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ON THE GROWTH OF NONEQUILIBRIUM SPATIAL CORRELATIONS IN A MODEL REACTION DIFFUSION SYSTEM: THE EFFECT OF THE DIFFUSIVE FLOW RELAXATION [*]

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The mesoscopic description of a system with chemical reactions predicts that if the detailed balance condition is not satisfied then nonequilibrium spatial correlations between concentrations of reactants may appear. The present work is concerned with the dynamics of their growth in a system which initially is well mixed. The discrepancy between the theory based on the master equation, in which Fick's law was assumed for the diffusive flow, and molecular dynamics simulations performed for a model system of "reacting" hard spheres was found in our previous work. Molecular dynamics indicates front-like expansion of correlations towards their stationary form, whereas the theory supports more uniform growth at all distances. In this paper, we introduce the relaxation of the diffusive flow towards Fick's law based on the Langevin approach in order to explain the front-like expansion of the spatial correlations.

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1. Introduction

It is known that the nonequilibrium spatial correlations between fluctuations in concentrations of reactants may appear in systems for which the detailed balance condition is not satisfied [1]. Most of the publications on this subject were concerned with the stationary correlations [2–5]. Recently Gorecki and Kitahara studied the dynamics describing the growth of nonequilibrium correlations using both the theory based on the master equation and molecular dynamics simulations [6]. They considered a stationary state of a system for which the detailed balance condition is not satisfied. Initially the average concentrations of reactants corresponded to their stationary values, but the reagents were randomly distributed in the system. In such a case the concentrations of reactants remain unchanged in time (they may fluctuate only), but the nonequilibrium correlations between reagents develop in space as reactions progress. Molecular dynamics simulations indicated front-like expansion of the spatial correlations, whereas the theory supported more uniform growth at all distances. This discrepancy seems remarkable in the case of faster reaction. Gorecki and Kitahara suggested that it comes mainly from the fact that the diffusive term in the master equation is evaluated according to Fick's law. When the time scale of the chemical reaction is sufficiently short, we have to take into account the time scale of relaxation of the diffusive flow towards the state which satisfies Fick's law.

This paper is concerned with a simple generalization of the conventional treatment for the case of fast reactions by considering the diffusive flow relaxation. We adopt the description based on the Langevin equations for the fluctuation of the concentration of reactants and the diffusive flow. These Langevin equations can be obtained by physically reasonable modification of the stochastic equations which are equivalent to the description adopted in [6].

The paper is organized as follows: in two following sections, we present the system and briefly discuss the description based on the master equation. Next we introduce the Langevin equations which are equivalent to the master equation in the Gaussian approximation and then modify them in order to take into account the diffusive flow relaxation.

From these Langevin equations the time evolution of the correlation functions of fluctuations in reagents' concentrations are derived. This result are compared with molecular dynamics simulations. We conclude the paper with a few remarks on our treatment and suggestions for the future work.

2. The model

The model which is considered below consists of the following reactions:

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

It was used in our previous papers on the stationary form of the correlations of fluctuations in reagents' concentrations [5] and the dynamics of their growth [6]. We shall assume that the reactions proceed in a closed system so the sum of the concentrations of X and Y (denoted x and Y respectively) is constant. The kinetic equations for system (1) read:

$$\begin{aligned} \frac{dx}{dt} &= -k_1x^2+k_{-1}xy-k_2xy+k_{-2}y^2=f(x,y)\,,\\ \frac{dy}{dt} &= k_1x^2-k_{-1}xy+k_2xy-k_{-2}y^2=-f(x,y)\,. \end{aligned} \tag{2}$$

It is clear that $x+y=c(=\text{const.})$ is a constraint of these kinetic equations. In the following we restrict our attention to a homogeneous, stationary state of the system (1). It is easy to prove that equations (2) admit a single such state $x_s, y_s; 0 \leq x_s, y_s \leq c$, which is always stable.

3. Previous results

At the beginning let us briefly illustrate the conventional mesoscopic description of spatial correlations between fluctuations in concentrations of reactants which is based on the master equation for a spatially distributed system. We consider a system composed of cells characterized by equal volume Ω and let X_i, Y_i denote the number of molecules of X and Y in the i-th cell. Information on time evolution of the system can be extracted from the probability distribution $P(\ldots, X_i, Y_i, \ldots, t)$ which describes the probability of finding X_i molecules of X and Y_i molecules of Y in the i-th cell at the time t. The master equation for the system can be derived by the standard method.

$$\frac{d}{dt}P=\left(\frac{d}{dt}\right)_{\text{chem}}P+\left(\frac{d}{dt}\right)_{\text{diff}}P\,. \tag{3}$$

The full representation of the transition probability for the chemical reaction and the diffusion is presented in [6]. It is important that the transition probability for the diffusion comes from the simple jump process between two cells, which gives Fick's law in the continuum limit.

