

ON NONEQUILIBRIUM SPATIAL CORRELATIONS IN
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We study the nonequilibrium spatial correlations of the density fluctuations for a selected reagent as well as the spatial correlations of its energetic states in a stationary state of a model chemical system. In the considered model the reagent of interest appears as a product of a binary process and vanishes as the result of a fast unimolecular decay. We present analytical formulae for all correlation functions for the case when the lifetime of the reagent is short enough to treat the motion of its molecules as a ballistic rather than a diffusive one. We demonstrate that the results obtained from these formulae agree well with correlations directly measured in molecular dynamics simulations.

PACS numbers: 05.40.-a, 82.20.Wt

1. Introduction

It is known [1–7] that spatial correlations between the density fluctuations of reagents may appear in a stationary state of an open chemical system. It is because a chemical reaction is a local process, so when products are created, they are obviously correlated in space. The contribution

* Presented at the XVI Marian Smoluchowski Symposium on Statistical Physics, Zakopane, Poland, September 6–11, 2003.

to correlations in positions and in velocities coming from a particular set of created product molecules vanishes in time because these molecules interact with other molecules of the system and correlations introduced by the reaction cross section are lost. In a stationary state of a nonequilibrium open system reactants are continuously supplied and products are continuously created. Due to the inflow of correlated particles the correlations calculated as the average over all molecules of a given type may be different from zero. It should be emphasized that such situation occurs in a nonequilibrium state of the system when the reactions are not exactly balanced by the possible inverse processes which convert products into reactants. If the detailed balance condition for all elementary processes is fulfilled then the amplitude of correlations is null.

A standard description of spatial correlations between the density fluctuations of reagents is based on the master equation for a spatially distributed system [8] and it assumes that the motion of molecules is diffusive. Within such approach one can easily show that the correlations can appear only if the detailed balance condition is not fulfilled [2, 5]. In a system with a single reagent of interest the spatial correlation in density fluctuation of X ($C_{XX}(r)$) depends on the distance between the X molecules, $r = |\mathbf{r} - \mathbf{r}'|$, as [2, 5]

$$C_{XX}(r) = \langle x(\mathbf{r}, t)x(\mathbf{r}', t) \rangle - \langle x \rangle^2 \sim \frac{1}{r} \exp \left(-\frac{r}{\sqrt{D\tau_p}} \right) \quad \text{for } r > 0, \quad (1)$$

where $x(\mathbf{r}, t)$ is the local concentration of X at point $\mathbf{r}$ and time t , D is the diffusion constant, and τ_p is the characteristic lifetime of X molecule. The bracket $\langle \cdot \rangle$ denotes the mean value. In an open stationary state which is away from a bifurcation point τ_p is finite ([8]).

In order to derive formula (1) one should assume that the motion of reagent X molecules is diffusive. Obviously this assumption fails when reactions are very fast. A step towards more accurate description of correlations characterizing products of chemical reactions has been recently made by the authors [9]. We have considered the case when the chemical reaction is fast (which means that τ_p is small if compared with the mean time between collisions t_C) and the spatial correlations are created by the ballistic flight of the products rather than by the diffusive motion. For such a case the Ornstein–Zernike type formula (1) does not work. We have derived the expressions that describe the correlations which appear as the result of ballistic motions of reactants. Such correlations may appear not only in the density fluctuations but also in the velocities of the X products. This prediction has been confirmed by computer simulations. In this work we show some of the results and discuss the applicability of ballistic approximation.

