Analysis of Models of Single-File Diffusion

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Abstract. Theoretical models of single-file transport in a homogeneous channel are considered. Three levels of channel populations were specified for which different approximations could be used. The results of these approximations are in good agreement with the results of a computer experiment (Aityan and Portnov 1986). At low populations, the pair correlation functions were negligibly small and allowed the use of linear approximation for unidirectional fluxes and populations. The value of the pair correlation function and the respective approximation for fluxes was obtained by the two-particles random-walk technique. At extremely high populations, the "divider" technique was proposed to describe the single-file transport. The divider technique allowed to explain the exponential shape of the pair correlation function $F^{AB}_{n,n+1}$ profile at extremely high populations. At medium populations the finite difference superposition approximation was valid.

Key words: Single-file transport — Unidirectional fluxes — Pair correlation function — Random-walk divider technique — Superposition approximation — Finite-difference equation

Introduction

In preceeding papers (Kohler and Heckmann 1980; Chizmadzhev and Aityan 1982; Aityan 1985) the theory of single-file diffusion has been developed. These studies essentially considered equations for the functions of channel population Θ (unary functions), including the pair correlation functions (in absence of long-range interactions), in order to allow for correlations of occupation of a single-file channel. Superposition approximation was used to close the equations. The superposition approximation is the most frequent approach used to solve various body problems. Usually, it is supposed to agree with the exact solution when interactions between particles are small (i.e. at low channel populations). However, as shown by a computer experiment (Aityan and Portnov 1986), the developed theory correctly describes the behaviour of the system even in superposition approximation in general. This approximation is valid only at low and medium population. At very high channel populations the superposition approximation works only qualitatively; it does not account for the flattening of the profiles of the pair correlation functions $F^{AB}_{n,n+1}$ describing probabilities of simultaneous occupation of the n-th well by particle A, and the $(n+1)$-th well by particle B, as observed in the computer experiment. Either at low channel populations the superposition approximation is not quite correct to describe the pair correlation function $F^{AB}_{n,n+1}$, but the expressions for unidirectional fluxes turned out to be correct owing to the negligible smalness of these correlation functions (Aityan and Portnov 1986). In the present paper we wish to propose methods to calculate unidirectonal fluxes, populations and pair correlation function $F^{AB}_{n,n+1}$ for small, high and medium populations.

1. The physics of the process

In order to distinguish the main features of the single-file nature of transport, we shall use the following model proposed by Aityan and Chizmadzhev (1981) and Aityan (1985). We shall suppose that the channel represents a successive set of equipotential wells separated by equipotential barriers. No more than one particle can be present in each well at a time. Particles are assumed to be noninteracting (i.e. the only interaction here is the forbiddingness of the coexistence of two and more particles in one well). We also supposed that the jump of particles from one well into the adjacent vacant well is determined by the rates (time probability densities) of jump $\nu_{\rightarrow}$ (from left to right) and $\nu_{\leftarrow}$ (from right to left). The difference between $\nu_{\rightarrow}$ and $\nu_{\leftarrow}$ in a homogeneous channel, i.e. in a channel in which all wells are alike, physically means the existence of an external field making the particles move predominantly in one direction. Furthemore, we assume that the bath to left of the channel contains particles of type A while the bath to the right of the channel contains particles of type B, each bath containing particles of only one type. The concentration of particles A in left solution will be denoted C_A, and that of particles B in the right solution C_B.

The passage of particles from the solution into the channel and backwards will be described by in-rates constants (k_{1A} and k_{1B}) and out-rates constants (k_{2A} and k_{2B}). We use formally different constants k_{1A}, k_{1B}, k_{2A}, k_{2B} so that the results shown in this section for ions can be used for holes in the high population case. The jump rate of a particle from solution into a vacant edge well will be $k_{1A}\,C_A$ and $k_{1B}\,C_B$ for the first and L-th well respectively, where L is the number of the right boundary well. The rates of passage of particles from the occupied boundary (1 and L) wells of the channel into the solution are k_{2A} and k_{2B}, respectively.

