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NONEQUILIBRIUM SPATIAL CORRELATIONS OF REAGENTS IN MODEL REACTION DIFFUSION SYSTEM[*,**]

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The mesoscopic description of systems with chemical reactions predicts that if the detailed balance condition is not satisfied then the nonequilibrium spatial correlations between concentrations of reactants may appear. The present work is concerned with molecular dynamics simulations of these correlations. The correlations appearing in a stationary state of a multicomponent chemical system and in a time dependent state of an "enzymatic" reaction are studied. Nonequilibrium correlations between reactants observed in simulations are compared with results of theory based on the master equation for a spatially distributed system.

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1. Introduction

Spatial correlations between concentrations of different reactants may appear in chemical systems as the result of statistical nature of diffusion in a multiparticle system and of the stochastic character of reactions at the microscopic level [1]. These correlations are unrelated directly to specific intermolecular interactions, but depend on the average quantities describing mass flows (diffusion, reaction rates). A simple theory, based on the spatially distributed master equation [2, 3] indicates that spatial correlations

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between concentrations of reactants may appear if the detailed balance condition is not satisfied which means that the system is out of equilibrium (and this is the reason that these correlations are called nonequilibrium ones). Nonequilibrium chemical phenomena has attracted a lot of scientific attention in the recent years, focusing community's interest on chemical oscillations and chaos [4–7]. It is expected that the presence of nonequilibrium spatial correlations may influence system's evolution [8], however a standard theoretical description of far-from-equilibrium chemical phenomena is based on kinetic equations for the average concentrations and completely neglects the problem. There are two factors justifying such simplification. First it is difficult to measure the correlations between molecules of different reagents directly in experiments. Second the range of applicability of the simplest theory dealing with nonequilibrium correlations, which is based on the master equation, is still a matter of studies. Moreover, even in the case of simple systems, this theory leads to complex partial differential equations, which describe time evolution of correlation functions.

Large scale computer simulations are very useful as idealized "experiments" in which we know all the details on chemical processes in the system and we have information on positions of all molecules in space. The first computer simulations of nonequilibrium spatial correlations were performed using the Bird technique for the stationary state of the first Schlogl model [9]. The results of molecular dynamics calculations were presented in [10, 11]. These simulations have shown that theory gives a correct quantitative picture of observed correlations, but, on the other hand if fails to predict quantitative characteristics of the amplitude and correlations length. The results presented in this paper continue research on nonequilibrium correlations in simple chemical models.

In this paper I shall consider two different problems. One of them are correlations in a multicomponent chemical system with two uncoupled processes. In such a case the theory predicts that there should be no correlations between reactants belonging to different processes and I have checked if this feature is confirmed by results of simulations. The second problem is related to time dependent correlations in the simplest "enzymatic" reaction.

This paper is organized as follows: a brief description of computer simulation method is given in Section 2. The next two Sections are concerned with the stationary and the time dependent correlations respectively. The final part (Section 5) contains discussion of obtained results.

2. Molecular dynamics simulations of nonequilibrium spatial correlations

Systems, which involve binary reactions only can be easily simulated using molecular dynamics technique for reacting hard spheres [12]. According to this method reactants are represented by spheres with the same mass (m) and diameters (σ). The chemical identities of spheres are described by an additional parameter which has no influence on the mechanical motion of a sphere. These assumptions imply that the diffusion constants of different reactants are the same.

Both reactive and nonreactive collisions between particles are considered in simulations. In order to control the values of rate constants for different reactions I introduced steric factors, which describe the probability that a collision between spheres representing reactants of a given process is reactive. If a collision of particles, which may lead to a reaction, occurs a random number generator is called and the obtained value is compared with the steric factor for the permitted process. Depending on this comparison the collision is regarded as reactive or not.

It is assumed that all reactive collisions are elastic from mechanical point of view, so no kinetic energy is released or consumed when a reaction occurs. Within this model a chemical reaction means only that the chemical identity parameter of the spheres involved is modified after a reactive collision. Therefore, the system of spheres as a whole is always in the thermal equilibrium with respect to the translational motion. Maintaining such equilibrium is very important from the computational point of view because it allows one to extend the size of simulations using a prerecorded equilibrium trajectory [10].

Any trajectory, which was calculated for a system of spheres characterized by the periodic boundary conditions, may be used to enlarge the size of simulations. Therefore the simulated system may be periodically expanded in any of the directions by any integer number of the box lengths. Of course, if chemical identities of molecules are neglected then such expansion does not bring us any new information. However, in a multicomponent chemical system, in which the translational motion is not related to chemical identity, the situation is different. First, different chemical composition may be initialized in various boxes by marking the equivalent (by periodicity) spheres in a different way. Secondly, steric factors (if they are not equal to unity) differentiate the time evolution in various boxes, as a collision between the equivalent objects may be reactive in one box and nonreactive in another. The periodic boundary conditions assure free motion of molecules between boxes.

In the following I assume that the activation energies for all considered reactions are equal to zero. The simulation technique may be easily adopted for any activation energies provided that the computation is long enough to give a large number of reactive collisions. However, it is well known [14, 15] that every thermally activated chemical reaction creates a nonequilibrium velocity distribution for the reagents involved and this effect is not taken into account by the theory based on the master equation for a spatially distributed system presented in the next Section.

At the beginning of simulations the chemical identities of all spheres are assigned in a random way, such that the concentrations of all reagents correspond to their assumed initial values. Next information on consecutive collisions is extracted from a prerecorded trajectory and the chemical identities of particles undergoing reactions are modified.

The information on nonequilibrium correlations between reactants is hidden in partial distribution functions, which are calculated from the statistics of intermolecular distances in the following way. Let us consider the interval of interesting intermolecular distances $[\sigma, R]$ which is divided into a number of subintervals of the same length Δ. Let us focus our attention on reactants N and M. At each moment of time simulations give us the average number of spheres representing reactant N which distance from a sphere representing reactant M lies within $[\sigma + i\Delta, \sigma + (i+1)\Delta]$. Let us denote this quantity as $G_{NM}(i)$. Similarly one may obtain the average number of spheres (without considering their chemical identity) which distance from a given one lies within the same interval $(G(i))$. In order to save computer time and cover the most important part of correlation functions the cutoff R in the range of considered distances between particles in simulations discussed below is between 2σ and 3σ.