2. The system

Let us consider a system composed of three reagents: A , X and S in which the following chemical processes take place



We assume that both the concentration of A and the sum of concentrations of S and X remain constant, which means that the reagent A is continuously supplied and the final product S is removed. We also assume that the mean concentration of X ($\langle x \rangle$), is much lower than that of A ($\langle a \rangle$). As a result, the collisions between X molecules are negligible and the role of inverse reaction: $X + X \rightarrow A + A$ can be neglected if compared to unimolecular decay (3). In order to simplify the problem we assume that all three reagents differ only by the chemical properties and their molecules are identical geometrically. From the kinetic theory point of view all the reagents are identical and the reaction is reduced to the change of chemical identify parameter which does not have influence on the motion. As a result, neglecting the chemical differences, the system is in the equilibrium state. Since $\langle x \rangle \ll \langle a \rangle$ the distribution function for the velocities of A particles can be approximated by the Maxwell–Boltzmann distribution.

For the case defined above, the master equation for a spatially distributed system gives [2,5] the spatial correlations of fluctuations in concentration of X in the following form

$$c_{XX}(r) = \frac{1}{\langle x \rangle^2} (C_{XX}(r) - \langle x \rangle \delta(x)) = \frac{k_2}{8\pi D \langle x \rangle r} \exp\left(-r\sqrt{\frac{k_2}{D}}\right). \quad (4)$$

In order to derive (4) one has to assume that the only transport process that drives motion of X molecules away is diffusion. In this paper, as mentioned in the Introduction, we assume an opposite situation: the reaction (3) is so fast (k_2 is large) that most of X molecules transforms into S before colliding with another molecule. As a consequence, the diffusion does not play any role and the correlations result only from the ballistic motion of a pair of X molecules that have been created in a single reactive collision.

The model considered in [9] assumes that the all molecules are represented by hard spheres of the diameters σ . The $A + A$ collisions are mechanically elastic and in addition to assumptions mentioned above we use the

Enskog-Boltzmann approximation for the A particle- A particle distribution function for colliding A molecules at the interparticle distance $|\mathbf{r} - \mathbf{r}'| = \sigma$

$$f_2(\mathbf{r}, \mathbf{v}, \mathbf{r}', \mathbf{v}') = \kappa_A f_0(v) f_0(v'), \quad (5)$$

where f_0 is the Maxwell-Boltzmann distribution function and κ_A is the value of the radial distribution at contact. We assume that the probability of reaction (2) (p_1^*) depends on velocities of colliding particles ($\mathbf{v}, \mathbf{v}'$) in the following way

$$p_1^*(\mathbf{v}_p, \mathbf{v}'_p) = \frac{\kappa_1}{|\mathbf{v}_p - \mathbf{v}'_p|} \exp \left(-\frac{m|\mathbf{v}_p - \mathbf{v}'_p|^2}{4kT} \left(\frac{1}{\xi} - 1 \right) \right) \quad (6)$$

with the obvious restriction that p_1^* should not be larger than 1. Here ξ and κ_1 are the parameters characterizing the reaction cross section.

The derivation of the formulae for spatial correlations in density fluctuations $c_{XX}(r)$ (compare (1), (4)), spatial correlations in velocities $J_{XX}(r)$ and spatial correlations in components of velocity projected on the line of sphere centers $I_{XX}(r)$ is based on the assumption that correlations appearing at the moment when product is created expand in space because the molecules of product fly apart up to the moment when one of them is transformed into S . The actual positions of product molecules are obtained from one-particle free motion propagator. The birth rate of product is calculated on the basis of kinetic theory for molecules modeled as hard spheres and the reaction cross section defined above (6). The procedure of averaging over all possible configurations of reacting molecules of A is straightforward, but tedious and it has been described in [9]. The final result is

$$c_{XX}(r) = \kappa_1 \chi_A \sigma^2 \langle a \rangle^2 \frac{1}{4\sqrt{\pi} \langle x \rangle^2} \int_0^{t_e} ds \frac{1}{s^3} e^{-2k_2 s} \int_{\frac{\sigma}{r}}^1 dz F(s, z), \quad (7)$$