To study the most characteristic features of single-file transport in the framework of this model, the problem of calculation of unidirectional fluxes is of particular interest. Let us assume that the particles in both the right and the left solution have the same kinetic properties (particles A in the left bath (solution) against particles B in the right bath (solution)). Supposing that there is a rapid mixing in the solutions, and the volumes of these solutions are large enough, then the channel will be in contact with particles B at its right edge and with particles A at the left one. Then the number of particles B passing per unit time to the left solution through the channel will be termed unidirectional flux j_B. Similarly, unidirectional flux j_A is defined as the number of particles A passing per unit time to the right solution. Obviously, the total particle flux j (the axis is directed from left to right, i.e. from A to B) is

$$j = j_A - j_B \tag{1}$$

We shall consider the case with no external field ($\nu_+ = \nu_- = \nu$). Let us present the general results obtained by Aityan (1985) for single-file diffusion of noninteracting particles in a discrete scheme. As has been shown by Aityan and Chizmadzhev (1981), Chizmadzhev and Aityan (1982), and Aityan (1985), the expressions for unidirectional fluxes contain the pair correlation functions. A jump between two adjacent wells within the channel can occur under the condition that one will is occupied and the other one is free:

$$j_A = \nu(F^{AO}_{n,n+1} - F^{OA}_{n,n+1}) \tag{2a}$$

where $F^{AO}_{n,n+1}$ ($F^{OA}_{n,n+1}$) is the probability that the n-th well is occupied by particle A and the $(n+1)$-th well is vacant (or vice versa).

Similarly, for j_B we obtain (the direction of j_B is opposite to that of j_A):

$$j_B = \nu(F^{OB}_{n,n+1} - F^{BO}_{n,n+1}) \tag{2b}$$

$F^{OB}_{n,n+1}$, $F^{BO}_{n,n+1}$ are defined similarly to $F^{OA}_{n,n+1}$, $F^{AO}_{n,n+1}$. For the total flux we have:

$$j = \nu(F^{10}_{n,n+1} - F^{01}_{n,n+1}) = j_A - j_B \tag{3}$$

where $F^{10}_{n,n+1}$ (the pair correlation function) is the probability that the n-th well is occupied by any particle and the $(n+1)$-th well is vacant. $F^{01}_{n,n+1}$ is defined similarly.

Obviously, in the steady-state case the fluxes (2) and (3) are independent of the well number n.

For fluxes calculated at the boundary of the channel we obtain:

$$\begin{aligned} j_A &= k_{1A}C_A\Theta^0_1 - k_{2A}\Theta^A_1 = k_{2B}\Theta^A_L\,, \\ j_B &= k_{2A}\Theta^B_1 = k_{1B}C_B\Theta^0_L - k_{2B}\Theta^B_L\,, \end{aligned} \tag{4}$$

where Θ^0_n, Θ^A_n, Θ^B_n (unary correlation functions) are the probabilities that the n-th well is vacant, occupied by a particle A or occuried by particle B, respectively. The unary functions Θ_n^A, Θ_n^B are also called populations. The correlation functions satisfy the normalization conditions:

$$\Theta_n^O + \Theta_n^A + \Theta_n^B = 1, \tag{5}$$

$$F_{n,n+1}^{AO} + F_{n,n+1}^{AB} + F_{n,n+1}^{AA} = \Theta_n^A, \tag{6a}$$

$$F_{n,n+1}^{BO} + F_{n,n+1}^{BB} + F_{n,n+1}^{BA} = \Theta_n^B, \tag{6b}$$

$$F_{n,n+1}^{OO} + F_{n,n+1}^{OB} + F_{n,n+1}^{OA} = \Theta_n^0, \tag{6c}$$

$$F_{n,n+1}^{OA} + F_{n,n+1}^{BA} + F_{n,n+1}^{AA} = \Theta_{n+1}^A, \tag{6d}$$

$$F_{n,n+1}^{OB} + F_{n,n+1}^{BB} + F_{n,n+1}^{AB} = \Theta_{n+1}^B, \tag{6e}$$

$$F_{n,n+1}^{OO} + F_{n,n+1}^{BO} + F_{n,n+1}^{AO} = \Theta_{n+1}^O, \tag{6f}$$

By virtue of Eq. (5) we use the function

$$\Theta_n \equiv 1 - \Theta_n^0 = \Theta_n^A + \Theta_n^B, \tag{7}$$

where Θ_n is the probability that the n-th well is occupied by any particle. Particle A cannot be located to the right of particle B because of the single-file character of diffusion within the channel. Therefore