The fact that simulated system has been obtained by periodic expansion simplifies calculations of spatial correlations, because it is sufficient to calculate interesting intermolecular distances between spheres within a single box and the distances between the equivalent pairs of spheres in other boxes are the same. Of course, because different chemical identities of spheres may be assigned in different boxes, the equivalent pairs may contribute to various $G_{NM}(i)$. It is convenient to calculate in simulations the partial distribution functions scaled to the equilibrium distribution function of spheres (χ_{NM}) rather than the partial distribution functions (g_{NM}) themselves. Let us notice that:

$$\chi_{NM}(r) = \frac{g_{NM}(r)}{g_{00}(r)} = \frac{G_{NM}(i)}{n} \frac{z_0}{G(i)}, \tag{1}$$

where g_{00} is the equilibrium distribution function of spheres at the considered packing fraction, n and z_0 denote the concentration of reactant N and the total concentration of spheres respectively and $r \in [\sigma + i\Delta, \sigma + (i+1)\Delta]$. The value of χ_{NM} is less affected by statistical fluctuations in the number of intermolecular distances belonging to intervals $[\sigma + i\Delta, \sigma + (i+1)\Delta]$ than the values of g_{NM} and g_{00} separately. Precise measurements of g_{00} may be performed in a separate program, which neglects chemical processes [16]. Next the partial distribution functions of reactants are calculated from:

$$g_{NM}(r) = \chi_{NM}(r) * g_{00}(r) \, . \tag{2}$$

If the system is in a stationary state then it is sufficient to average g_{NM} along the calculated trajectory. If concentrations are time dependent then it is necessary to fix time intervals covering interesting range of concentrations and to calculate the scaled correlation functions in each interval separately. For a time dependent system the data obtained from a single reaction path usually do not give an accurate result and the procedure have to be repeated.

3. Correlations in a stationary state of a model multicomponent system

Let us consider a system composed of four reagents: A, B, C and D in which two separate groups of chemical processes take place:

$$A + A \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} A + B\,, \tag{3a}$$

$$A + B \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} B + B\,, \tag{3b}$$

$$C + C \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} C + D\,, \tag{4a}$$

$$C + D \underset{k_{-4}}{\overset{k_4}{\rightleftharpoons}} D + D\,. \tag{4b}$$

The spatial correlations in a two component system with reactions (3) or (4) were the subject of [10]. Here I check if the presence of an uncoupled chemical process may influence correlations between reagents of another process. Let us consider a stationary state of a system with reactions (3), (4) and let us assume that the detailed balance condition is not satisfied in each of these reactions. This assumption is necessary for existence of nonequilibrium correlations (see [10]). It indicates that there are unspecified processes (for example interaction with light or small particles which do not affect motion of the considered reagents), which keep the system out of equilibrium. The precise definition of these processes is not necessary for the following discussion.

The mesoscopic description of spatial correlations is based on the master equation for a spatially distributed system [17]. Let us consider a system composed of cells characterized by volume Ω and let A_i, B_i, C_i, D_i denote the number of molecules of A,B,C and D in the i-th cell. Information on time evolution of the system can be extracted from the probability distribution $P(..., A_i, B_i, C_i, D_i, ..., t)$ which describes the probability of finding A_i molecules of A, B_i molecules of B,C_i molecules of C, and D_i molecules of D in the i-th cell at the time t. The master equation for the system (3), (4) reads:

$$\frac{d}{dt}P = \left(\frac{d}{dt}\right)_{\text{chem}} P + \left(\frac{d}{dt}\right)_{\text{diff}} P\,, \tag{5}$$

where

$$\begin{aligned}
&\left(\frac{d}{dt}\right)_{\text{chem}} P(..., A_i, B_i, C_i, D_i, ..., t) \\
&= \sum_{\substack{\text{cells}\\ i}} - \left(\frac{2k_1}{\Omega}\frac{1}{2}A_i(A_i-1) + \frac{k_{-1}}{\Omega}A_iB_i + \frac{k_2}{\Omega}A_iB_i + \frac{2k_{-2}}{\Omega}\frac{1}{2}B_i(B_i-1)\right) * \\
&\qquad *P(..., A_i, B_i, C_i, D_i, ..., t) \\
&+ \left(\frac{2k_1}{\Omega}\frac{1}{2}(A_i+1)A_i + \frac{k_2}{\Omega}(A_i+1)(B_i-1)\right) P(..., A_i+1, B_i-1, C_i, D_i, ..., t) \\
&+ \left(\frac{k_{-1}}{\Omega}(A_i-1)(B_i+1) + \frac{2k_{-2}}{\Omega}\frac{1}{2}(B_i+1)B_i\right) P(..., A_i-1, B_i+1, C_i, D_i, ..., t) \\
&- \left(\frac{2k_3}{\Omega}\frac{1}{2}C_i(C_i-1) + \frac{k_{-3}}{\Omega}C_iD_i + \frac{k_4}{\Omega}C_iD_i + \frac{2k_{-4}}{\Omega}\frac{1}{2}D_i(D_i-1)\right) * \\
&\qquad *P(..., A_i, B_i, C_i, D_i, ..., t) \\
&+ \left(\frac{2k_3}{\Omega}\frac{1}{2}(C_i+1)C_i + \frac{k_4}{\Omega}(C_i+1)(D_i-1)\right) P(..., A_i, B_i, C_i+1, D_i-1, ..., t) \\
&+ \left(\frac{k_{-3}}{\Omega}(C_i-1)(D_i+1) + \frac{2k_{-4}}{\Omega}\frac{1}{2}(D_i+1)D_i\right) P(..., A_i, B_i, C_i-1, D_i+1, ..., t)
\end{aligned} \tag{6}$$

and

$$\begin{aligned}
&\left(\frac{d}{dt}\right)_{\text{diff}} P(..., A_i, B_i, C_i, D_i, ..., t) \\
&= \sum_{\substack{\text{cells}\\ i,j}} -(d^a_{ij}A_i + d^b_{ij}B_i + d^c_{ij}C_i + d^d_{ij}D_i)P(..., A_i, B_i, C_i, D_i, ..., t) \\
&+d^a_{ji}(A_j+1)P(..., A_j+1, B_j, C_j, D_j, ..., A_i-1, B_i, C_i, D_i, ..., t) \\
&+d^b_{ji}(B_j+1)P(..., A_j, B_j+1, C_j, D_j, ..., A_i, B_i-1, C_i, D_i, ..., t) \\
&+d^c_{ji}(C_j+1)P(..., A_j, B_j, C_j+1, D_j, ..., A_i, B_i, C_i-1, D_i, ..., t) \\
&+d^d_{ji}(D_j+1)P(..., A_j, B_j, C_j, D_j+1, ..., A_i, B_i, C_i, D_i-1, ..., t)\,.
\end{aligned} \tag{7}$$

The factors: $2k_1, k_{-1}, k_2, 2k_{-2}, 2k_3, k_{-3}, k_4$ and $2k_{-4}$ denote the probabilities that a corresponding reaction of (3), (4) occurs within a time unit and $d^a_{ij}, d^b_{ij}, d^c_{ij}, d^d_{ij}$ describe the probability of a diffusive jump of a particle of A, B, C or D, respectively between the i-th and the j-th cells.

