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REMARK ON LARGE SCALE COMPUTER SIMULATIONS OF MODEL CHEMICAL SYSTEMS

JERZY GÓRECKI

Institute of Physical Chemistry, Polish Academy of Sciences, Kasprzaka 44/52, PL-01-224 Warsaw, Poland

ABSTRACT: A new numerical technique, which may be useful for large scale microscopic simulations of model chemical systems is presented. The method allows one to study systems composed of millions of particles using a small computer. It may be applied to model a wide range of nonequilibrium phenomena associated with chemical reactions. A few applications of the method, namely: a homogeneous oscillations of concentrations, a chemical wave front propagation and nonequilibrium spatial correlations of reagents in a steady state of a chemical system, are briefly discussed.

I. INTRODUCTION

It is surprising that complex behaviour of a chemical system, which is composed of an enormous number of individual molecules of reagents linked together by complicated interactions, can be usually succesfully desribed on the basis of kinetic equations using such simple variables as concentrations and temperatures. The equations may be also applied for fast chemical processes, giving a reasonable approximation for the observed evolution. However, for very fast chemical phenomena the nonequilibrium effects may play an important role [1]. In the case of nonlinear systems the presence of fluctuations may significantly influence system's evolution [2]. The standard methods of chemical kinetics do not take into account nonequilibrium effects nor fluctuations. Therefore, generalization of these methods is important for the future development of chemical kinetics. Many theoretical papers concerned with this problem have been published in the recent years. [3, 4].

However, it is difficult to test new theoretical ideas by comparing them with experimental results because the real reactions are extremly complex and usually we do not know all the elementary processes involved. Even for the Belousov-Zhabotinskii reaction, which has been intensively studied for about 40 years, we are not able to name the ellementary processes and give their rate constants.

Large scale computer simulations of chemical systems allow us to test theories using idealized, model reaction schemes and thus, they play the role of "experiments" in which, contrary to the real experiments, all the elementary reaction steps are known. The most popular simulation techniques are the Bird method [5] and the lattice-gas cellular automaton [6]. These methods allow us to study the time evolution of systems

composed of millions of particles. Moreover, they are fast enough to give us information on collective phenomena like chemical oscillations [7], front propagation [8, 9] or Turing structures [10], for which characteristic times are much longer than the characteristic time describing intermolecular interactions. In order to speed up simulations, it is usually assumed that a parameter, which describes chemical properties of a particle, has no influence on its mechanical motion. This parameter may be regarded as a "colour", which allows us to distinguish different reagents and it changes if a collision is considered as reactive, but it does not affect interactions between particles.

However, both methods mentioned above involve serious approximations. In the Bird technique the pairs of colliding particles are randomly selected. The criterium for a collision involves velocities only and it does not take into account particle's positions. Therefore, the technique is appropriate for systems characterized by a very low density. Considering a lattice gas automaton one assumes a special geometry of a simulated system: particles may occupy nodes of a lattice only. Within a single time step a particle jumps to one of the neighboring nodes, thus the speed of every particle is the same. As one may expect this method may not be applied if energetic effects associated with a chemical reaction (a thermal activation for example) are considered.

In this note I would like to present a new numerical technique, which allows for large scale computer simulations and which is free of simplifications mentioned above. There is no doubt molecular dynamics is the most appropriate for microscopic simulations [11]. However, this method is the most time consuming and its direct application in the case of a large system requires supercomputing facilities. The method presented below may be adopted even on a personal computer and it allows us to study systems as large, as those treated with the use of the Bird method or reactive lattice gas automaton. It originates from the molecular dynamics technique for reactive hard spheres [12]. The particles are represented by hard spheres and the collisions are regarded as elastic. Each sphere is assigned a parameter which describes its chemical properties. Some of the collisions are considered as reactive, according to the assumed chemical processes. The chemical identity parameters of colliding spheres are updated after every reactive collision.

A step towards more efficient simulations was suggested in [13] and then successfully used to calculate the influence of nonequilibrium effects on a rate constant in a system with a thermally activated reaction [14]. It was based on an observation that if the mechanical motion of particles is separated from chemical processes then a trajectory of a chemical system is the same as the one for an equilibrated system of hard spheres. Thus, many different reaction paths are created from a single equilibrium trajectory (which may be recorded on a computer disk) by assigning the chemical identity parameters to all particles and checking if successive collisions are reactive or not.