$$\begin{aligned} J_{XX}(r) &= \langle \mathbf{v}_X(\mathbf{r}, t) \cdot \mathbf{v}_X(\mathbf{r}', t) \rangle \\ &= \kappa_1 \chi_A \sigma^2 \langle a \rangle^2 \frac{1}{4\sqrt{\pi}} \int_0^{t_e} ds \frac{1}{s^3} e^{-2k_2 s} \int_{\frac{\sigma}{r}}^1 dz \left[\frac{3}{2} - \frac{\left(\frac{\sigma}{r}\right)^2 + 1 - 2\frac{\sigma}{r} z}{4} \frac{r^2}{s^2} \right] F(s, z), \end{aligned} \quad (8)$$

$$\begin{aligned} I_{XX}(r) &= \left\langle \frac{(\mathbf{v}_X(\mathbf{r}, t) \cdot (\mathbf{r} - \mathbf{r}'))(\mathbf{v}_X(\mathbf{r}', t) \cdot (\mathbf{r} - \mathbf{r}'))}{(\mathbf{r} - \mathbf{r}')^2} \right\rangle \\ &= \kappa_1 \chi_A \sigma^2 n_A^2 \frac{1}{4\sqrt{\pi}} \int_0^{t_e} ds \frac{1}{s^3} e^{-2k_2 s} \int_{\frac{\sigma}{r}}^1 dz \left[\frac{1}{2} - \frac{\left(\frac{\sigma}{r} z - 1\right)^2}{4} \frac{r^2}{s^2} \right] F(s, z), \end{aligned} \quad (9)$$

where

$$F(s, z) = \frac{z - \frac{\sigma}{r}}{\sqrt{\left(\frac{\sigma}{r}\right)^2 + 1 - 2\frac{\sigma}{r}z}} \exp \left[-\frac{\left(\frac{\sigma}{r}\right)^2 + 1 - 2\frac{\sigma}{r}z}{4\xi} \frac{r^2}{s^2} \right] \quad (10)$$

and t_e — the upper limit of integration over time can be estimated as the mean free time between collisions because of the assumption on the ballistic motion of molecules. In the following we calculate t_e from the formula

$$t_e = t_C = \frac{\sqrt{\pi}\sigma}{24\eta\sqrt{\frac{k_B T}{m}}}, \quad (11)$$

where η is the packing fraction.

3. Correlations in molecular dynamics simulations

The molecular dynamics (MD) simulations [10] were performed for two models of interparticle interactions: hard spheres (the diameter σ) and soft spheres surrounded by weakly interacting (the friction constant $\lambda = 0.1$) Brownian medium. The hard sphere system was simulated using the method of prerecorded trajectory [11]. The basic system contained $N_0 = 1000$ –5832 particles and the trajectory was expanded by 5 box lengths which resulted in the total number of particles involved, $N = 125000$ –729000. The soft sphere system was simulated on $N = 32768$ particles interacting via the following potential

$$u(r) = \begin{cases} 4\epsilon\left[\left(\frac{\sigma}{r}\right)^6 - 1\right]\left(\frac{\sigma}{r}\right)^{12\alpha} + u_0 & \text{for } r \leq R_c\sigma \\ 0 & \text{for } r > R_c\sigma \end{cases} \quad (12)$$

The cut-off distance, R_c , was adjusted such that the derivative of $u(r)$ is 0 at $r/s = R_c$. Simulations were performed for $\alpha = 1$ (weak potential) and $\alpha = 2$ (strong potential). The two values of α enabled us to test consistency of the obtained results. An increase of α should make the results closer to that of the hard sphere system. The presence of the Brownian medium has been realized by mixing the standard Verlet leapfrog method of solving second order differential equations [10] with the Euler–Maruyama approximation for the stochastic term [12]. As a result one obtains the following procedure that has been used to simulate time evolution of the coordinates of the i -th soft sphere