Calculating the average of $\frac{N_i}{\Omega}$ one obtains the kinetic equations for concentration of reactant N. In the following we shall denote these quantities by $a(\boldsymbol{r})$,$b(\boldsymbol{r})$,$c(\boldsymbol{r})$ and $d(\boldsymbol{r})$ where $\boldsymbol{r}$ instead of i denotes the position in our system. Considering the continuum limit, according to the standard approach [17], one may replace the diffusion term by the Laplacian of the appropriate concentration. Thus the averaging gives:

$$\frac{da}{dt} = -k_1 a^2 + k_{-1}ab - k_2 ab + k_{-2}b^2 + D\nabla^2 a = f(a,b) + D\nabla^2 a\,, \tag{8a}$$

$$\frac{db}{dt} = k_1 a^2 - k_{-1}ab + k_2 ab - k_{-2}b^2 + D\nabla^2 b = -f(a,b) + D\nabla^2 b\,, \tag{8b}$$

$$\frac{dc}{dt} = -k_3 c^2 + k_{-3}cd - k_4 cd + k_{-4}d^2 + D\nabla^2 c = g(c,d) + D\nabla^2 c\,, \tag{8c}$$

$$\frac{dd}{dt} = k_3 c^2 - k_{-3}cd + k_4 cd - k_{-4}d^2 + D\nabla^2 d = -g(c,d) + D\nabla^2 d\,, \tag{8d}$$

where we assumed that the diffusion constants for all reactants are the same. It is clear that $a + b = z_1(=\text{const.})$ and $c + d = z_2(=\text{const.})$ are constraints of these kinetic equations. In the following we restrict our attention to a homogeneous, stationary state of the system (3), (4). It is easy to prove that equations (8) admit a single such state a_s, b_s, c_s, d_s; which is always stable. In the stationary state the concentrations of reactants satisfy the following relationships:

$$k_1 a_s^2 - k_{-1}a_s b_s + k_2 a_s b_s - k_{-2}b_s^2 = 0\,, \tag{9a}$$

$$-k_3 c_s^2 + k_{-3}c_s d_s - k_4 c_s d_s + k_{-4}d_s^2 = 0\,. \tag{9b}$$

The equations which describes the time evolution of spatial correlations of reactant's concentration can be derived in a direct way from the master equation (Eq.(5)) [2, 3]. Let us consider the correlation functions of fluctuations of concentrations defined as:

$$\Sigma_{NM}(i,j,t) = \Omega\left\langle \left(\frac{N_i}{\Omega} - n_s\right)\left(\frac{M_j}{\Omega} - m_s\right)\right\rangle_t$$

$$= \Omega \sum_{\text{cells}} \left(\frac{N_i}{\Omega} - n_s\right)\left(\frac{M_j}{\Omega} - m_s\right) P(\ldots, A_j, B_j, C_j, D_j, \ldots, A_i, B_i, C_i, D_i, \ldots, t)\,, \tag{10}$$

where M and N denote one of reactants. The index t denotes that the averaging is taken with the probability distribution: $P(\ldots, A_j, B_j, C_j, D_j, \ldots,$ $A_i, B_i, C_i, D_i, \ldots, t)$ which depends on time.

A tedious, but direct calculation leads to equations describing the dynamics of $\Sigma_{NM}(i,j,t)$. In a homogeneous system the correlation functions depend on the distance between boxes i and j only. Introducing new correlation functions σ_{nm}, which do not take into account fluctuations within a single cell:

$$\begin{aligned}
\sigma_{aa}(|\boldsymbol{r}-\boldsymbol{r}'|,t) &= \Sigma_{AA}(\boldsymbol{r},\boldsymbol{r}',t) - a_s\delta(\boldsymbol{r},\boldsymbol{r}')\\
\sigma_{bb}(|\boldsymbol{r}-\boldsymbol{r}'|,t) &= \Sigma_{BB}(\boldsymbol{r},\boldsymbol{r}',t) - b_s\delta(\boldsymbol{r},\boldsymbol{r}')\\
\sigma_{cc}(|\boldsymbol{r}-\boldsymbol{r}'|,t) &= \Sigma_{CC}(\boldsymbol{r},\boldsymbol{r}',t) - c_s\delta(\boldsymbol{r},\boldsymbol{r}')\\
\sigma_{dd}(|\boldsymbol{r}-\boldsymbol{r}'|,t) &= \Sigma_{DD}(\boldsymbol{r},\boldsymbol{r}',t) - d_s\delta(\boldsymbol{r},\boldsymbol{r}')\\
\sigma_{ab}(|\boldsymbol{r}-\boldsymbol{r}'|,t) &= \Sigma_{AB}(\boldsymbol{r},\boldsymbol{r}',t)\\
\sigma_{ac}(|\boldsymbol{r}-\boldsymbol{r}'|,t) &= \Sigma_{AC}(\boldsymbol{r},\boldsymbol{r}',t)\\
\sigma_{ad}(|\boldsymbol{r}-\boldsymbol{r}'|,t) &= \Sigma_{AD}(\boldsymbol{r},\boldsymbol{r}',t)\\
\sigma_{bc}(|\boldsymbol{r}-\boldsymbol{r}'|,t) &= \Sigma_{BC}(\boldsymbol{r},\boldsymbol{r}',t)\\
\sigma_{bd}(|\boldsymbol{r}-\boldsymbol{r}'|,t) &= \Sigma_{BD}(\boldsymbol{r},\boldsymbol{r}',t)\\
\sigma_{cd}(|\boldsymbol{r}-\boldsymbol{r}'|,t) &= \Sigma_{CD}(\boldsymbol{r},\boldsymbol{r}',t)
\end{aligned} \tag{11}$$