The method mentioned above gives reaction paths for a chemical system with the same number of particles as the one for which the equilibrium trajectory was recorded. However, if the equilibrium trajectory is obtained for the periodic boundary conditions, then a spatial extension of system's size is possible. The periodic boundary conditions mean that the simulated system is regarded as an elementary cell in an infinite system, which is invariant with respect to the translations by the vectors corresponding to cell's edges. Knowing the evolution within a single (elementary) cell we have the information about positions and velocities for particles in the whole system. Therefore, a prerecorded trajectory gives us the evolution of a system which is expanded by a number of edge lengths in each direction. Of course, the periodic boundary conditions remain satisfied for the expanded system. If a chemical identity of molecules is neglected than such expansion does not bring us any new information, as the motion in all replicas of the elementary cell is identical. Moreover, it may lead to wrong conclusions because the correlations extending over a single cell are affected by artificially introduced periodicity. However, for a multicomponent chemical system, in which the motion is not related to chemical identity, the situation is different. First, different chemical compositions may be initialized in various cells by marking the equivalent (by periodicity) spheres in a different way. Secondly, a steric factor (probability that a collision is reactive), if it is not equal to unity, differentiate the time evolution in various cells, because a collision between the equivalent particles may be reactive in one cell and nonreactive in another. Because of the periodic boundary conditions a free flow of molecules between the neighboring cells is ensured. Thus, one obtains the evolution of a system which is much larger than the original one. Let us also notice that the number of collisions per particle, which decides about the time scale of simulated processes, is the same for both the original and the expanded systems.

The suggested method is extremely efficient from the computer point of view. In the case of chemically reacting hard spheres only times of collisions and identities of colliding objects have to be recorded in order to restore a trajectory. Next, when an expanded system is created one needs only one large array to store the chemical identities of all particles (one may use logical or short integer variables), whereas the other quantities as velocities, positions and moments of collisions are periodic in space and they do not require a large memory. In practice on my home computer with 16Mb of RAM, I may easily perform simulations involving 10^7 particles. I believe that similar scale of computation is too difficult for the largest existing computers if the "orthodox" technique is applied.

II. SIMULATIONS OF AN OSCILLATING SYSTEM

The simplest model of an oscillating chemical system consists of three following reactions [15]:

$$A + B \xrightarrow{k_1} A + A \tag{1a}$$

$$B + C \xrightarrow{k_2} B + B \tag{1b}$$

$$C + A \xrightarrow{k_3} C + C \tag{1c}$$

If the reactions proceed in a closed system, the sum of concentrations of A, B and C (denoted as a, b and c respectively) is costant ($a + b + c = n_0$). Therefore we have:

$$a \in [0, n_0],\ b \in [0, n_0],\ c \in [0, n_0]$$

The kinetic equations for a system (1) read:

$$\frac{da}{dt} = k_1 ab - k_3 ac \tag{2a}$$

$$\frac{db}{dt} = k_2 bc - k_1 ab \tag{2b}$$

$$\frac{dc}{dt} = k_3 ca - k_2 bc \tag{2c}$$

There are three degenerated stationary states of system (2):

$$\{a = n_0, b = 0, c = 0\},\ \{a = 0, b = n_0, c = 0\},\ \{a = 0, b = 0, c = n_0\}$$

and there exists another stationary state, in which concentrations of all reagents are different from zero:

$$\{a = \frac{k_2}{k_1 + k_2 + k_3},\ b = \frac{k_3}{k_1 + k_2 + k_3},\ c = \frac{k_1}{k_1 + k_2 + k_3}\}.$$

If $a \neq 0$, $b \neq 0$ and $c \neq 0$ then the set of equation (2) can be transformed to the form:

$$\frac{d\ln(a)}{dt} = k_1 b - k_3 c \tag{3a}$$

$$\frac{d\ln(b)}{dt} = k_2 c - k_1 b \tag{3b}$$

$$\frac{d\ln(c)}{dt} = k_3 a - k_2 c \tag{3c}$$

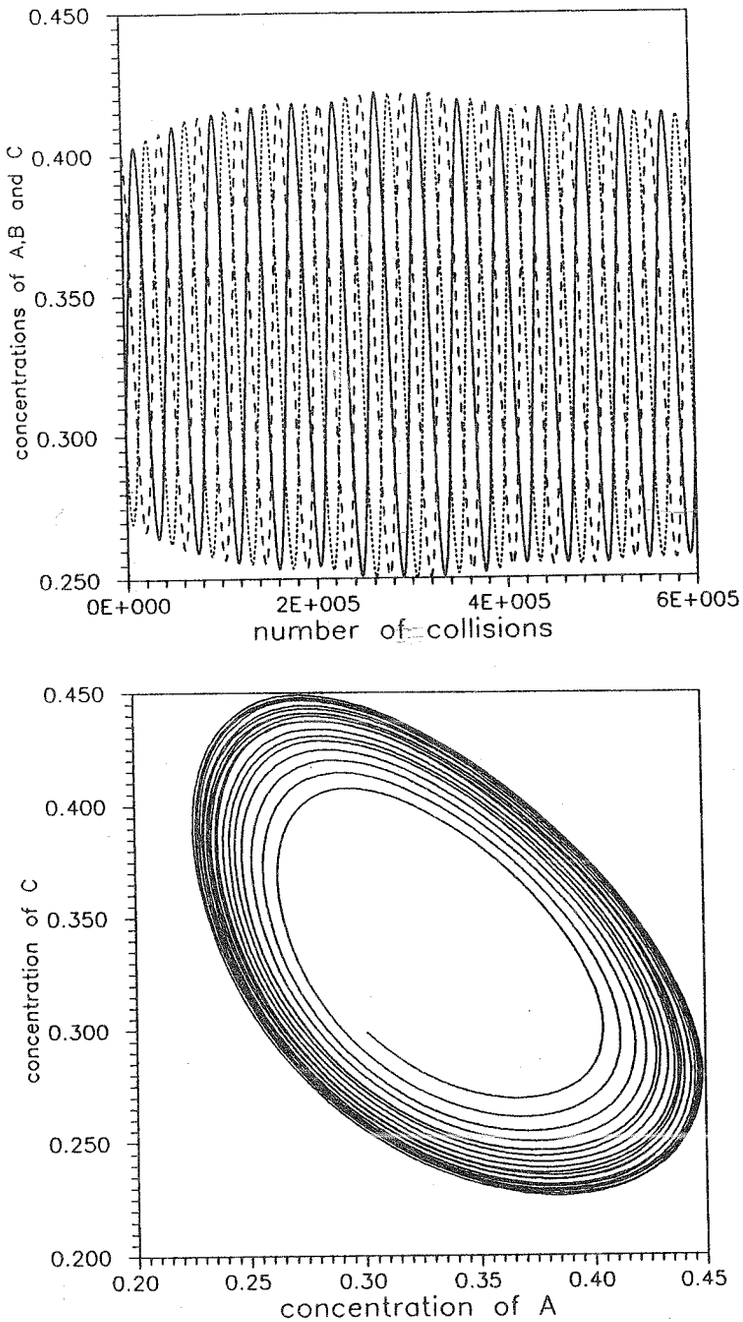

Fig. 1. An oscillating trajectory obtained in molecular dynamics simulations for system (1). The concentrations of A, B and C as functions time are plotted using solid, dashed and dotted lines respectively (Fig. 1A). The same trajectory is represented on the phase space ($a \times c$) in Fig. 1B.

From (3) it follows that:

$$\frac{d\ln(a^{k_2}b^{k_3}c^{k_1})}{dt} = 0$$

Thus for an initial condition $a(t=0)$, $b(t=0)$, $c(t=0)$ different than a stationary state, the system (1) oscillates along the trajectory defined by the condition:

$$a(t)^{k_2}b(t)^{k_3}c(t)^{k_1} = a(t=0)^{k_2}b(t=0)^{k_3}c(t=0)^{k_1} \tag{4}$$

These oscillations can be easily modelled by molecular dynamics. Figure 1A shows time evolution of the system (1) for 9 600 000 spheres (the original trajectory, calculated for 1200 spheres at the packing fraction $\eta = 0.35$ was expanded by 20 box's edge lengths in each direction). Initialy the system is composed of 2 880 000 spheres denoting A and C ($a(t=0) = c(t=0) = 0.3$) and 3 840 000 spheres representing $B(b(t=0) = 0.4)$. The steric factors for all raections (1) are the same and equal to 0.2. Any oscillating trajectory defined by Eq. (4) is unstable and this unstability is reflected by changes in the amplitude of oscillations seen in Figure 1A. The influence of internal fluctuations on a trajectory is also clearly visible on its representation in the phase space ($a \times c$).

III. PROPAGATION OF A CHEMICAL WAVE FRONT

The chemical wave front propagation may be regarded as the simplest manifestation of an organized spatio-temporal behaviour in a nonhomogeneous chemical system. Here I consider the wave front which appears in a system with reaction describing quadratic autocatalysis:

$$A + B \xrightarrow{k} A + A \tag{5}$$

For reaction (5) both states: composed of pure A and composed of pure B are stationary; the first one is stable and the other is unstable. In a nonhomogeneous system a front of concentration propagates into regions composed of pure B.