The equations which describe the growth of spatial correlations of fluctuations in reactants' concentrations can be derived in a direct way from the master equation by assuming a Gaussian multivariate probability for intensive excess variables

$$\delta x_i = \frac{X_i}{\Omega} - x_s, \qquad \delta y_i = \frac{Y_i}{\Omega} - y_s, \tag{4}$$

following the method by van Kampen [7]. Here we assumed that the average concentrations of reactants (x_s, y_s) correspond to the homogeneous steady state.

Considering the continuum limit, according to the standard approach [1,7], the stationary correlation functions have the following form:

$$\begin{aligned}\big\langle (n(\boldsymbol{r}) - n_s)\,(m(\boldsymbol{r}') - m_s)\big\rangle \;&=\; n_s\,\delta_{nm}\,\delta(\boldsymbol{r}-\boldsymbol{r}') \\ &\quad - \frac{C^{NM}}{8\pi D}\frac{1}{|\boldsymbol{r}-\boldsymbol{r}'|}\exp(-\kappa|\boldsymbol{r}-\boldsymbol{r}'|)\,,\end{aligned} \tag{5}$$

where n and m denote the concentrations of the reagents N and M. The constants C^{NM} and κ are related to the chemical dynamics and diffusion. For reaction (1) they read

$$C^{XX} = C^{YY} = -C^{XY} \equiv C = 2(k_1 x_s^2 - k_{-1} x_s y_s)\,, \tag{6}$$

$$\kappa = \sqrt{\frac{a}{D}}\,, \tag{7}$$

where

$$a = \left(\frac{\partial f}{\partial y}\right)_{x_s y_s} - \left(\frac{\partial f}{\partial x}\right)_{x_s y_s} > 0. \tag{8}$$

It is obvious that if the detailed balance condition is satisfied then all constants C^{NM} are equal to zero. Thus the second term in Eq. (5) which gives the spatial correlation with the correlation length $1/\kappa$ may appear in a stationary state only if the detailed balance condition is not hold.

Then we show the equation which describes the dynamics of the correlation functions. Let us introduce new time-dependent correlation functions σ_{nm} defined as follows:

$$\sigma_{nm}(|\,\boldsymbol{r}-\boldsymbol{r}'\,|, t) = \big\langle (n(\boldsymbol{r}) - n_s)(m(\boldsymbol{r}') - m_s)\big\rangle_t - n_s\delta_{nm}\delta(\boldsymbol{r}-\boldsymbol{r}')\,, \tag{9}$$

assuming that the system is homogeneous. Its Fourier transform is denoted as $\sigma_{nm}(\boldsymbol{k}, t)$. For reactants which are perfectly mixed the initial condition reads:

$$\sigma_{xx}(\boldsymbol{k}, t=0) = \sigma_{yy}(\boldsymbol{k}, t=0) = \sigma_{xy}(\boldsymbol{k}, t=0) = 0\,. \tag{10}$$

This initial condition leads a condition for the solution

$$\sigma_{xx}(\boldsymbol{k}, t) = \sigma_{yy}(\boldsymbol{k}, t) = -\sigma_{xy}(\boldsymbol{k}, t)\,. \tag{11}$$

Using this condition one finally obtains the equation for σ_{xx}

$$\frac{d}{dt}\sigma_{xx}(\boldsymbol{k},t) = -2a\sigma_{xx}(\boldsymbol{k},t) - C - 2D\boldsymbol{k}^2\sigma_{xx}(\boldsymbol{k},t)\,. \tag{12}$$

The analytical solution for $\sigma_{xx}(\mid \boldsymbol{r}-\boldsymbol{r}' \mid, t)$ can be obtained from Eq. (12) and it was presented in [6].

4. The Langevin equations for the diffusive flow relaxation

First of all we derive the Langevin equations which are equivalent to the description based on the master equation in the Gaussian approximation which was mentioned in the previous section. Let us denote $\delta n(\boldsymbol{r}) = n(\boldsymbol{r}) - n_s$ as the local fluctuation of the concentrations of reactants N (N is X or Y), and $\boldsymbol{J}_n$ as local diffusive flow of reactants N. Then the dynamics of δn and $\boldsymbol{J}_n$ is given as follows:

$$\frac{d}{d\,t}\begin{pmatrix}\delta x(\boldsymbol{r},t)\\ \delta y(\boldsymbol{r},t)\end{pmatrix} = \begin{pmatrix} f_{x,s} & f_{y,s}\\ -f_{x,s} & -f_{y,s}\end{pmatrix}\begin{pmatrix}\delta x(\boldsymbol{r},t)\\ \delta y(\boldsymbol{r},t)\end{pmatrix} - \nabla\cdot\begin{pmatrix}\boldsymbol{J}_x(\boldsymbol{r},t)\\ \boldsymbol{J}_y(\boldsymbol{r},t)\end{pmatrix} + \begin{pmatrix}\xi_x(\boldsymbol{r},t)\\ \xi_y(\boldsymbol{r},t)\end{pmatrix},$$

$$\begin{pmatrix}\boldsymbol{J}_x(\boldsymbol{r},t)\\ \boldsymbol{J}_y(\boldsymbol{r},t)\end{pmatrix} = -D\nabla\begin{pmatrix}\delta x(\boldsymbol{r},t)\\ \delta y(\boldsymbol{r},t)\end{pmatrix} + \begin{pmatrix}\boldsymbol{R}_x(\boldsymbol{r},t)\\ \boldsymbol{R}_y(\boldsymbol{r},t)\end{pmatrix}, \tag{13}$$

where we have used abbreviated notation

$$f_{n,s} = \left(\frac{\partial f}{\partial n}\right)_{x_s y_s}.$$

The variables $\xi_n(\boldsymbol{r},t)$ and $\boldsymbol{R}_n(\boldsymbol{r},t)$ are Gaussian random forces characterized by:

$$\langle \xi_n(\boldsymbol{r},t)\rangle = 0\,, \qquad \langle \boldsymbol{R}_n(\boldsymbol{r},t)\rangle = \boldsymbol{0}\,, \tag{14}$$

and

$$\left\langle \xi_n(\boldsymbol{r},t)\, R_{m\alpha}(\boldsymbol{r}',t')\right\rangle = 0\,,$$

$$\begin{aligned}
&\begin{pmatrix}\langle \xi_x(\boldsymbol{r},t)\xi_x(\boldsymbol{r}',t')\rangle & \langle \xi_x(\boldsymbol{r},t)\xi_y(\boldsymbol{r}',t')\rangle\\ \langle \xi_y(\boldsymbol{r},t)\xi_x(\boldsymbol{r}',t')\rangle & \langle \xi_y(\boldsymbol{r},t)\xi_y(\boldsymbol{r}',t')\rangle\end{pmatrix} = \begin{pmatrix}1 & -1\\ -1 & 1\end{pmatrix}\\
&\times\left[a\,\frac{f_{x,s}x_s - f_{y,s}y_s}{f_{x,s}-f_{y,s}} - C\right]\delta(\boldsymbol{r}-\boldsymbol{r}')\,\delta(t-t')\,,\\
&\begin{pmatrix}\langle R_{x\alpha}(\boldsymbol{r},t)R_{x\beta}(\boldsymbol{r}',t')\rangle & \langle R_{x\alpha}(\boldsymbol{r},t)R_{y\beta}(\boldsymbol{r}',t')\rangle\\ \langle R_{y\alpha}(\boldsymbol{r},t)R_{x\beta}(\boldsymbol{r}',t')\rangle & \langle R_{y\alpha}(\boldsymbol{r},t)R_{y\beta}(\boldsymbol{r}',t')\rangle\end{pmatrix} = \begin{pmatrix}x_s & 0\\ 0 & y_s\end{pmatrix}\\
&\times 2D\,\delta_{\alpha\beta}\,\delta(\boldsymbol{r}-\boldsymbol{r}')\,\delta(t-t')\,.
\end{aligned} \tag{15}$$

It is easy to check that these equations give the same time evolution of the correlation function as Eq. (12).

Now let us propose a simple modification of these Langevin equations which takes into account the diffusive flow relaxation to Fick's law. We slightly modify the Langevin equations as follows:

$$\frac{d}{dt}\begin{pmatrix}\delta x(\boldsymbol{r},t)\\ \delta y(\boldsymbol{r},t)\end{pmatrix}=\begin{pmatrix}f_{x,s} & f_{y,s}\\ -f_{x,s} & -f_{y,s}\end{pmatrix}\begin{pmatrix}\delta x(\boldsymbol{r},t)\\ \delta y(\boldsymbol{r},t)\end{pmatrix}-\nabla\cdot\begin{pmatrix}\boldsymbol{J}_x(\boldsymbol{r},t)\\ \boldsymbol{J}_y(\boldsymbol{r},t)\end{pmatrix}+\begin{pmatrix}\xi_x(\boldsymbol{r},t)\\ \xi_y(\boldsymbol{r},t)\end{pmatrix},$$