and considering the continuous space variables $\boldsymbol{r}$ and $\boldsymbol{r}'$ instead of the discrete ones i and j one obtains equations describing dynamics of σ_{mn}:

$$\begin{aligned}
\frac{d}{dt}\sigma_{ac}(\boldsymbol{r},t) =& 2D\nabla^2\sigma_{ac} + (-2k_1a + k_{-1}b - k_2b - 2k_3c + k_{-3}d - k_4d)\,\sigma_{ac}\\
&+ (k_{-1}a - k_2a + 2k_{-2}b)\,\sigma_{bc} + (k_{-3}c - k_4c + 2k_{-4}d)\,\sigma_{ad}\,,
\end{aligned} \tag{12}$$

$$\begin{aligned}
\frac{d}{dt}\sigma_{ad}(\boldsymbol{r},t) =& 2D\nabla^2\sigma_{ad} + (-2k_1a + k_{-1}b - k_2b - 2k_{-4}d + k_4c - k_{-3}c)\,\sigma_{ad}\\
&+ (k_{-1}a - k_2a + 2k_{-2}b)\,\sigma_{bd} + (k_4d - k_{-3}d + 2k_3c)\,\sigma_{ac}\,,
\end{aligned} \tag{13}$$

$$\begin{aligned}
\frac{d}{dt}\sigma_{bc}(\boldsymbol{r},t) =& 2D\nabla^2\sigma_{bc} + (-2k_{-2}b + k_2a - k_{-1}a - 2k_3c + k_{-3}d - k_4d)\,\sigma_{bc}\\
&+ (k_2b - k_{-1}b + 2k_1a)\,\sigma_{ac} + (k_{-3}c - k_4c + 2k_{-4}d)\,\sigma_{bd}\,,
\end{aligned} \tag{14}$$

$$\begin{aligned}
\frac{d}{dt}\sigma_{bd}(\boldsymbol{r},t) =& 2D\nabla^2\sigma_{bd} + (-2k_{-2}b + k_2a - k_{-1}a - 2k_{-4}d + k_4c - k_{-3}c)\,\sigma_{bd}\\
&+ (k_2b - k_{-1}b + 2k_1a)\,\sigma_{ad} + (k_4d - k_{-3}d + 2k_3c)\,\sigma_{bc}\,.
\end{aligned} \tag{15}$$

It follows from Eqs. (12)–(15) that if at the beginning there are no cross correlations between reagents involved in different pairs of reactions:

$$\sigma_{ac}(\boldsymbol{r},t=0) = \sigma_{ad}(\boldsymbol{r},t=0) = \sigma_{bc}(\boldsymbol{r},t=0) = \sigma_{bd}(\boldsymbol{r},t=0) \equiv 0 \tag{16}$$

then these correlations will not develop and the relationship (16) will be valid for any time. The initial condition for my simulations describes randomly distributed reagents and therefore it is expected that cross correlations listed above vanish.

Equations describing time evolution of correlations between reactants involved in the same group of reactions are exactly the same as derived in [11] and they read:

$$\begin{aligned}\frac{d}{dt}\sigma_{aa}(\boldsymbol{r},t) =& 2D\nabla^2\sigma_{aa} + 2\left(-2k_1a + k_{-1}b - k_2b\right)\sigma_{aa} \\ &+ 2\left(2k_{-2}b + k_{-1}a - k_2a\right)\sigma_{ab} + 2\left(k_2ab - k_{-2}b^2\right)\delta(\boldsymbol{r}),\end{aligned} \tag{17}$$

$$\begin{aligned}\frac{d}{dt}\sigma_{ab}(\boldsymbol{r},t) =& 2D\nabla^2\sigma_{ab} + \left(2k_1a - k_{-1}b + k_2b\right)\sigma_{aa} \\ &+ \left(-2k_1a + k_{-1}b - k_2b - 2k_{-2}b + k_{-1}a - k_2a\right)\sigma_{ab} \\ &+ \left(2k_{-2}b + k_{-1}a - k_2a\right)\sigma_{bb} - 2\left(k_2ab - k_{-2}b^2\right)\delta(\boldsymbol{r}),\end{aligned} \tag{18}$$

$$\begin{aligned}\frac{d}{dt}\sigma_{bb}(\boldsymbol{r},t) =& 2D\nabla^2\sigma_{bb} + 2\left(-2k_{-2}b + k_2a - k_{-1}a\right)\sigma_{bb} \\ &+ 2\left(2k_1a + k_2b - k_{-1}b\right)\sigma_{ab} + 2\left(k_2ab - k_{-2}b^2\right)\delta(\boldsymbol{r}),\end{aligned} \tag{19}$$

and by symmetry

$$\begin{aligned}\frac{d}{dt}\sigma_{cc}(\boldsymbol{r},t) =& 2D\nabla^2\sigma_{cc} + 2\left(-2k_3c + k_{-3}d - k_4d\right)\sigma_{cc} \\ &+ 2\left(2k_{-4}d + k_{-3}c - k_4c\right)\sigma_{cd} + 2\left(k_4cd - k_{-4}d^2\right)\delta(\boldsymbol{r}).\end{aligned} \tag{20}$$

$$\begin{aligned}\frac{d}{dt}\sigma_{cd}(\boldsymbol{r},t) =& 2D\nabla^2\sigma_{cd} + \left(2k_3c - k_{-3}d + k_4d\right)\sigma_{cc} \\ &+ \left(-2k_3c + k_{-3}d - k_4d - 2k_{-4}d + k_{-3}c - k_4c\right)\sigma_{cd} \\ &+ \left(2k_{-4}d + k_{-3}c - k_4c\right)\sigma_{dd} - 2\left(k_4cd - k_{-4}d^2\right)\delta(\boldsymbol{r}),\end{aligned} \tag{21}$$

$$\begin{aligned}\frac{d}{dt}\sigma_{dd}(\boldsymbol{r},t) =& 2D\nabla^2\sigma_{dd} + 2\left(-2k_{-4}d + k_4c - k_{-3}c\right)\sigma_{dd} \\ &+ 2\left(2k_3c + k_4d - k_{-3}d\right)\sigma_{cd} + 2\left(k_4cd - k_{-4}d^2\right)\delta(\boldsymbol{r}).\end{aligned} \tag{22}$$

