Springer, Berlin 1983)
8. B. G. Kistiakowsky, *J. Am. Chem. Soc.* **50** (1928) 2315
9. L. M. Raff, D. L. Thompson, L. B. Sims and R. N. Porter,
J. Chem. Phys. **56** (1972) 5998
10. R. Der, A. Markel and H.-J. Cserwon, *Chem. Phys. Lett.* **53**, (1980) 427
R. Der, R. Haberlandt and A. Merkel, *Chem. Phys. Lett.* **53** (1980) 437

1. The probability distribution of time intervals elapsing between successive reactive collisions (HS potential, $T=594.4^\circ\text{K}$, $n_0 = 1.86 \text{ mol/l}$, $E_a = 13.31 \text{ kJ/mol}$, 380 reactive collisions).
2. The reaction rate as a function of the activation energy E_a at $T = 594.4^\circ\text{K}$.
 - a) HS potential, $n_0 = 1.08 \text{ mol/l}$, solid line: Arrhenius curve.
 - b) LJ potential $n_0 = 1 \text{ mol/l}$, dashed line: Arrhenius curve
 - c) as b), but $n_0 = 5 \text{ mol/l}$
 - d) as b), but $n_0 = 7 \text{ mol/l}$
3. The reaction rate as a function of the density for $E_a = 0$ at $T = 594.4^\circ\text{K}$. Triangles are computer simulation for HS potential, filled circles are computer simulations for LJ potential and open circles are the experimental data of Kistiakowsky [8]. The solid line is the value of $\log g(\sigma, n_0)$.
4. As Fig. 3, but for $E_a = 13.31 \text{ kJ/mol}$.

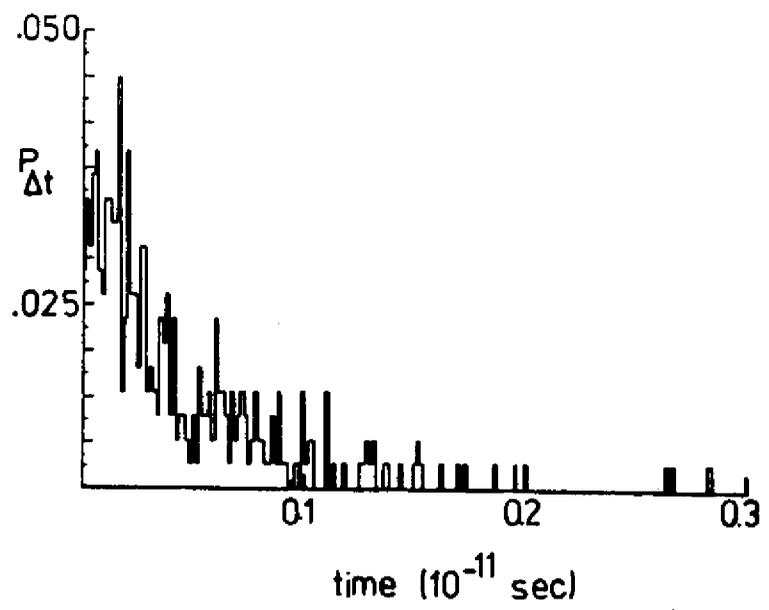


Fig. 1

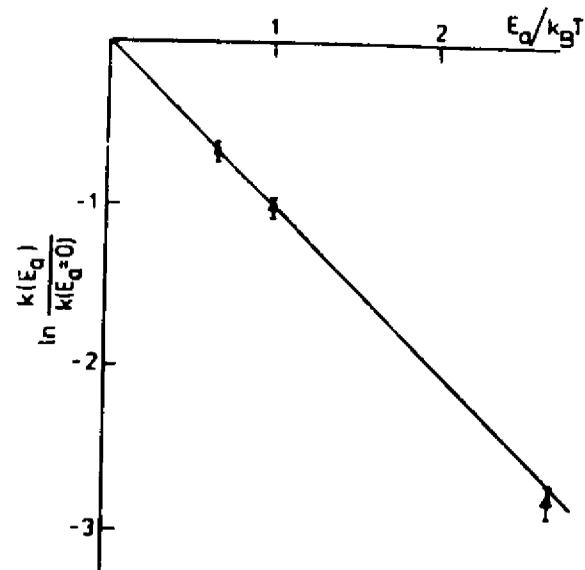


Fig. 2(a)