$$\frac{d}{dt}\begin{pmatrix}\boldsymbol{J}_x(\boldsymbol{r},t)\\ \boldsymbol{J}_y(\boldsymbol{r},t)\end{pmatrix}=-\gamma\left\{\begin{pmatrix}\boldsymbol{J}_x(\boldsymbol{r},t)\\ \boldsymbol{J}_y(\boldsymbol{r},t)\end{pmatrix}+D\nabla\begin{pmatrix}\delta x(\boldsymbol{r},t)\\ \delta y(\boldsymbol{r},t)\end{pmatrix}\right\}+\gamma\begin{pmatrix}\boldsymbol{R}_x(\boldsymbol{r},t)\\ \boldsymbol{R}_y(\boldsymbol{r},t)\end{pmatrix}, \tag{16}$$

where $\boldsymbol{R'}_n(\boldsymbol{r},t)=\gamma\boldsymbol{R}_n(\boldsymbol{r},t)$ and

$$\begin{aligned}\left\langle R'_{n\alpha}(\boldsymbol{r},t)\,R'_{m\beta}(\boldsymbol{r}',t')\right\rangle &= 2\gamma^2 D n_s\,\delta_{nm}\,\delta_{\alpha\beta}\,\delta(\boldsymbol{r}-\boldsymbol{r}')\,\delta(t-t')\\ &= 2\gamma\frac{k_BT}{m}n_s\,\delta_{nm}\,\delta_{\alpha\beta}\,\delta(\boldsymbol{r}-\boldsymbol{r}')\,\delta(t-t')\,. \end{aligned}\tag{17}$$

In Eq. (17) we have assumed Einstein's relation $D=k_BT/m\gamma$ where k_B is the Boltzmann constant and m is the mass of the reactants (where we have assumed that reactants X and Y have the same mass.). The relation (17) corresponds to the fluctuation-dissipation relation which can be obtained from the consideration based on nonequilibrium thermodynamics of multicomponent systems [8]. In this treatment $\tau_f\equiv 1/\gamma$ determines the time scale of diffusive flow relaxation to Fick's law. In the limit $\tau_f\to 0\,(\gamma\to\infty)$ we recover the description by Eqs (13) and (15).

5. Results

The spatial correlations of fluctuations in reactants' concentrations can be calculated from Eqs (16) with initial conditions:

$$\begin{aligned}\left\langle\delta n(\boldsymbol{r},0)\,\delta m(\boldsymbol{r}',0)\right\rangle &= n_s\,\delta_{nm}\,\delta(\boldsymbol{r}-\boldsymbol{r}')\,,\\ \left\langle J_{n\alpha}(\boldsymbol{r},0)\,J_{m\beta}(\boldsymbol{r}',0)\right\rangle &= \frac{k_BT}{m}\,n_s\,\delta_{nm}\,\delta_{\alpha\beta}\,\delta(\boldsymbol{r}-\boldsymbol{r}')\,,\\ \left\langle\delta n(\boldsymbol{r},0)\,J_{m\beta}(\boldsymbol{r}',0)\right\rangle &= 0\,,\end{aligned}\tag{18}$$

where the first condition corresponds to the initial perfectly mixed state and the second condition comes from the equilibrium distribution at initial time.

A tedious but straightforward calculation leads to the following result

$$\begin{aligned}\left\langle \delta n(\boldsymbol{r},t)\,\delta m(\boldsymbol{r}',t)\right\rangle &= \lim_{t\to\infty}\left\langle \delta n(\boldsymbol{r},t)\,\delta m(\boldsymbol{r}',t)\right\rangle \\ &+ C^{NM}\int \frac{d^3\boldsymbol{k}}{(2\,\pi)^3}\,\frac{\mathrm{e}^{i\,\boldsymbol{k}\cdot(\boldsymbol{r}-\boldsymbol{r}')}}{(a-\gamma)^2-4\gamma D k^2} \\ &\times\left[\mathrm{e}^{-2\lambda_+ t}\,\frac{(\lambda_+-\gamma)^2}{2\,\lambda_+}+\mathrm{e}^{-2\lambda_- t}\,\frac{(\lambda_--\gamma)^2}{2\,\lambda_-}-\mathrm{e}^{-(a+\gamma)t}\,\frac{2\gamma D k^2}{a+\gamma}\right], \qquad (19)\end{aligned}$$

where

$$\lambda_\pm = \frac{1}{2}\left[(a+\gamma)\pm\sqrt{(a-\gamma)^2-4\gamma D k^2}\,\right], \qquad (20)$$

and

$$\begin{aligned}\lim_{t\to\infty}\left\langle \delta n(\boldsymbol{r},t)\,\delta m(\boldsymbol{r}',t)\right\rangle &= \left[n_s\,\delta_{nm}-\frac{C^{NM}}{2(a+\gamma)}\right]\delta(\boldsymbol{r}-\boldsymbol{r}') \\ &- \frac{C^{NM}}{8\pi D}\,\frac{\gamma}{a+\gamma}\,\frac{1}{|\boldsymbol{r}-\boldsymbol{r}'|}\,\mathrm{e}^{-\kappa|\boldsymbol{r}-\boldsymbol{r}'|}\,. \qquad (21)\end{aligned}$$

This term survives in the limit $t\to\infty$ and it corresponds to the stationary spatial correlation function. We obtained some correction to the well-known result (5) which are of the order of $1/\gamma$. The second term contains three kinds of modes which decay exponentially to zero with time scales $\mathrm{Re}(\lambda_+)$, $\mathrm{Re}(\lambda_-)$ and $(a+\gamma)$ respectively.