$$\mathbf{v}_i\left(t + \frac{\Delta t}{2}\right) = \mathbf{v}_i\left(t - \frac{\Delta t}{2}\right) - \frac{\Delta t}{m} \left(\sum_{j=1}^N \frac{\partial u(\mathbf{r}_{ij})}{\partial \mathbf{r}_{ij}} + \lambda \mathbf{v}_i(t) \right) + \bar{\boldsymbol{\theta}}_i \sqrt{\frac{2\lambda k_B T \Delta t}{m}}, \quad (13)$$

$$\mathbf{r}_i(t + \Delta t) = \mathbf{r}_i(t) + \mathbf{v}_i\left(t + \frac{\Delta t}{2}\right) \Delta t, \quad (14)$$

where

$$\mathbf{v}_i(t) = \left(\mathbf{v}_i \left(t - \frac{\Delta t}{2} \right) + \mathbf{v}_i \left(t + \frac{\Delta t}{2} \right) \right) / 2 \quad (15)$$

$\mathbf{r}_{ij} = \mathbf{r}_i - \mathbf{r}_j$, Δt is the time step and $\bar{\boldsymbol{\theta}}_i$ is a three dimensional random variable normally distributed (variance equal to 1).

The parameters of reaction cross sections were selected such that $\langle x \rangle$ was small ($\sim 3\%$) for all the considered systems which satisfies the assumptions of theory. For both hard and soft spheres we considered two kinds of systems: the low-density system ($N/V = 0.04545$, $\kappa_1 = 0.025$, $\xi = 0.8$, $k_2 = 0.0716$, $t_C = 3.1$), and the high-density one ($N/V = 0.2441$, $\kappa_1 = 0.1$, $\xi = 0.6$, $k_2 = 1.396$, $t_C = 0.57$). The values of parameters are given in the reduced units [10]. The correlation functions c_{XX} , J_{XX} and I_{XX} were measured directly during a simulation run.

The results obtained from the simulations are compared with those calculated from (7)–(9) in figures 1–3. The double integration in (7)–(9) has been performed numerically. Both integrals were calculated using the Gauss–Legendre quadrature with a few hundred nodes. It has been checked that the accuracy of such numerical integration is sufficient. The figure notation is such that the letter (a) marks results for a low density system and the letter (b) corresponds to a high density ones. In all figures the thin line with symbols represents results of calculations and the thick lines show correlations measured in simulations (the solid line — for hard spheres, the short and long dashed correspond to hard and soft potentials, respectively). The comparison clearly shows that for all considered cases the theory agrees quite well with the numerical experiments. One should especially emphasize the successful prediction of the correlations in velocities (J_{XX} and I_{XX} in Figs. 2 and 3), because these correlations cannot be obtained from the standard master equation formalism. In all figures the largest differences between simulations for soft spheres and the theory are observed at short distances. The differences come from the fact that formulae (7)–(9) are derived for hard spheres which interact only at collisions and their velocities between collisions do not change. In the case of a soft potential the kinetic energy of interacting molecules decreases at short distances because the potential energy is positive. Therefore, because of slow relative motion, the correlations at short distances are increased with respect to the theoretical predictions. Of course, the agreement between theory and simulations performed for hard spheres is very good.