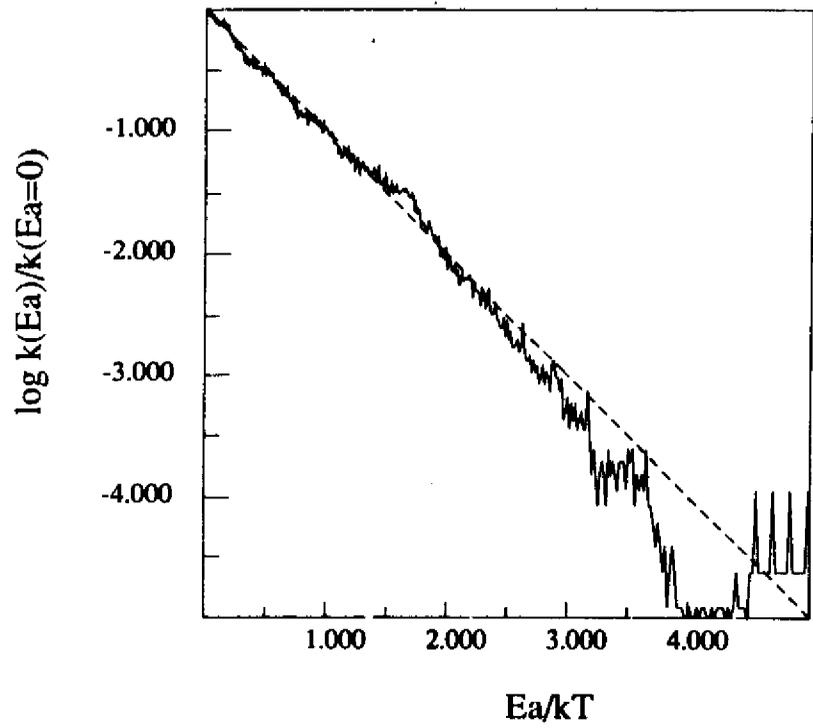


Fig. 2(b)

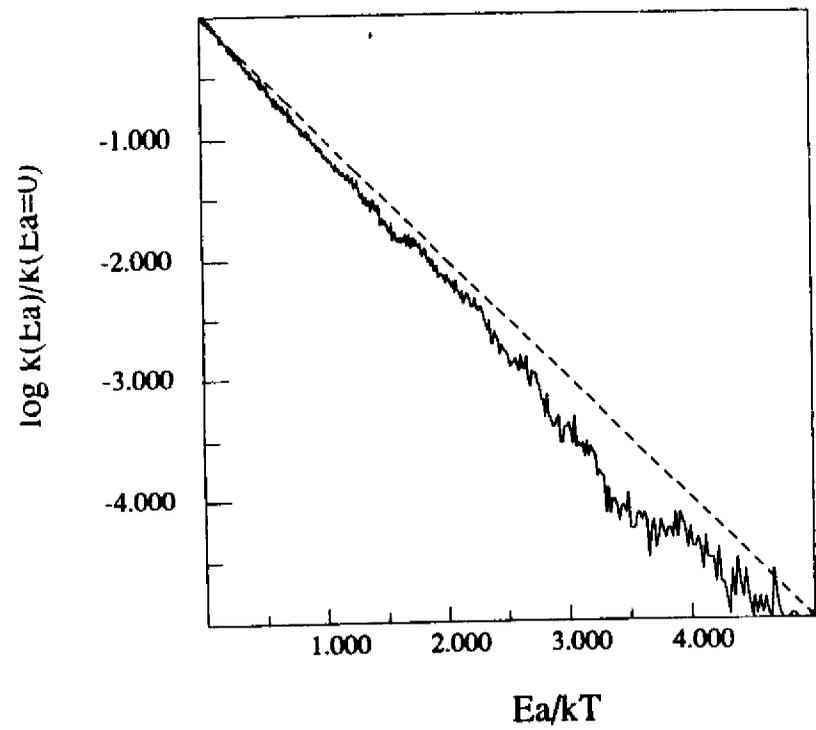


Fig. 2(c)