In the special case $a=\gamma$, the inverse Fourier transform of Eq. (19) can be done analytically leading to the expression

$$\begin{aligned}\left\langle \delta n(\boldsymbol{r},t)\,\delta m(\boldsymbol{r}',t)\right\rangle &= n_s\delta_{nm}\delta(\boldsymbol{r}-\boldsymbol{r}')-\frac{C^{NM}}{4a}\left(1-\mathrm{e}^{-2at}\right)\delta(\boldsymbol{r}-\boldsymbol{r}') \\ -C^{NM}&\frac{\mathrm{e}^{-2at}}{32\pi a D}\frac{1}{|\boldsymbol{r}-\boldsymbol{r}'|}\left[\delta\left(t-\frac{|\boldsymbol{r}-\boldsymbol{r}'|}{2\sqrt{aD}}\right)-\delta\left(t+\frac{|\boldsymbol{r}-\boldsymbol{r}'|}{2\sqrt{aD}}\right)\right] \\ -\theta&\left(t-\frac{|\boldsymbol{r}-\boldsymbol{r}'|}{2\sqrt{aD}}\right)\frac{C^{NM}}{16\pi D}\frac{1}{|\boldsymbol{r}-\boldsymbol{r}'|}\mathrm{e}^{-\kappa|\boldsymbol{r}-\boldsymbol{r}'|}, \qquad (22)\end{aligned}$$

where $\theta(t)$ is the step function. The first term of Eq. (22) corresponds to Poisson distribution and the second term gives the correction to Poisson distribution. The fourth term has the stationary value inside the region $|\boldsymbol{r}-\boldsymbol{r}'|<2\sqrt{aD}\,t$. Thus this term represents the wave front with the velocity $2\sqrt{aD}$. The third term gives the delta function localized at the wave front. This delta function should be smeared in some extent by appropriate cut off for the wave number because our phenomenological treatment is not valid in the microscopic length. Anyway this term gives the quite large peak at the wave front which was not observed in the previous molecular dynamics simulations [6].

6. Molecular dynamics simulations of nonequilibrium spatial correlations

Molecular dynamics simulations in the special case $\gamma = a$ are performed using the same technique which was applied in our previous paper [6]. The technique is based on the concept of "reactive" hard spheres (see for example [9]). According to it all the reagents are represented by identical hard spheres (masses and diameters are the same) and their motion is ruled by a standard dynamics with all the collisions regarded as elastic. The additional parameter, which has no influence on the mechanical motion, labels the chemical properties of spheres. We consider both reactive and nonreactive collisions between spheres. A chemical reaction may occur if particles representing appropriate reagents collide. In order to describe a stochastic character of chemical processes a random number is called for each collision which may lead to a reaction and its value is compared with the steric factor for the appropriate process. If the value is not larger than the steric factor the collision is regarded as a reactive one and the chemical identity parameters of the spheres involved are modified. In simulations we assume that the activation energies for all reactions (1) are equal to zero.

Simulations performed within the reactive hard spheres technique can be very efficient if one uses a prerecorded trajectory which describes a system characterized by the periodic boundary conditions. In such a case the trajectory can be used as the data base on consecutive collisions and the boundary conditions allow to extend the size of simulated system by treating the original box within the system is enclosed as the elementary cell in a periodically expanded system. This technique was used in our previous studies on nonequilibrium spatial correlations [5, 6].

In the following we discuss the results which have been obtained by periodic extension of a system of $N = 500$ hard spheres placed in a cubic box with the side length $d = 14.7\sigma$ where σ is the diameter of a sphere. The packing fraction is $\eta = 0.0824$. This system was expanded by 10 box lengths in each direction so the total number of molecules is 500000. For such system the average time between successive collisions of a particle is equal to 1.29 ps. In the following we give all values of time in this unit unless it is directly specified.

Both reactants X and Y are represented by spheres with the mass ($m =$ 32 a.u.) and diameter ($\sigma = 5$ Å). The temperature equals 300 K and remains constant during simulations.