From the assumed reaction scheme (5) it follows that sum of densities of A and B (denoted as a and b respectively) remains constant ($a + b = n_0$). Therefore the system may be completely described by a single concentration – for example a. The "classical" approach to the problem is based on a reaction-diffusion equation, which for reaction (5) has the form [16]:

$$\frac{\partial a}{\partial t} = kab + D\nabla^2 a = ka(n_0 - a) + D\nabla^2 a \tag{6}$$

where k denotes the rate constant. It is convenient to describe front propagation using the scaled variables: concentration $\alpha = a/n_0$, rate constant $\kappa = n_0 k (\kappa = n_0 k_0)$, time $\tau = \kappa t$

and the space variable $\xi = \sqrt{\kappa/Dr}$, where D is the diffusion constant. In these new variables Eq. (6) reads:

$$\frac{\partial \alpha}{\partial \tau} = \alpha(1 - \alpha) + \nabla^2 \alpha \tag{7}$$

The studies on equation (7) (and especially on its one dimensional version) have a long history originating from works by Fisher [17] and Kolmogorov et. al. [18] (for a chronography of research on chemical fronts see [19]). Let us consider a stationary wave front propagating along the x-axis with a constant velocity ν. A stationary front profile may be described in the reference frame moving together with it:

$$\alpha(\xi,\gamma) = \alpha(\xi_x,\gamma) = \alpha(\zeta) \tag{8}$$

where $\zeta = \xi_x - \nu\tau$. The front profile as a function of ς variable satisfies equation:

$$\nu \frac{\partial \alpha}{\partial \zeta} + \frac{\partial^2 \alpha}{\partial \zeta^2} + \alpha(1 - \alpha) = 0 \tag{9}$$

This equation admits solutions which are stable with respect to local perturbations for all velocities, which are greater or equal than the critical one $\nu_{min} = 2$ (or in non-scaled variables $\nu_{min} = 2\sqrt{\kappa D}$). The particular solution of Eq. (6) which corresponds to ν_{min} is very important because it was shown by Mc Kean [20] that a step-function initial distribution of A evolves into a wave front propagating with this minimal velocity. This result was later generalized by Bramson [21] and by Merkin and Needhan [22], who proved that velocity of any front originating from an initial condition, such that the concentration of A vanishes for all ζ greater than ζ_0, converges to the solution propagating with ν_{min}. Unfortunately, the analytical solution for the profile corresponding to the minimum velocity is not known.

The shape of fronts profile is uniquely related to the scaled velocity. If one considers the inflection point of $\alpha(\zeta)$ then the following relationship between α and ν is hold:

$$v = \nu\sqrt{\kappa D} = -\sqrt{\kappa D}\,\alpha(1 - \alpha)\left(\frac{\partial \alpha}{\partial \zeta}\right)^{-1} \tag{10}$$

An alternative description of a wave front propagation comes from the recently developed methods of extended irreversible thermodynamics [4, 23]. For reaction (6) the coupled equations for the density of A and for the accompanying diffusion flow read:

$$\frac{\partial a}{\partial t} = ka(n_0 - a) - \nabla J_a$$

$$\frac{\partial J_a}{\partial t} = -L(J_a + D\nabla a) \tag{11}$$

where J_a denotes the diffusion flow associated with a. Eqs (11) may be considered as describing processes in two different time scales: a slow one for the conserved variable a and fast one for a non conserved variable J_a. If the relaxation of J_a is infinitely fast ($L \to \infty$) then the second equation gives:

$$J_a = -D\nabla a$$

and the set of equation (11) reduces to Eq. (7). Using the same rules of scaling as before, defining the scaled diffusion flow as $\iota_\alpha = J_a/n_0$ and assuming that a front depends only on ξ one obtains:

$$\frac{\partial \alpha}{\partial \tau} = \alpha(1 - \alpha) - \frac{\partial}{\partial \xi}\frac{\iota_\alpha}{\sqrt{\kappa D}}$$

$$\frac{\kappa}{L}\frac{\partial}{\partial \tau}\frac{\iota_\alpha}{\sqrt{\kappa D}} = -\frac{\partial}{\partial \xi}\alpha - \frac{\iota_\alpha}{\sqrt{\kappa D}} \tag{12}$$

Finding an analytical solution of this set of equations seems difficult, however an approximation for fronts velocity can be obtained if one assumes that κ/L (reaction-diffusion number) is small. In this case we can assume that:

$$\frac{\iota_\alpha}{\sqrt{\kappa D}} \cong -\frac{\partial}{\partial \xi}\alpha + \frac{\kappa}{L}\frac{\partial}{\partial \tau}\frac{\partial}{\partial \xi}\alpha \tag{13}$$

and the equation for wave front is:

$$\frac{\partial \alpha}{\partial \tau} = \alpha(1 - \alpha) + \frac{\partial^2}{\partial^2 \xi}\alpha - \frac{\kappa}{L}\frac{\partial^3}{\partial \tau \xi^2}\alpha \tag{14}$$