In the case of stationary (time independent) correlations the solution of Eqs.(17)–(22) is simple and reads [3, 10]:

$$\begin{aligned}\sigma_{aa}(\boldsymbol{r},t=\infty) =&\sigma_{bb}(\boldsymbol{r},t=\infty) = -\sigma_{ab}(\boldsymbol{r},t=\infty)\\ &= \frac{(k_1 a_s^2 - k_{-1}a_s b_s)}{4\pi D}\frac{1}{\mid r\mid}\exp\left(-\kappa_1 \mid \boldsymbol{r}' \mid\right),\end{aligned} \tag{23}$$

$$\begin{aligned}\sigma_{cc}(\boldsymbol{r},t=\infty) =&\sigma_{dd}(\boldsymbol{r},t=\infty) = -\sigma_{cd}(\boldsymbol{r},t=\infty)\\ &= \frac{(k_3 c_s^2 - k_{-3}c_s d_s)}{4\pi D}\frac{1}{\mid r\mid}\exp\left(-\kappa_2 \mid \boldsymbol{r}' \mid\right),\end{aligned} \tag{24}$$

where the constants κ_1, κ_2 are defined as follows:

$$\kappa_1^2 =\frac{1}{D}(2k_1 a_s - (k_{-1} - k_2)(b_s - a_s) + 2k_{-2}b_s)\,, \tag{25}$$

$$\kappa_2^2 =\frac{1}{D}(2k_3 c_s - (k_{-3} - k_4)(d_s - c_s) + 2k_{-4}d_s)\,, \tag{26}$$

and they are positive because the steady state of system (3), (4) is a stable one.

The theory presented above predicts that if spatial correlation between reactants of different reactions are initially absent then they will not develop in time and the correlation function for reactants involved in one group of reactions is not influenced by reactions of different group. Now let me compare these results with molecular dynamics simulations. They were performed for the system of 500, 000 spheres, which was obtained by periodic expansion of a trajectory calculated for 500 spheres. The packing density of the considered system was 0.082. The steric factors for corresponding reactions were:

$$\begin{aligned}k_1 &= 0.2, & k_{-1} &= 0.1, & k_2 &= 0.1, & k_{-2} &= 0.1\,,\\ k_3 &= 0.4, & k_{-3} &= 0.2, & k_4 &= 0.1, & k_{-4} &= 0.4\,.\end{aligned}$$

The partial radial distribution functions calculated in simulations satisfy the relationship:

$$\begin{aligned}&{a_s}^2 g_{AA} + {b_s}^2 g_{BB} + {c_s}^2 g_{CC} + {d_s}^2 g_{DD}\\ &+ 2\left(a_s b_s g_{AB} + a_s c_s g_{AC} + a_s d_s g_{AD} + b_s c_s g_{BC} + b_s d_s g_{BD} + c_s d_s g_{CD}\right)\\ &= \left(a_s + b_s + c_s + d_s\right)^2 g_{00}\,,\end{aligned} \tag{27}$$

whereas for the correlation functions σ_{NM} we have:

$$\sigma_{AA}+\sigma_{BB}+\sigma_{CC}+\sigma_{DD}+2\left(\sigma_{AB}+\sigma_{AC}+\sigma_{AD}+\sigma_{BC}+\sigma_{BD}+\sigma_{CD}\right) = 0 \tag{28}$$

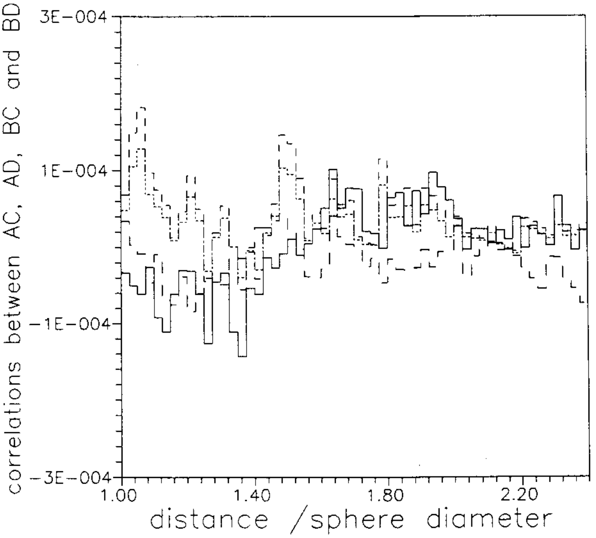

Fig. 1. Results of molecular dynamics simulations of correlation functions between reactants belonging to different reaction groups (3), (4);σ_{AC} — the dotted line, σ_{AD} — the short dashed line, σ_{BC} - the long dashed line and σ_{AB} — the solid line. All correlation functions are scaled by the square of the total density of particles.

Relationship (28) is automatically satisfied if one identifies:

$$\sigma_{NM} = n_s m_s (g_{NM} - g_{00}) \tag{29}$$

The results of molecular dynamics simulations for the system (3), (4) are presented in Figs. 1–5. The correlation functions for reactants belonging to different reaction groups are shown in Fig. 1. As predicted by the theory they are very small and fluctuate around zero. The correlation functions $\sigma_{AA}, \sigma_{AB}, \sigma_{BB}$ are shown in Fig. 2. Here also the theory gives correct relationships between correlations, because the absolute values of all these functions are the same; moreover the function σ_{AB} is positive whereas σ_{AA} and σ_{BB} are negative as seen from (23). The similar relationships are satisfied by σ_{CC}, σ_{CD} and σ_{DD} as seen in Fig. 3.