The parameter γ is obtained from the diffusion constant using Einstein's relation. The diffusion constant D is calculated from simulation data by measuring the average square of a particle's displacement as a function of time. The parameter a is calculated from Eq. (8) where the reaction rate constants k_i's are obtained from the observed collision rate multiplied by corresponding steric factors s_i's.

Two sets of steric factors for which the condition $\gamma = a$ is satisfied are selected.

$$\begin{aligned} s_1 &= 0.32, \;\; s_{-1} = 0.16, \;\; s_2 = 0.08, \;\; s_{-2} = 0.32, \\ \text{and} \qquad s'_1 &= 0.16, \;\; s'_{-1} = 0.08, \;\; s'_2 = 0.36, \;\; s'_{-2} = 0.52. \end{aligned}$$

For both sets of steric factors the concentrations of X at its stationary state are the same and they are equal to: $x_s = ((\sqrt{65} - 7)/2)c$.

At the beginning of simulations the chemical identities of spheres are assigned in a random way, such that the concentrations of X and Y correspond to their stationary values x_s, y_s. Because of random distribution of reactants we may expect that the no spatial correlations of concentrations are present in initial state.

The spacial correlation $\sigma_{nm}(\mid \boldsymbol{r} - r' \mid, t)$ is defined in such a way that the hard sphere correlation is removed out. The details of calculations are shown in [6].

$$\begin{aligned} \sigma_{nm}(\mid \boldsymbol{r} - r' \mid, t) &= n_s m_s g_0(\mid \boldsymbol{r} - \boldsymbol{r}' \mid) \left(\frac{g_{NM}(\mid \boldsymbol{r} - \boldsymbol{r}' \mid, t)}{g_0(\mid \boldsymbol{r} - \boldsymbol{r}' \mid, t)} - 1 \right) \\ &= \left[\frac{n_s}{c} \frac{m_s}{c} g_0(\mid \boldsymbol{r} - \boldsymbol{r}' \mid) \left(\frac{g_{NM}(\mid \boldsymbol{r} - \boldsymbol{r}' \mid, t)}{g_0(\mid \boldsymbol{r} - \boldsymbol{r}' \mid, t)} - 1 \right) \right] c^2, \quad (23) \end{aligned}$$

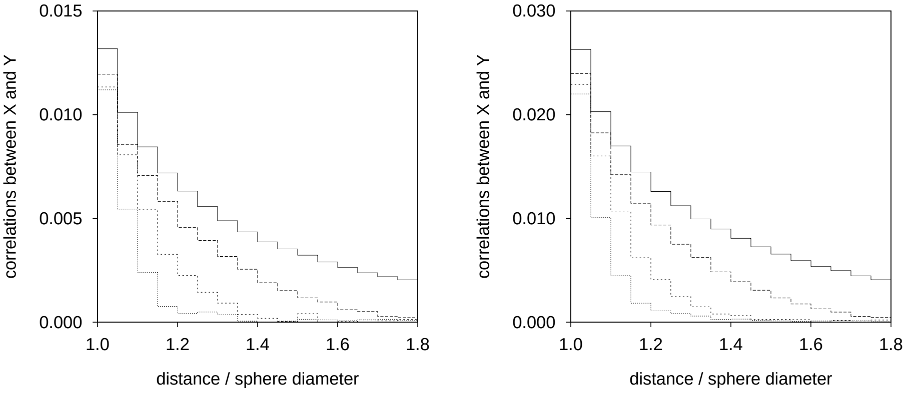
where $g_0(r)$ is the radial distribution function for the system of spheres at the given packing fraction. Let us mention that from the computational point of view it is more convenient to calculate the partial radial distribution functions scaled to $g_0(r)$ rather than $g_{NM}(r)$ itself because in the first case the fluctuations in the sample of interatomic distances cancel out.

Unlike the theory, the simulations do not give us the values of correlation functions for a specified distance at a given moment of time but the average over an interval of distances and an interval of times. In our simulations $g_0(r, t)$ and $g_{NM}(r, t)$ are averaged within the space interval $[\sigma + i\Delta, \sigma + (i + 1)\Delta]$ where $\Delta = 0.05\sigma$ and the time interval $[j\Delta_t, (j + 1)\Delta_t]$ where $\Delta_t = 0.02$ ps. In the figures we refer to such correlation functions as functions depending on r and t which denote a point within the selected interval of spaces and the average time $t = (2j + 1)\Delta_t/2$. In order to make a consistent comparison between theory and simulations we have averaged the theoretical results over space and time as follows:

$$\sigma_{nm}(i, j) = \frac{1}{\Delta \Delta_t} \int\limits_{\sigma + i\Delta}^{\sigma + (i+1)\Delta} dr \int\limits_{j\Delta_t}^{(j+1)\Delta_t} dt \, \sigma_{nm}(r, t), \qquad (24)$$

and such results are shown in Figs 2 and 3.