Assuming the stationary form of front solution (Eq. (8)) one obtains the following relationship between the derivatives at the inflexion point of the profile:

$$\left(\frac{\partial \alpha}{\partial \zeta}\right)_i, \quad \left(\frac{\partial^3 \alpha}{\partial \zeta^3}\right)_i$$

and the front's velocity:

$$v = \nu\sqrt{\kappa D} = -\sqrt{\kappa D}\,\alpha(1 - \alpha)\left(\frac{\partial \alpha}{\partial \zeta}\right)_i^{-1} \frac{1}{1 - \frac{\kappa}{L}\left(\frac{\partial^3 \alpha}{\partial \zeta^3}\right)_i \left(\frac{\partial \alpha}{\partial \zeta}\right)_i^{-1}} \tag{15}$$

Let assume that in the case of small κ/L the shape of the front, described in the scaled variables, is the same as the solution obtained for $\kappa/L = 0$ (and thus it is described by the shape corresponding to the minimum stable velocity). Using Eq. (10) we obtain the following rule of velocity scaling with respect to the steric factor s_F

$$\frac{\sqrt{s_F}}{\nu} = \frac{1}{2\sqrt{\kappa_0 D}}(1 - s_F\gamma) \tag{16}$$

where γ denotes

$$-\frac{\kappa_0}{L}\left(\frac{\partial^3\alpha}{\partial\zeta^3}\right)_i\left(\frac{\partial\alpha}{\partial\zeta}\right)_i^{-1}$$

and it is easy to show that γ is positive. The assumption on the independence of shape of profile on s_F leads to the conclusion that the value of γ is constant for all systems characterized by the same diffusion constant and collision frequency.

Let us notice that the results given by the classical, parabolic reaction diffusion equation and by the extended irreversible thermodynamics are qualitatively different. The first method says that the scaled speed of a front is constant, in the second this speed is an increasing function of s_F

The simulation were performed by a periodic expansion of an equilibrium trajectory, which was recorded for a system composed of 500 hard spheres characterized by the mass m = 32 *a.u* and diameter the σ = 5 Å. The average kinetic energy of spheres corresponded to temperature 300 K, but this value is not very important, as temperature may be easily changed by rescaling time. The trajectory was recorded for spheres placed in a cubic box with the side lenght $d = 14.7\sigma$ and thus the packing fraction was $\eta = 0.0824$.

The expanded system was initialized as homogeneous in *x*- and *y*-directions, which means that the initial average concentrations of *A* and *B* in all the cells characterized by the same range of the *z*-variable were the same. The periodic boundary conditions were used in *x*- and *y*-directions. In order to observe front propagation the initial concentration of reactants were nonhomogeneous in the *z*-direction. Part of the simulations started form an initial concentrations described by a step-function: all the spheres, for which $z \le z_0$ were marked as *A*, all the others as *B*. In other simulations there was a wide interval of *z* (usually about 100 σ in lenght) within which the initial concentrations of both reactants were different from zero. A modified periodic boundary conditions (the chemical identity parameter of a sphere crossing the boundary of an expanded system was reversed) were used in the *z*-direction. To analyze the results, the system was divided into slices perpendicular to the *z*-axis (500 total). The fraction of particles representing each of reactants is averaged within every slice. The simulation were performed for a system expanded by 14 side lengths in *x*- and in *y*-directions and by 100 side lengths in the z-direction. Thus, the total number of spheres considered was 9 800 000.

Fig. 2. shows a typical time evolution of a fronts of concentration. The steric factor used was $s_F = 0.22$. As Fig. 2. shows, a well developed, stationary concentration profile appears within less than 100 ps. Observing the distance travelled by a front as a function of time it is easy to obtain the phase velocity as a function of the rate constant (in practice I focused my attention on the shift of a point corresponding to $\alpha = 0.5$). For simulations performed at the same packing fraction, the diffusion constant does not change. By substituting the values of the diffusion constant

$$(D = 0.62\frac{\sigma^2}{ps})$$

and of the collision frequency

$$(\kappa_0 = 0.766\frac{1}{ps})$$

to the expression for the minimum stable velocity one obtains that:

$$\frac{v}{\sqrt{s_F}} = 2\sqrt{\kappa_0 D} = 1.378\frac{\sigma}{ps}$$

or

$$\frac{\sqrt{s_F}}{v} = 0.726\frac{ps}{\sigma}$$

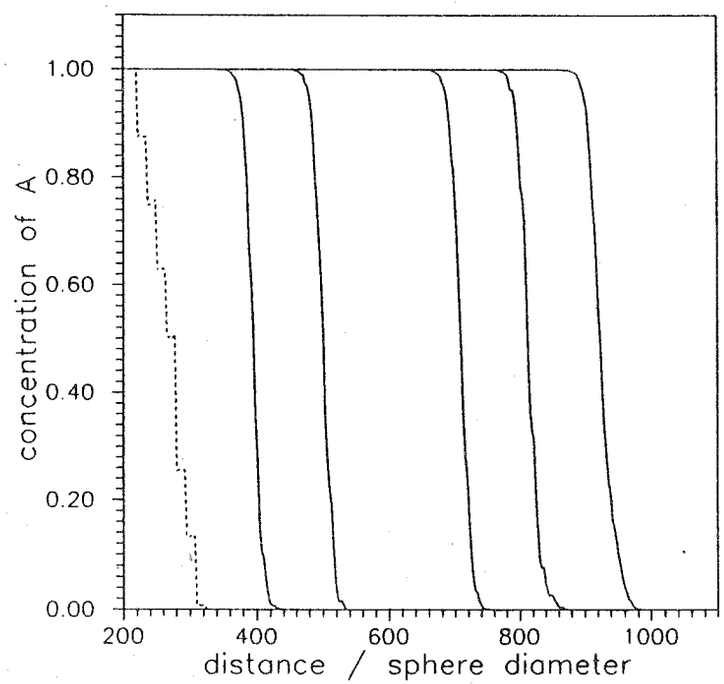

Fig. 2. The profile of concentration of *A* as a function of *z*-variable for a few selected moments of time. The dashed line shows the initial concentration of *A*. The solid lines from left to right correspond to times: 104 ps, 208 ps, 416 ps, 519 ps and 622 ps.

For the slowest reaction the minimum stable velocity is a good approximation of the observed speed of a front. However, the velocity scaled by a square root of the steric

factor is an increasing function of s_F. This effect cannot be explained on the basis of a standard parabolic reaction-diffusion equation (6).

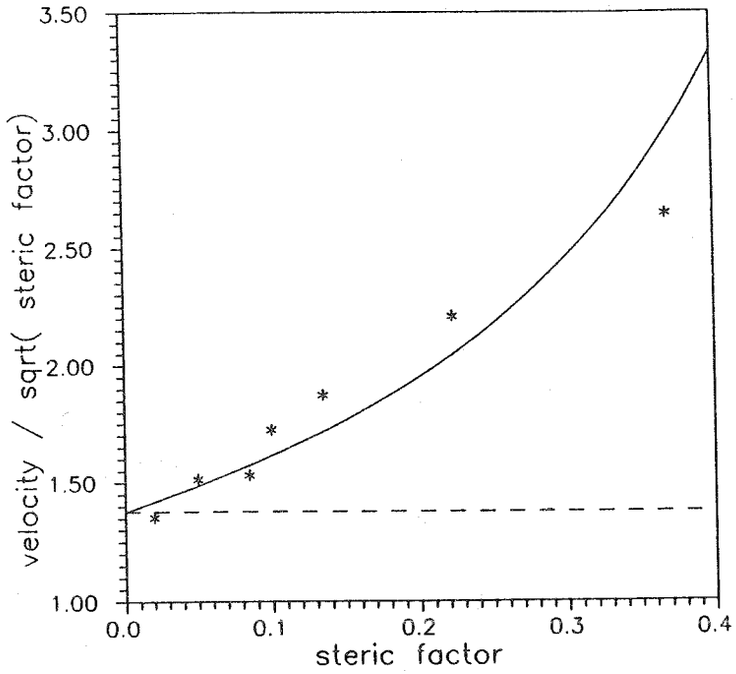

Fig. 3. The front velocity scaled by $\sqrt{s_F}$ as a function of the steric factor; stars mark the results of simulations, the dashed line shows the minimum stable velocity and the solid line is a numerical fit based on Eq. (16) ($\gamma = 1.006$).

One can adjust the modified expression for velocity (Eq. (16)) to the results of simulations. If one uses the value of $2\sqrt{\kappa_0 D}$ given above then for $\gamma = 1.066$ a good approximation for the observed velocities is achieved. The comparison between theory and simulations is presented in Fig. 3. Similar results supporting a hyperbolic reaction diffusion equation (Eq. (11)), rather than the parabolic one (Eq. (6)) have been recently obtained for chemical fronts propagating in a system characterized by higher packing fraction ($\eta = 0.14$, [24]).

IV. NONEQUILIBRIUM SPATIAL CORRELATIONS IN A CHEMICAL SYSTEM

Another interesting application of periodically expanded molecular dynamics is concerned with spatial correlations between concentrations of reactants, which correlations may appear in a steady state of a chemical system if the detailed balance condition is not satisfied [25]. This feature justifies calling these correlations as nonequilibrium one.