$$F_{n,n+1}^{BA} \equiv 0. \tag{8}$$

Using Eqs. (2), (6), and (8) we get:

$$\begin{aligned} \frac{1}{v} j_A &= \Theta_n^A - \Theta_{n+1}^A - F_{n,n+1}^{AB}, \\ \frac{1}{v} j_B &= \Theta_{n+1}^B - \Theta_n^B - F_{n,n+1}^{AB}, \\ \frac{1}{v} j &= \Theta_n - \Theta_{n+1} \end{aligned} \tag{9}$$

Eqs. (9) show that the total flux under the conditions of single-file diffusion in absence of any field is exactly the same as in the case of ordinary diffusion (Aityan 1985). The expression for the unidirectional fluxes differs from the usual diffusion by the term $F_{n,n+1}^{AB}$.

With the known relationships between the correlation function $F_{n,n+1}^{AB}$ and Θ_n^A, Θ_n^B, we can find j_A and j_B by solving equations for $\Theta_n^{A,B}$ and $F_{n,n+1}^{AB}$ (9), where $F_{n,n+1}^{AB}$ is a known function of Θ_n^A and Θ_n^B.

Now let us consider some special cases when the set of finite-differences equations (4), (9) can be easily solved.

2. Low populations

At low populations

$$\Theta_n \ll 1/L \tag{10}$$

the probability of the occurrence of more than one particle within the channel is low; the correlation function $F^{AB}_{n,n+1}$ in Eqs. (9) can be thus neglected, and the single-file transport is determined by free diffusion. The profiles of populations Θ^A_n and Θ^B_n, obtained from Eqs. (4) and (9) for the case of low populations are described by the linear expressions:

$$\begin{aligned} \Theta^A_n &= \frac{\left(1 + \frac{L-n}{\nu} k_{2B}\right) k_{1A} C_A}{k_{2A} + k_{2B} + \frac{L-1}{\nu} k_{2A} k_{2B}}, \\ \Theta^B_n &= \frac{\left(1 + \frac{n-1}{\nu} k_{2A}\right) k_{1B} C_B}{k_{2A} + k_{2B} + \frac{L-1}{\nu} k_{2A} k_{2B}}. \end{aligned} \tag{11}$$

For the case of a "rapid" exchange at the boundary

$$k_{2A}, k_{2B}, k_{1A} C_A, k_{1B} C_B \gg \nu, \tag{12}$$

expressions (11) become

$$\Theta^A_n = \frac{L-n}{L-1} \frac{k_{1A} C_A}{k_{2A}}, \quad \Theta^B_n = \frac{n-1}{L-1} \frac{k_{1B} C_B}{k_{2B}}. \tag{13}$$

For the unidirectional fluxes in the general case we have:

$$\begin{aligned} j_A &= \frac{k_{1A} C_A / k_{2A}}{k_{2A}^{-1} + k_{2B}^{-1} + (L-1)\nu^{-1}}, \\ j_B &= \frac{k_{1B} C_B / k_{2B}}{k_{2A}^{-1} + k_{2B}^{-1} + (L-1)\nu^{-1}}, \\ j &= \frac{k_{1A} C_A / k_{2A} - k_{1B} C_B / k_{2B}}{k_{2A}^{-1} + k_{2B}^{-1} + (L-1)\nu^{-1}} \end{aligned} \tag{14}$$

Thus, the fluxes are expressed in a form similar to the Ohm law (as it should be for the linear case); the role of the resistance is played by inverse values of the