A time evolution of the functions σ_{xy} obtained from MD simulations for the steric factors (s_i) and (s'_i) is presented in figures 1(a) and 1(b). In the previous and present simulations the relationship (11) is hold, thus, we show the results for σ_{xy} only. This function is plotted using a dashed line for four selected moments of time (the dash length is an increasing function of time) and it is compared with the stationary correlation function σ_{xy} (solid line). It can be noticed that short distance correlations grow first and the long distance correlations appear later.



(a) (b)

Fig. 1. The time evolution of $\frac{\sigma_{xy}}{c^2}$ with rates s_i — (a) and s'_i — (b) obtained in molecular dynamics simulations. The correlations are shown for three moments of time: 0.078 (the dotted line), 0.155 (the short dashed line), 0.372 (the long dashed line). The solid line represents stationary correlation function.

In order to introduce more detailed description of correlation dynamics let us introduce the scaled correlation function in the form:

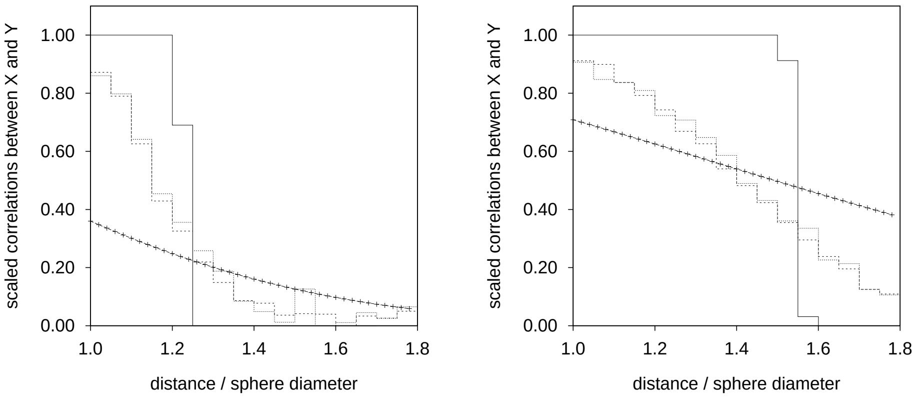
$$\nu(r,t) = \frac{\sigma_{nm}(r,t)}{\sigma_{nm}(r,t=\infty)}\,. \tag{25}$$

As the time progresses $\nu(r,t)$ changes from 0 to 1 for every r.

The theoretical result for $\gamma = a$ (Eq. (22)) gives the scaled correlation in the form:

$$\nu_{\gamma=a}(r,t) = \frac{1}{2a}\,\delta\left(t - \frac{|\boldsymbol{r}-\boldsymbol{r}'|}{2\sqrt{aD}}\right) + \theta\left(t - \frac{|\boldsymbol{r}-\boldsymbol{r}'|}{2\sqrt{aD}}\right). \tag{26}$$

$\nu_{\gamma=a}(r,t)$ as a function of distance for two selected moments of time is presented in Fig. 2(a) ($t = 0.155$) and Fig. 2(b) ($t = 0.372$). In these figures, the dashed line represents the result of simulations with the set (s_i) and the



(a) (b)

Fig. 2. The scaled correlation function $\nu(r,t)$; comparison of molecular dynamics simulations with the theory for two selected moments of time $t = 0.155$ — (a) and $t = 0.372$ — (b). The scaled correlation obtained from simulations with the set (s_i) (the dashed line) and (s'_i) (the dotted line) is presented. The dashed line with points represents the previous theoretical result which is calculated from Eq. (12). The solid line represents our present theory (Eq. (26)) without the delta function. The following values were used to evaluate Eq. (12) and (26): $D = 0.628\sigma^2\,\mathrm{ps}^{-1}$ and $a(=\gamma) = 0.496$ ps^{-1}.

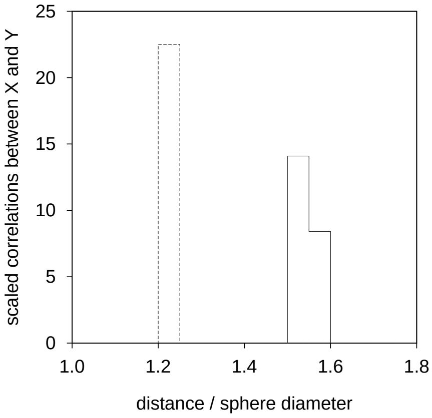


Fig. 3. The contribution of the delta function in the scaled correlation function $\nu(r,t)$ (Eq. (26)) for two moments of time: 0.155 (the dashed line), 0.372 (the solid line). The following values were used to evaluate Eq. (12) and (26): $D = 0.628\sigma^2\,\mathrm{ps}^{-1}$ and $a(=\gamma) = 0.496$ ps^{-1}.