Let us consider two coupled reactions:

$$X + X \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} X + Y$$
$$X + Y \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} Y + Y \tag{17}$$

On the basis of a master equation, which treats diffusion as a jump process and a chemical reaction as a birth-and-death process one may show that the nonequilibrium spatial correlations have the form [26]:

$$<(n(\mathbf{r}) - n_s)(m(\mathbf{r}') - m_s)>_{chem} =$$
$$= n_s \delta_{NM} \delta(\mathbf{r} - \mathbf{r}') + \frac{C_{NM}}{8\pi D} \frac{1}{|\mathbf{r} - \mathbf{r}'|} \exp(-\kappa |\mathbf{r} - \mathbf{r}'|) \tag{18}$$

where $n(\mathbf{r})$ and $m(\mathbf{r})$ denote the concentrations of the reagents X and Y at the point $\mathbf{r}$ and n_s, m_s are their concentrations in a steady state of (17). The constants C_{NM} and κ are related to the chemical dynamics and diffusion and for reactions (17) they read:

$$C_{XX} = -2(k_1 x_s^2 - k_{-1} x_s y_s)$$
$$C_{XY} = 2(k_1 x_s^2 - k_{-1} x_s y_s)$$
$$C_{YY} = -2(k_1 x_s^2 - k_{-1} x_s y_s) \tag{19}$$

and

$$\kappa^2 = \frac{1}{D}(-2k_1 x_s + (k_{-1} - k_2)(y_s - x_s) - 2k_{-2} y_s) \tag{20}$$

The results of simulations performed for various sets of rate constants and different packing fractions are discussed in paper of Górecki et al. ([27]) and here I shall refer to them. Typical partial radial distribution functions for reagents X and Y as well as the equilibrium radial distribution function for the considered system of spheres are shown in Figure 4. The results were obtained from an equilibrium trajectory describing a system composed of 1331 spheres and characterized by the mass $m = 32$ *a.u.* and the diameter $\sigma = 5A$. The packing fraction was $\eta = 0.51$. This system was expanded by 8 edge lengths in each direction, thus the total number of particles was 681472.

The fact that our system was obtained by a periodic expansion simplifies the calculation of intermolecular distances. Now it is sufficient to know the distances for particles within a single cell only because distances between corresponding particles within the other cells are the same. However, because the chemical composition is various in different cells, the equivalent pairs of spheres may contribute to different partial distribution functions. The steric factors for reactions (17) were: $s_1 = 0.8$, $s_{-1} = 0.4$,

$s_2 = 0.2$, $s_{-2} = 0.8$. It is easy to see that the partial radial distribution functions are distinctly different from the equilibrium radial distribution function. Extracting the equilibrium correlations from the partial ones ([27]) one can obtain information on nonequilibrium correlations caused by the presence of chemical raections. The range of nonequilibrium correlations ($\sim 0.15\sigma$) is of the order of the mean free path (0.05σ for $\eta = 0.51$). I would like to stress that in all simulations, in which the detailed balance condition was satisfied, the partial distribution functions were the same as the equilibrium distribution function and thus the nonequilibrium chemical correlations vanish.

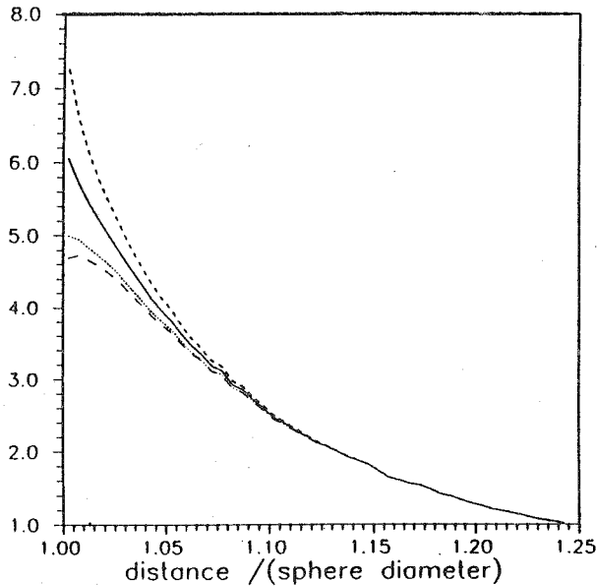

Fig. 4. The comparison between the radial distribution function for the equilibrated system of spheres (solid line, $\eta = 0.51$) and the partial radial distribution functions of reagents of (17): g_{XX} (dotted line, the second curve from the bottom), g_{XY} (short dashed line, the upper curve), g_{YY} (long dashed). The steric factors for reactions (17) are: [$s_1 = 0.8$, $s_{-1} = 0.4$, $s_2 = 0.2$, $s_{-2} = 0.8$].