The functional form of correlation functions ($\frac{Y}{r}\exp(-\kappa r)$) predicted by theory Eqs. (23), (24) fits well the observed correlation functions as it is shown for σ_{AB} and σ_{CD} in Figs. 4 and 5, respectively. The dashed lines represent results of simulations and the solid ones show numerical approximation based on the form given above. The amplitude Y and decay constant κ were chosen to fit the short distance part of correlation functions ($r \in [\sigma, 1.5 * \sigma]$), where the accuracy of simulation result is the highest. It may be noticed that the κ overestimates the decay of correlations for long

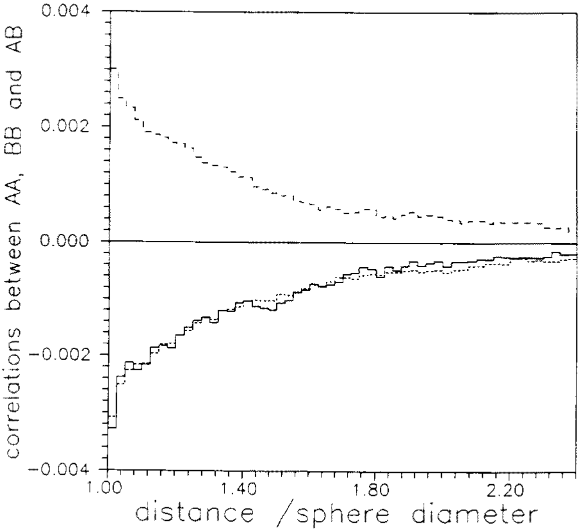

Fig. 2. Results of molecular dynamics simulations of correlation functions between reactants belonging to the reaction group (3);σ_{AA} — the dotted line, σ_{AB} — the dashed line, σ_{BB} — the solid line. All correlation functions are scaled by the square of the total density of particles.

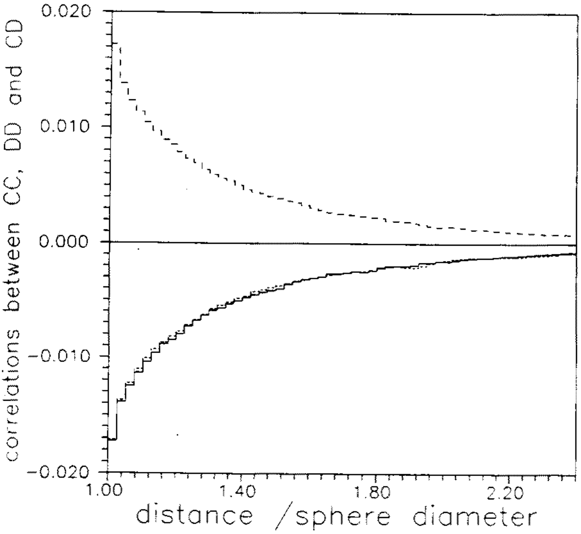

Fig. 3. Results of molecular dynamics simulations of correlation functions between reactants belonging to the reaction group (4);σ_{CC} — the dotted line, σ_{CD} — the dashed line, σ_{DD} — the solid line. All correlation functions are scaled by the square of the total density of particles.

distances. The similar effect was observed for the other simulated systems [9, 10]. On the other hand, if the decay constant fits the long distance correlations then the decay at short distances are underestimated. Formulae (25) and (26) may be used to calculate the decay constants. Using the diffusion constant, the rate constants and the densities of the simulated system one obtains:

$$\kappa_{1,\mathrm{theory}} = 0.417\tfrac{1}{\sigma}, \quad \kappa_{2,\mathrm{theory}} = 0.704\tfrac{1}{\sigma},$$

whereas the numerical fit gives us:

$$\kappa_{1,\mathrm{fit}} = 1.4\tfrac{1}{\sigma}, \quad \kappa_{2,\mathrm{fit}} = 2.0\tfrac{1}{\sigma}.$$

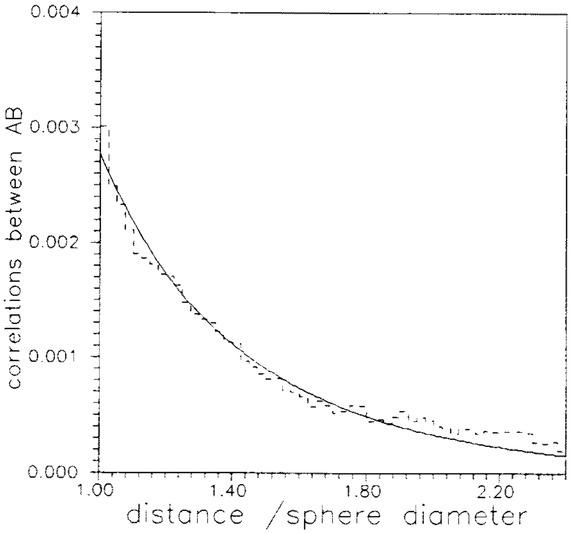

Fig. 4. The comparison between molecular dynamics simulations of σ_{AB} (the dashed line) and its numerical fit based on the function $\frac{Y}{r}\exp(-\kappa r)$ (the solid line).

Although the theory underestimates the short distance decay constant by the factor of three, the ratio of the decay constants predicted by theory: $\kappa_{2,\mathrm{theory}}/\kappa_{1,\mathrm{theory}} = 1.69$ is quite well represented by simulation results ($\kappa_{2,\mathrm{fit}}/\kappa_{1,\mathrm{fit}} = 1.43$).

The formulae (23) and (24) cannot be literally used to describe correlations measured in simulations, because they are valid for any distance, whereas in simulations, because of the excluded volume effect, correlations have no meaning for $r \leq \sigma$. However, we can compare the ratio of amplitudes of correlations associated with different groups of reactions predicted

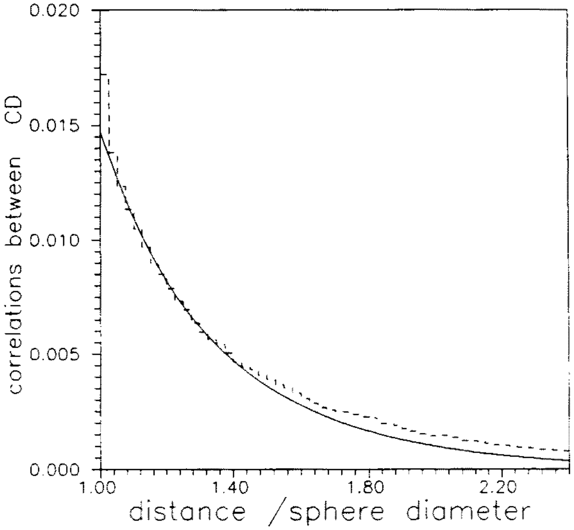

Fig. 5. The comparison between molecular dynamics simulations of σ_{CD} (the dashed line) and its numerical fit based on the function $\frac{Y}{r}\exp(-\kappa r)$(the solid line).

by the theory for $r = 0$ with the simulation results for $r = \sigma$. The theoretical value is 6.29 whereas simulations give 5.50. The agreement is remarkable, considering the simplicity of theoretical approach.