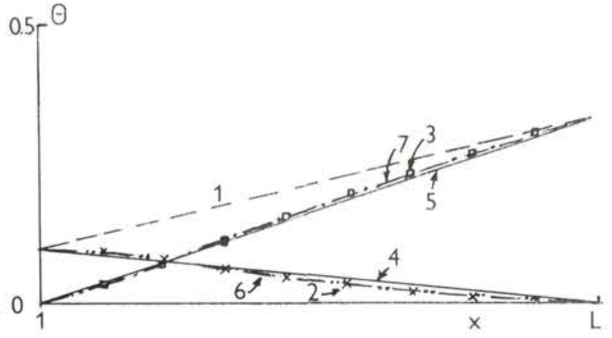

Fig. 1. Population profiles at $\Theta_l^A = 0.0909$, $\Theta_l^B = 0.3333$ (low populations): (1) — Θ_n, (2) — Θ_n^A, computer experiment, (3) — Θ_n^B, computer experiment, (4) — Θ_n^A, linear approximation, (5) — Θ_n^B, linear approximation (6) — Θ_n^A, superposition approximation, (7) — Θ_n^B, superposition approximation; $L = 10$.

reaction rates. The validity of results (13), (14) was checked by a computer experiment, described by Aityan and Portnov (1986). Expression (13) turns out to be valid for population profiles over a considerably large range of conditions at the boundary (see Fig. 1). Fig. 1 shows that even for not small populations ($\Theta_l^A = 0.09$, $\Theta_L^B = 0.33$) the linear approximation plots for Θ_n^A (curve 4) and Θ_n^B (curve 5) practically coincide with the computer experiment (points: $2 - \Theta_n^A$; $3 - \Theta_n^B$). Total populations Θ are calculated accurately, their profile is always linear (curve 1).

3. The pair correlation function $F_{n,n+1}^{AB}$ at low populations

In zero approximation at low populations the pair correlation functions are negligibly small. Let us take the following approximation. Consider a pair correlation function $F_{m,n}^{AB}$ which is the probability of both the m-th and n-th well to be occupied by particle A and B respectively. Under the condition that there can be no more than two particles in the channel at a time we can write for this function the kinetic equations:

$$\frac{d}{dt} F_{m,n}^{AB} = \nu[F_{m+1,n}^{AB} + F_{m-1,n}^{AB} + F_{m,n+1}^{AB} + F_{m,n-1}^{AB} - 4F_{m,n}^{AB}] \quad (15)$$

for

$$1 < m < n - 1 < L - 1$$

For the functions $F^{AB}_{m,m+1}$, corresponding to neighbouring particles, the equations take the form (the single-file condition is taken into account):

$$\frac{d}{dt}F^{AB}_{m,m+1} = \nu[F^{AB}_{m-1,m+1} + F^{AB}_{m,m+2} - 2F^{AB}_{m,m+1}] \tag{16}$$

for

$$1 < m < L - 1$$

The boundary conditions make the remaining equations take the form:

$$\frac{d}{dt}F^{AB}_{1,n} = k_{1A}C_A\Theta^B_n + \nu(F^{AB}_{1,n-1} + F^{AB}_{1,n+1} + F^{AB}_{2,n}) - (3\nu + k_{2A})F^{AB}_{1,n} \tag{17}$$

at $2 < n < L$;

$$\frac{d}{dt}F^{AB}_{m,L} = k_{1B}C_B\Theta^A_m + \nu(F^{AB}_{m+1,L} + F^{AB}_{m-1,L} + F^{AB}_{m,L-1}) - (3\nu + k_{2B})F^{AB}_{m,L} \tag{18}$$

at $1 < m < L-1$;

$$\frac{d}{dt}F^{AB}_{1,L} = k_{1B}C_B\Theta^A_1 + k_{1A}C_A\Theta^B_L + \nu(F^{AB}_{1,L-1} + F^{AB}_{2,L}) - (2\nu + k_{2A} + k_{2B})F^{AB}_{1,L}; \tag{19}$$

$$\left.\begin{aligned} \frac{d}{dt}F^{AB}_{1,2} &= k_{1A}C_A\Theta^B_2 + \nu F^{AB}_{1,3} - (\nu + k_{2A})F^{AB}_{1,2} \\ \frac{d}{dt}F^{AB}_{L-1,L} &= k_{1B}C_B\Theta^A_{L-1} + \nu F^{AB}_{L-2,L} - (\nu + k_{2B})F^{AB}_{L-1,L} \end{aligned}\right\} \tag{20}$$