A test for the functional form of correlations (Eq. (18)) is shown in Figure 5. and the results were obtained for a system of 614400 spheres at $\eta = 0.29$. They correspond to two sets of steric factors; the curves closer to the x-axis were obtained for $s_1 = 0.4$, $s_{-1} = 0.2$, $s_2 = 0.2$, $s_{-2} = 0.2$, the other curves are for: $s_1 = 0.8$, $s_{-1} = 0.4$, $s_2 = 0.2$, $s_{-2} = 0.8$. The results of simulations are in a good agreement with the theory: the correlations between like- and unlike- reagents have the opposite signs (Eq. (19)), but the rates of their decay are the same (Eq. (20)). Moreover, the functional form of correlations, given by Eq. (18) is confirmed (the best fit for the simulation data in the form (18) is plotted using the short dashed line on Fig. 5). However, the quantitative analysis of results exhibits differences. At very short distances the correlations decay slightly faster than Eq. (20) predicts. This effect was also observed in simulations performed by Nicolis et al. [28], who were using the Bird technique. Moreover, the theory based

on the master equation does not take the excluded volume effect into account and the observed amplitudes of correlations are larger than it is given by Eq. (19) (see disscusion in [27]).

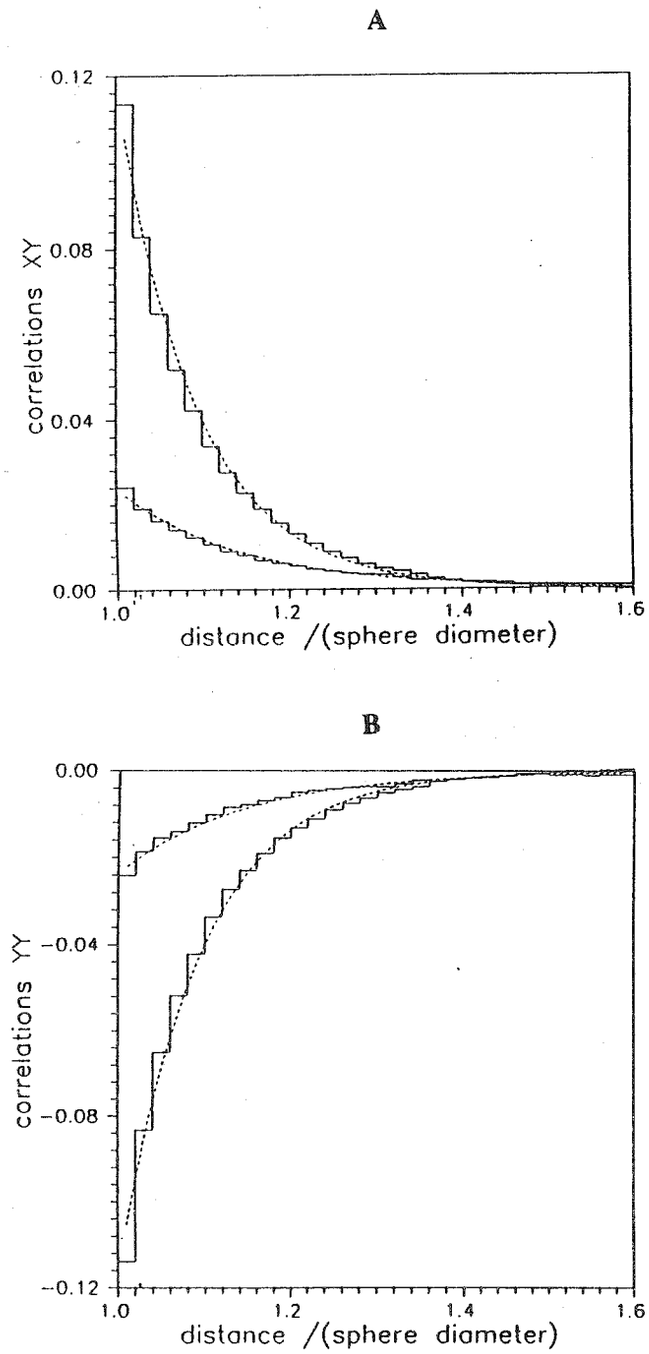

Fig. 5. The nonequilibrium spatial correlations $< nm >_{chem}$ (with the density factor $(x_s + y_s)^2$ excluded) for a system characterized by $\eta = 0.29$; the solid line shows the data obtained in simulations, whereas the dashed line is the best fit based on Eq. (18). The pair of curves which is closer to the x-axis corresponds to [$s_1 = 0.4$, $s_{-1} = 0.2$, $s_2 = 0.2$, $s_{-2} = 0.2$], the other to [$s_1 = 0.8$, $s_{-1} = 0.4$, $s_2 = 0.2$, $s_{-2} = 0.8$]. A shows correlations between X and Y; B – correlations between Y and Y.

V. CONCLUSIONS

The applications of periodically expanded molecular dynamics technique discussed above show that the method allows one to perform simulations, which seems to be very difficult if the standard molecular dynamics is used. The scale of simulations is large enough to measure interesting quantities with the accuracy, which makes comparison with theory possible. The author believes that the method will find a lot of new applications, important for further development of chemical kinetics, in near future.

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