4. Correlations in a time dependent state of a model system

Now let us consider another system composed of three reagents: A, B and E in which the simplest "enzymatic" reaction takes place:

$$A + E \xrightarrow{k} B + E\,. \tag{30}$$

The master equation for the process (30) has the same form as in the previous case (5) but now:

$$\left(\frac{d}{dt}\right)_{\mathrm{chem}} P(\ldots, A_i, B_i, E_i, \ldots, t) = \sum_{\substack{cells\\ i}} -\frac{k}{\Omega} A_i E_i P(\ldots, A_i, B_i, E_i, \ldots, t)$$

$$+\frac{k}{\Omega}(A_i + 1) E_i P(\ldots, A_i + 1, B_i - 1, E_i, \ldots, t)\,, \tag{31}$$

and

$$\begin{aligned}
&\left(\frac{d}{dt}\right)_{\mathrm{diff}} P(\ldots, A_i, B_i, E_i, \ldots, t) \\
&= \sum_{\substack{\text{cells}\\ i,j}} -(d^a_{ij} A_i + d^b_{ij} B_i + d^e_{ij} E_i) P(\ldots, A_i, B_i, E_i, \ldots, t) \\
&\quad + d^a_{ji}(A_j + 1) P(\ldots, A_j + 1, B_j, E_j, \ldots, A_i - 1, B_i, E_i, \ldots, t) \\
&\quad + d^b_{ji}(B_j + 1) P(\ldots, A_j, B_j + 1, E_j, \ldots, A_i, B_i - 1, E_i, \ldots, t) \\
&\quad + d^c_{ji}(E_j + 1) P(\ldots, A_j, B_j, E_j + 1, \ldots, A_i, B_i, E_i - 1, \ldots, t)\,. \qquad (32)
\end{aligned}$$

The kinetic equation for the time evolution of concentrations has the form:

$$\frac{da}{dt} = -\frac{db}{dt} = -kae\,, \tag{33}$$

where, like in the previous case, the small letters denote concentrations of corresponding reactants. The solution of Eq.(33) is simple:

$$a(t) = a(t = 0)\exp(-ket)\,, \tag{34a}$$

$$b(t) = b(t = 0) + a(t = 0)(1 - \exp(-ket))\,. \tag{34b}$$

Time evolution of correlation functions of concentration's fluctuations are given by the set of equations:

$$\frac{d}{dt}\sigma_{ee}(\boldsymbol{r}, t) = 2D\nabla^2\sigma_{ee}\,, \tag{35}$$

$$\frac{d}{dt}\sigma_{ae}(\boldsymbol{r}, t) = 2D\nabla^2\sigma_{ae} - ke\sigma_{ae} - ka\sigma_{ee} - kae\delta(\boldsymbol{r})\,, \tag{36}$$

$$\frac{d}{dt}\sigma_{be}(\boldsymbol{r}, t) = 2D\nabla^2\sigma_{be} + ke\sigma_{ae} + ka\sigma_{ee} + kae\delta(\boldsymbol{r})\,, \tag{37}$$

$$\frac{d}{dt}\sigma_{ab}(\boldsymbol{r}, t) = 2D\nabla^2\sigma_{ab} + ke\sigma_{aa} - ke\sigma_{ab} + ka\sigma_{ae} - ka\sigma_{be}\,, \tag{38}$$

$$\frac{d}{dt}\sigma_{aa}(\boldsymbol{r}, t) = 2D\nabla^2\sigma_{aa} - 2ke\sigma_{aa} - 2ka\sigma_{ae}\,, \tag{39}$$

$$\frac{d}{dt}\sigma_{bb}(\boldsymbol{r}, t) = 2D\nabla^2\sigma_{bb} + 2ke\sigma_{ab} + 2ka\sigma_{be}\,. \tag{40}$$

In the simulated system all correlation functions are equal to zero at $t = 0$. Eq.(35) says that if there are no correlations between the enzyme molecules at $t = 0$ (as in simulations) then they will never develop in time so $\sigma_{ee}(t) \equiv 0$. The solution of the other equations is simple if one transforms them to the reverse space. The time evolution of Fourier transforms of σ_{nm} is described by:

$$\frac{d}{dt}\sigma_{ae}(q,t) = -2D(2\pi q)^2\sigma_{ae}(q,t) - ke\sigma_{ae}(q,t) - kae\,, \tag{41}$$

$$\frac{d}{dt}\sigma_{be}(q,t) = -2D(2\pi q)^2\sigma_{be}(q,t) + ke\sigma_{ae}(q,t) + kae\,, \tag{42}$$

$$\begin{aligned}\frac{d}{dt}\sigma_{ab}(q,t) = &-2D(2\pi q)^2\sigma_{ab}(q,t) + ke\sigma_{aa}(q,t)\\ &- ke\sigma_{ab}(q,t) + ka\sigma_{ae}(q,t) - ka\sigma_{be}(q,t)\,,\end{aligned} \tag{43}$$

$$\frac{d}{dt}\sigma_{aa}(q,t) = -2D(2\pi q)^2\sigma_{aa}(q,t) - 2ke\sigma_{aa}(q,t) - 2ka\sigma_{ae}(q,t)\,, \tag{44}$$

$$\frac{d}{dt}\sigma_{bb}(q,t) = -2D(2\pi q)^2\sigma_{bb}(q,t) + 2ke\sigma_{ab}(q,t) + 2ka\sigma_{be}(q,t)\,. \tag{45}$$

For the initial condition:

$$\sigma_{aa}(q,t=0)=\sigma_{ab}(q,t=0)=\sigma_{bb}(q,t=0)=\sigma_{ae}(q,t=0)=\sigma_{be}(q,t=0)=0$$

the solution of Eqs. (41)–(45) reads:

$$\sigma_{ae}(q,t) = -\sigma_{be}(q,t) = -\frac{kea(t)}{2D(2\pi q)^2}(1-\exp(-2D(2\pi q)^2 t))\,, \tag{46}$$

$$\begin{aligned}\sigma_{aa}(q,t) = \sigma_{bb}(q,t) = &-\sigma_{ab}(q,t)\\ = &-\frac{2k^2ea^2(t)}{(2D(2\pi q)^2)^2}\left(1-(1+2D(2\pi q)^2 t)\right)\exp(-2D(2\pi q)^2 t)).\end{aligned} \tag{47}$$