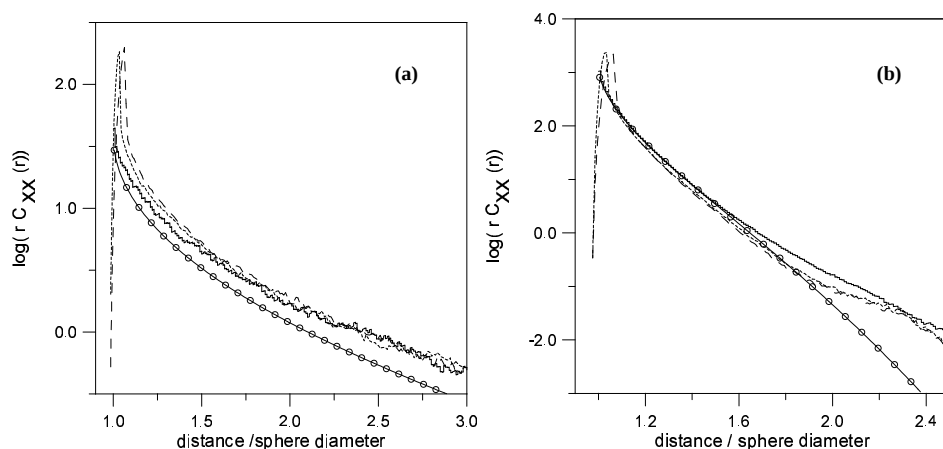


Fig. 1. The nonequilibrium spatial correlations, $c_{XX}(r)$, as a function of the interparticle distance for (a) the low and (b) the high density system. The thick solid line — the hard spheres, the short dashed line — the soft spheres and the strong potential, the long dashed line — the soft spheres and the weak potential, the solid line with circles — the theoretical result.

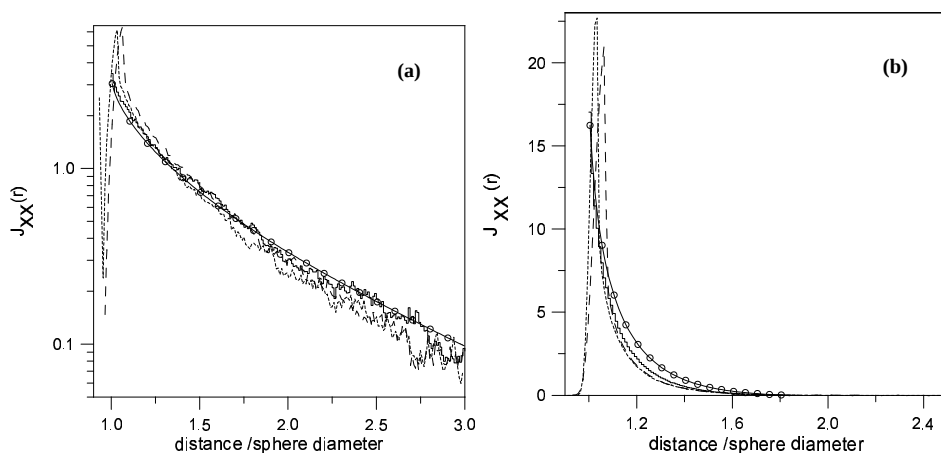


Fig. 2. The velocity-velocity correlation function, $J_{XX}(r)$, as a function of the interparticle distance for (a) the low and (b) the high density system. Notations as in Fig. 1.

The comparison between Fig. 1(a) and 1(b) shows that, for low r , the theory describes the spatial correlations for the high-density system (Fig. 1(b)) more accurately than for the low density one (Fig. 1(a)). The reason is that for the high density system k_2 is sufficiently large to believe that the assumption on molecules of X disappearing during a free flight is satisfied

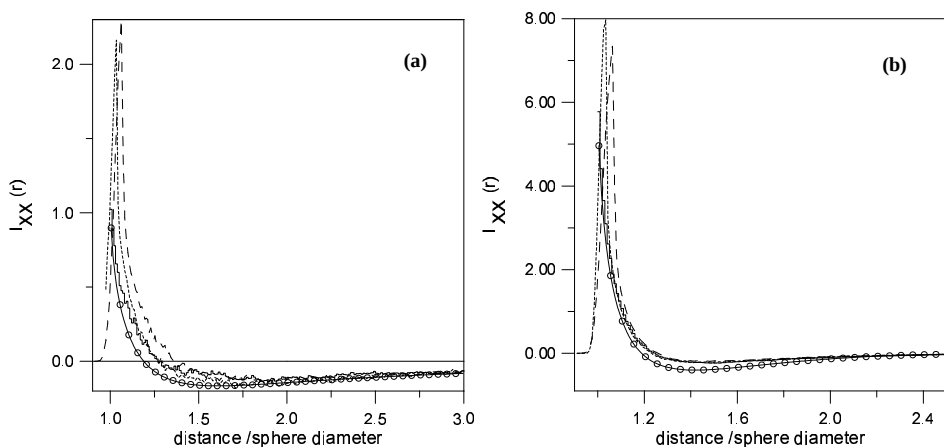


Fig. 3. The radial velocity–radial velocity correlation function, $I_{XX}(r)$, as a function of the interparticle distance for (a) the low and (b) the high density system. Notations as in Fig. 1.