Naturally, these equations generalize the random-walk kinetics for one particle to the case of two particles random walk. At the same time equations (17)—(20) allow for the fact that the two-particles state can be constructed only from the one-particle state. Since equation (15) is homogeneous it is natural to try to solve it in the form of linear combination of functions

$$F^{AB}_{m,n} \sim \xi^m \eta^n \tag{21}$$

However, by substituting (21) into (15) and (16) we get two similar values for each constant (ξ and η)

$$\xi_{1,2} = \eta_{1,2} = 1 \tag{22}$$

The theory of linear finite-difference equations shows that in this case (when the proper values of equations are equal) the solution must be linear for both m and n. In the general case it is rather awkward but it principally does not cause

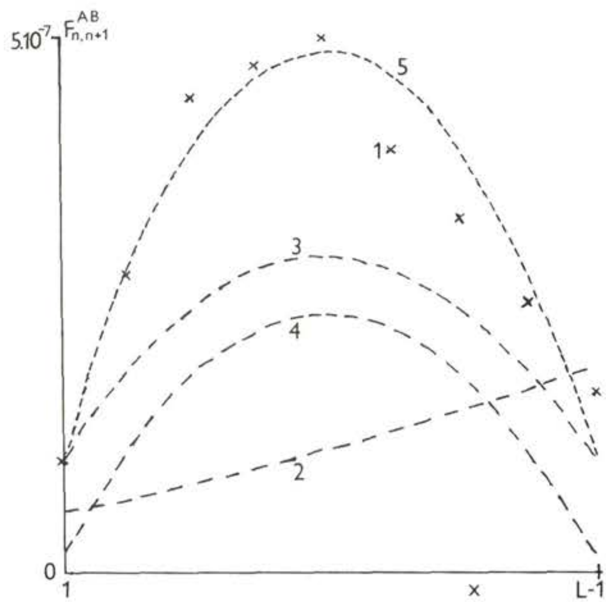

Fig. 2. Profile of the pair correlation function $F^{AB}_{n,n+1}$ for extremely low populations. $\Theta^{A}_{1} = 0.001$, $\Theta^{B}_{L} = 0.002$; (1) — computer experiment, (2) — the divider method approximation, (3) — "discrete" superposition approximation (the present study), (4) — "continuous" superposition approximation (Aityan 1984), (5) — $F^{AB}_{n,n+1}$, calculated by the random-walk method. $L = 10$.

difficulties. We consider the case of "rapid" boundaries (12) studied by Aityan and Portnov (1986); the boundary conditions in this case are slightly different from the above analysed boundary conditions (17)—(20). Condition (12) provides the independence of the boundary wells population

$$F^{AB}_{1,n} = \Theta^{A}_{1}\Theta^{B}_{n},\ F^{AB}_{m,L} = \Theta^{A}_{m}\Theta^{B}_{L} \tag{23}$$

and this must be used as boundary conditions instead of (17)—(20). Finally, solving the system (15), (16), (23), we get:

$$F^{AB}_{m,n} = \frac{\Theta^{A}_{1}\Theta^{B}_{L}}{L-1}\left[\frac{2(m-1)(L-n)}{L-2} + n - m\right] \tag{24}$$

and

$$F^{AB}_{n,n+1} = \frac{\Theta^{A}_{1}\Theta^{B}_{L}}{(L-1)(L-2)}[2(n-1)(L-n-1) + L - 2] \tag{25}$$

At a sufficient channel length we have:

$$F^{AB}_{n,n+1} \approx 2\Theta^{A}_{n}\Theta^{B}_{n} \tag{26}$$

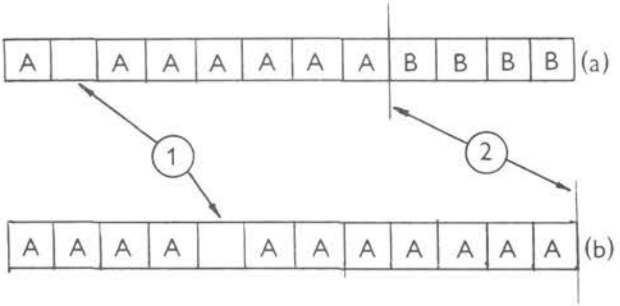

Fig. 3. Channel populations at high boundary wells populations. (1) — "hole", (2) — "divider". a) — divider within the channel, b) — divider at the channel boundary.