In simulations I considered a system of 691,200 spheres, which was obtained by a periodic extension of a trajectory obtained for 400 spheres placed in a cube with the side length 12.5σ (therefore the packing fraction was 0.107). At the beginning 40% of all spheres are marked as E, all the others correspond to reactant A. The steric factor for reaction (30) is equal to 0.2. The results shown in Figs. 6 and 7 were obtained after averaging over 140 different reaction paths. Fig. 6 shows the correlation functions σ_{EE}, σ_{AE} and σ_{BE} at the moment of time when $b = 0.1$. As predicted by the theory the values of σ_{EE} obtained in simulations are very close to zero, which reflects the fact that there are no nonequilibrium correlations, which are introduced by the presence of reaction (30). The correlation functions σ_{AE} and σ_{BE} are plotted using the solid and the dotted lines in the same figure. Their signs are opposite and their magnitudes are almost the same as follows from Eq. (46). The same results were obtained for the other values of b at which the correlation functions were studied (see also Fig. 7).

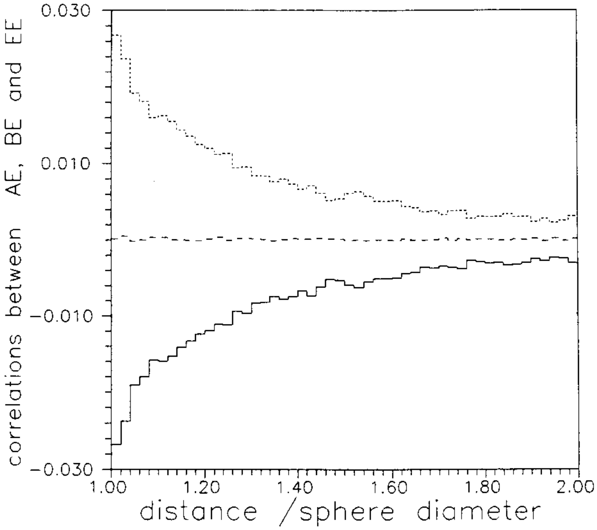

Fig. 6. Results of molecular dynamics simulations of correlation functions between the enzyme and reactants for the process (30); σ_{BE} — the dotted line, σ_{EE} — the dashed line, σ_{AE} — the solid line. The correlations were calculated for $b = 0.1$ and they are scaled by the square of the total density of particles.

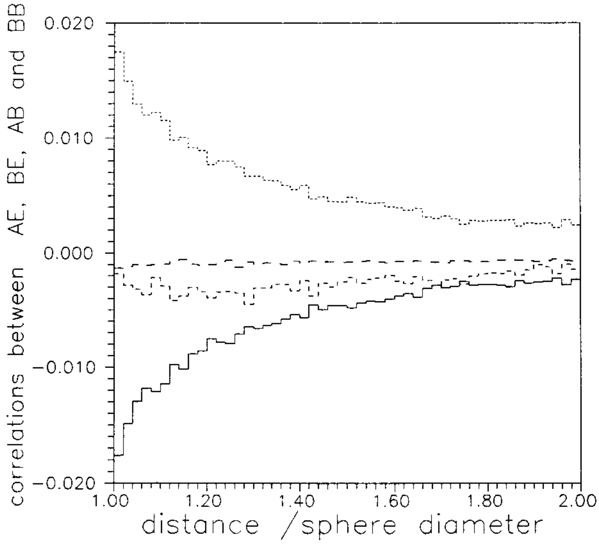

Fig. 7. Results of molecular dynamics simulations of correlation functions between the reagents of the process (30); σ_{BE} — the dotted line, σ_{BB} — the short dashed line, σ_{AB} — the long dashed line, σ_{AE} — the solid line. The correlations were calculated for $b = 0.3$ and they are scaled by the square of the total density of particles.

The correlation functions σ_{AE} and σ_{BE} are the most important because they appear directly as the result of chemical reaction (notice the source term $kae\delta(\mathbf{r})$ in Eqs. (36), (37)). These correlation functions become the source for the correlations between molecules of A and B (Eqs. (38)–(40)). As expected, it is observed in simulations that the correlation functions σ_{AE} and σ_{AB} grow first and the functions σ_{AA},σ_{AB} and σ_{BB} appear later. Moreover the absolute value of σ_{AE} (or σ_{BE}) is larger than for the other functions. The correlation functions σ_{AB} and σ_{BB} are shown in Fig. (7). According to the theory (Eq. (47)) the sign of σ_{AB} is opposite than those of σ_{AA},σ_{BB} but all these functions should have the same absolute values. The results for $b = 0.3$ (Fig. 7) show that both σ_{AB} and σ_{BB} are negative and their values are different. A disagreement with Eq. (47) was observed for other moments of time and also for simulations performed for reaction (30) proceeding in a system characterized by different density. The origin of this discrepancy is a subject of further studies.

5. Conclusions

In this paper I presented a numerical technique based on the model of reactive hard spheres, which may be used for molecular dynamics simulations of nonequilibrium spatial correlations between molecules involved in chemical reactions. The method was applied to two simple models of reactions. The results of simulations were compared with a simple theory based on the master equation for a spatially distributed system. Although the detailed qualitative comparison between both methods is not possible because the excluded volume effect is neglected by the theory it was interesting to study if there is a qualitative agreement between results.

A model with two independent reaction groups was considered as an example of a chemical system in a stationary state. In this case a good qualitative agreement between correlations measured in molecular dynamics simulations and these described by theory was obtained. The correlation functions computed in simulations obey the symmetries predicted by the theory. Moreover, the calculated values of the decay constants and of the ratio between amplitudes of correlations related to different groups reaction give a fair approximation for results of simulations.

The interpretation of results obtained for time dependent correlations related to a simple enzymatic reaction is more complex . The most important correlation functions between reactants and enzyme are correctly (qualitatively) described by theory. There is however a discrepancy in correlations between substrate and product because the functions obtained in simulations do not obey the symmetries predicted by theory. The effect may be associated with a limited size of simulated system, but further investigation of this problem is necessary.

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