($t_C k_2 \sim 0.8$), whereas for the low density system this value is too small ($t_C k_2 \sim 0.22$). As a result, for the low-density system, the diffusive motion of product is not negligible, which disagrees with the assumption of the theory. The influence of this restriction of the theory is clearly seen in Fig. 4 which compares $c_{XX}(r)$ obtained from the hard sphere simulations in a high density system and the theory for two cases corresponding to different κ_1 and k_2 . In these cases κ_1 and k_2 are scaled such that the concentration of product remains the same (~ 0.03) and $t_C k_2$ are equal to 1.6 and 0.27, respectively. The remaining parameters of the two systems are the same as for the high-density system. It is clearly seen that for a smaller k_2 the consistency between theory and simulations becomes worse.

The rigorous fulfillment of the assumptions requires $t_C k_2$ to be around one (or higher). However, for a typical reaction this quantity is many times lower. Therefore, the role of diffusive processes in creation of spatial correlations can not be usually neglected. However, even if the molecules diffuse, the presented formulae (7)–(9) can be applied to estimate the contribution to the correlation functions coming from the ballistic motion. At short distances this contribution may be dominant even if $t_C k_2$ is much lower than 1. This is seen by comparing amplitudes of $c_{XX}(r)$ at $r = \sigma$ obtained from (4) and (6) for low-density and high-density systems considered above. The values resulting from the ballistic theory are about 30 (for the high-density) and 200 (for the low-density) times higher than those evaluated from the diffusive theory (4). Therefore, one may expect that the theory based on the assumption that the motion of molecules is ballistic gives the right strength

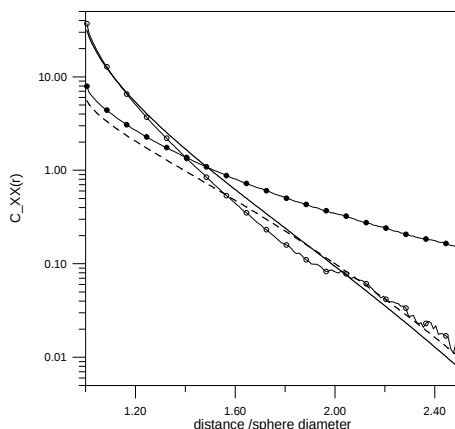


Fig. 4. The nonequilibrium spatial correlation function, $c_{XX}(r)$, as a function of the interparticle distance for two different values of k_2 . The thick solid line and the line with empty circles correspond to simulations and theory for $k_2 = 2.8$, respectively. The results of simulations and theory for $k_2 = 0.3$ are shown by the thick dashed line and the line with filled circles, respectively.

of correlations at short distances also when the quantity $t_C k_2$ is orders of magnitude smaller than 1.

4. Conclusions

We have demonstrated that the presented theory of nonequilibrium correlations created by a chemical reaction correctly describes the results of computer experiments for extremely fast reactions when the lifetime of product molecules is of the order of the mean free time between collisions. In a general case the developed theory gives the contribution to the correlation functions which comes from the ballistic motion of molecules. This contribution is neglected by the standard theory based on the master equation for a reaction-diffusion system, but it seems dominant at short distances even if reactions are slow. It would be important to match both approaches together and we hope to present some results on this subject in near future.

This work was partially supported by the grant 5P03B 139 20 provided by the Polish State Committee for Scientific Research (KBN).

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