The estimated correlation function is in good agreement with the results of the computer experiment (Aityan and Portnov (1986)). Fig. 2 shows that expression (25) (curve 5) is on quantitative agreement with the computer experiment (crosses) while the superposition approximation (Aityan 1985) (curves 3 and 4) gives only qualitative agreement. The spread of the points is considerable because of negligible probability of the AB pair formation. The number of iterations in the computer experiment is shown in Table.

With the help of the results obtained we can calculate the first non-linear component in unidirectional fluxes:

$$j_A = \frac{v\Theta_1^A}{L-1}\left(1 - \frac{L+6}{3}\Theta_1^B\right) \tag{27}$$

Expression (27) shows that at low populations the deviation from linearity is about two times larger than it follows from the superposition approximation of the pair correlation function $F_{n,n+1}^{AB}$ (Aityan 1985). The results for fluxes are in agreement with those of the computer experiment as well (see Table, lines 1—6, 18, 19, 23).

4. Extremely high populations

Now consider the case of an extremely high population. In this case almost the whole of the channel will be occupied (Fig. 3) and the transport process will be determined by the motion of holes. We consider a case with the concentrations in the solutions being so high that the probability of the occurrence of more than one hole within the channel excluding the utmost wells is negligibly small. This is observed on the condition that

$$\Theta_n^0 = 1 - \Theta_n \ll 1/L \tag{28}$$

Table. Logarithm of unidirectional flux (-ln (j_A))

N	L	A / 1	B / L	Linear approximation	Divider method	Superposition "discrete" approximation	Superposition "continous" approximation	Computer "experiment"	Interactions number (mln) comp. exper.
1	2	3	4	5	6	7	8	9	10
1.	10	0.00100	0.00100	9.10498	9.68440	9.10702	9.21200	9.10328	1.0
2.	10	0.00100	0.00200	9.10498	12.92084	9.10906	9.21368	9.12747	4.0
3.	10	0.00990	0.00990	6.81234	7.42753	6.83268	6.93440	6.84830	0.6
4.	10	0.09090	0.09090	4.59512	5.51141	4.79523	4.85924	4.90236	1.0
5.	10	0.09090	0.16666	4.59512	8.74284	4.99300	5.00770	5.17342	1.0
6.	10	0.09090	0.33333	4.59512	14.40909	5.56296	5.39080	5.98493	0.5
7.	10	0.23076	0.23076	3.66356	5.03587	4.24600	4.20236	4.42817	0.5
8.	10	0.33333	0.50000	3.29583	8.34963	5.19961	4.55106	5.42227	0.5
9.	10	0.50000	0.50000	2.89037	5.08759	4.67928	4.08079	4.60953	0.6
10.	10	0.50000	0.60000	2.89037	6.92103	5.71095	4.44429	5.43926	1.0
11.	10	0.50000	0.70588	2.89037	9.68340	7.22360	4.89070	6.62187	1.0
12.	10	0.50000	0.83333	2.89037	14.59564	9.56061	5.48883	9.69032	0.5
13.	10	0.85714	0.88235	2.35137	7.15583	13.15944	4.84708	6.72491	0.5
14.	10	0.99010	0.99010	2.20717	8.79207	16.24002	5.52315	8.74868	10.0
15.	10	0.99850	0.99900	2.19872	12.67542	19.52741	5.05130	12.50719	0.5
16.	10	0.99875	0.99900	2.19847	11.88068	19.52715	5.04973	12.02042	2.5
17.	10	0.99900	0.99900	2.19822	11.08341	15.72024	5.04313	11.08342	8.5
18.	15	0.00100	0.00100	9.54681	10.17237	9.54967	9.61831	0.53926	2.5
19.	15	0.00200	0.00300	8.85366	12.73003	8.86227	8.93018	8.82046	0.5
20.	15	0.23076	0.23076	4.10539	5.81015	4.98164	4.36602	5.18075	1.0
21.	15	0.75000	0.75000	2.92674	6.57182	10.28105	6.23218	5.83737	1.8
22.	15	0.99010	0.99010	2.64900	9.75256	19.97770	7.45232	9.71369	4.0
23.	7	0.00990	0.00990	6.40687	6.94337	6.42239	6.57283	6.42972	1.0
24.	7	0.50000	0.50000	2.48490	4.27666	3.70830	3.33230	3.85604	1.0
25.	7	0.66666	0.83333	2.19722	7.35203	6.57883	3.75277	6.00706	1.0
26.	7	0.75000	0.75000	2.07944	4.76502	4.86228	3.38572	4.49717	1.0
27.	7	0.90909	0.90909	1.88707	5.69373	7.40703	3.46407	5.79315	1.0
28.	7	0.99900	0.99900	1.79275	10.16726	17.17724	3.58885	10.18957	1.0