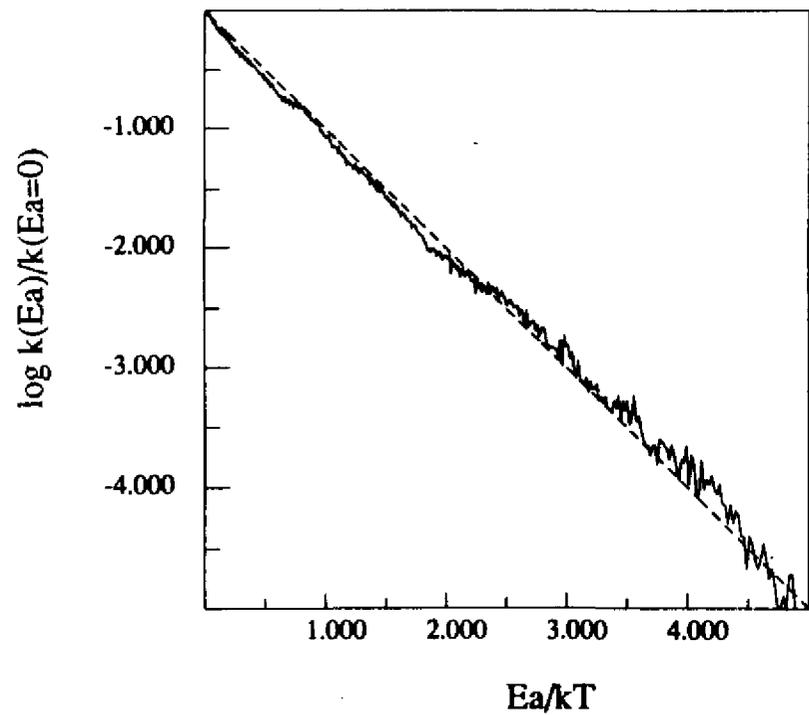


Fig. 2(d)

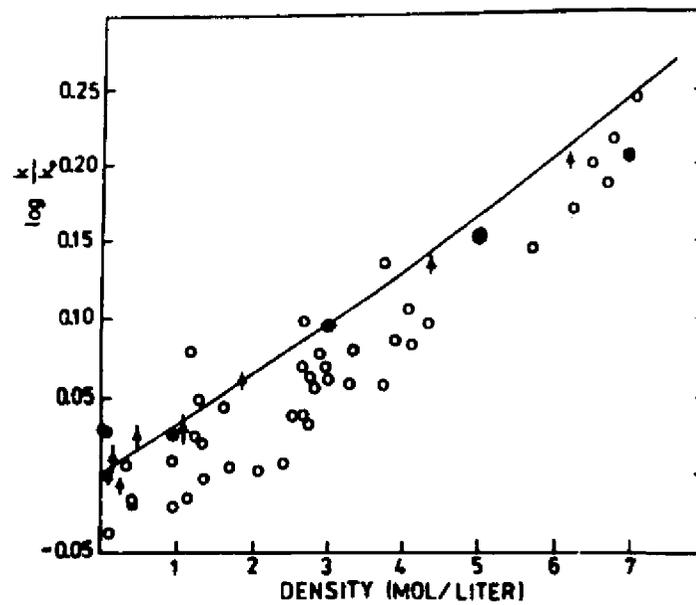


Fig. 3

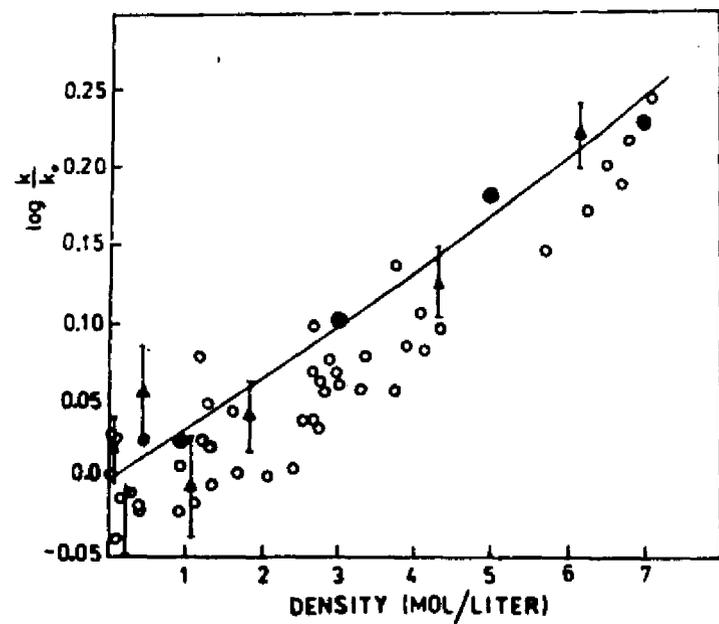


Fig. 4