dotted line corresponds to (s_i'). Although the sets of steric factors are different the results agree very well what confirms that the scaled distribution functions depend on D and a only. The dashed line with points represents the previous theoretical result which is calculated from Eq. (12) using D which is observed in simulations. It is clear that the theory based on master equation underestimates correlation at short distances, but overestimates them at large ones. The solid line represents the result of our present theory (Eq. (26)) without the delta function. The contribution of the delta function is quite large; we show the contribution of the delta function only in Fig. 3. The delta functions and the step functions in Figs 2 and 3 are averaged within space-time subintervals which is adopted in the simulation.

When we compare our theoretical results with the results of molecular dynamics simulations using a hard sphere model, we face a problem: on one hand the correlation functions obtained from simulations have the physical meaning for distances larger than the sphere diameter, on the other hand the correlation functions in our theory are defined for any distance because we consider the continuum limit of submacroscopic cells. In simulations we observe that in a system which is initially well mixed the correlations start to grow instantaneously after reactions start. Unlike it is for the standard theory, in our new approach the correlations are localized in space and at the distance equal to the sphere diameter they appear after $t_\sigma = \frac{\sigma}{2\sqrt{aD}}$. For the values of parameters used in simulations t_σ is much longer than the times for which the correlations in Figs 2 are shown. In order to take the excluded volume into account we rescaled time by transformation $t \to t + t_\sigma$ and the solid line in Figs 2 show the second term of solution (26) which corresponds to the rescaled time. This approach is equivalent to considering an initial condition for Eqs (16), which corresponds to its solution $n(r, t_\sigma), \boldsymbol{J}_n(r, t_\sigma)$ of Eqs (16) with the initial condition (18). However such procedure may be only applied for the special case $\gamma = a$ and in the general case the theory should be improved such that the excluded volume effect is included in equations for the time evolution of concentrations and the corresponding diffusive flows.

The part of $\nu_{\gamma=a}(r,t)$ which is represented by the step function reflects the fact that correlations fully develop at short distance first and then it spread out. If the rescaled time is used it gives much better approximation of the simulation results than the standard theory (Figs 2). However there is still a large difference between our present theory and simulations. First, the sharp peak at wave front which comes out of the δ function contribution in Eq. (26) has not been observed in simulations. Secondly, the second term of the theoretical result overestimates correlation at short distances and underestimates them at long distances.

7. Conclusions

In this paper we have taken the diffusive flow relaxation into account in order to describe a fast reaction. The Langevin equations for concentration fluctuations and diffusive flows, which have been modified such that the information on the time scale of the diffusive flow relaxation is included, have been presented. Using these equations we have calculated the time evolution of the spatial correlations between fluctuations in concentrations of reactants. It has been found that the stationary correlations Eq. (21) includes some corrections to the well-known result (Eq. (5)) which are of the order of $1/\gamma$.

In the special case $\gamma = a$, an analytical solution for the correlation functions has been obtained. On its basis we calculated the scaled correlation function (Eq. (26)). It comes out that $\nu_{\gamma=a}$ can be written as a sum of step-like wave front propagating with the velocity $2\sqrt{aD}$ and the delta-function peak localized at the edge of wave front. The contribution from a propagating wave front reflects some features of correlations observed in simulations: the correlation function approaches its stationary form at short distances first and then spreads out. However, the step-function-like wave front clearly overestimates correlations at short distances and underestimates them at long distances. On the other hand no trace of the delta-function-like peak localized at the wave front has been found in molecular dynamics simulations. We think that the discrepancies show the limitation of sub-macroscopic description of nonequilibrium spatial correlations in molecular dynamics simulations. We have compared the theory with simulations for distances being a fraction of the sphere diameter, which, for the parameters used, is of the order of the mean free path. In this range of distances there is no justification of sub-macroscopic description based on the master equation and its Gaussian approximation for intensive valuables.

The generalization which we have presented here seems to be not sufficient to describe the dynamics at so short time and space scales. We believe that it can be done within the theory which takes the excluded volume effect into account. On the other hand a good agreement between the theory based on the master equation and the molecular dynamics simulations for distances exceeding the sphere diameter observed in [5] suggests that the theory presented in this paper may be better suited for explaining the growth of correlations at large distances than the conventional mesoscopic description.

In the following we are going to study solutions of Eq. (19) for an arbitrary γ. The results will be compared with simulations of correlations growth at long distances. The problem of the description of nonequilibrium spatial correlations at short distances will be considered in future works.

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