The interface between particle A and B within the channel (we shall call it the divider) can be shifted by one well to the right (to the left) under the condition that a hole should pass trough the channel from right to left (from left to right). For particle A, the jump from the L-th well into the solution (unidirectional flux), is equivalent to a hole entering the channel from the right side. If subsequently this hole leaves the channel in opposite direction into the right solution, then the L-th well would be occupied by a particle B. We shall obtain quite analogous results if we consider particle B presents in the first well. The following notation will be used hereafter: Z_A-the number of holes that entered the channel from the left bath per unit time; there of: Z_A^+-those that have left the channel to the right, Z_A^--those that have left the channel to the left. Z_B-the number of holes that have entered the channel from the right bath per unit time; there of: Z_B^+-those that left the channel to the left, Z_B^--those that have left the channel to the right.

If we denote p_n the probability that the divider is located between the n-th and $(n+1)$-th well, and p_0 (p_L) is the probability that the channel is free of particles A, (B) i. e. the divider is located on the right boundary, then the motion of the divider will be described by the following equations:

$$\begin{gathered}\frac{d}{dt}p_n = Z_B^+ p_{n-1} + Z_A^+ p_{n+1} - (Z_A^+ + Z_B^+)p_n, \quad 1 < n < L-1; \\ \frac{d}{dt}p_1 = (Z_A^- + Z_B^+)p_0 + Z_A^+ p_2 - (Z_A^+ + Z_B^+)p_1; \\ \frac{d}{dt}p_{L-1} = (Z_B^- + Z_A^+)p_L + Z_B^+ p_{L-2} - (Z_A^+ + Z_B^+)p_{L-1}; \\ \frac{d}{dt}p_0 = Z_A^+ p_1 - (Z_A^- + Z_B^+)p_0; \quad \frac{d}{dt}p_L = Z_B^+ p_{L-1} - (Z_B^- + Z_A^+)p_L.\end{gathered} \tag{29}$$

Note that in approximation (28)

$$F_{n,n+1}^{AB} = p_n \tag{30}$$

This description does not consider fluctuations of the divider position in the process of Brownian motion of holes within the channel. The duration time of hole wandering in the channel as compared to the time interval between two subsequent entrances of a hole into the channel may become the criterion of the approximation validity.

We would like to stress the interesting specific features of equations (29) for $\frac{dp_1}{dt}$ and $\frac{dp_{L-1}}{dt}$. The equations for $\frac{dp_1}{dt}$ and $\frac{dp_{L-1}}{dt}$ have, in comparison with equations for $\frac{\mathrm{d}p_n}{\mathrm{d}t}$ $(1 < n < L-1)$, additional terms $Z_A^- p_0$ and $Z_B^- p_L$. The occurrence of these additional terms arises from the fact that a hole that has entered the channel, e.g., from the left bath, and has left the channel again to the left, exchanges the left boundary particles in the channel (A or B) for a particle of type A. If the divider is located inside the channel or at the right-side boundary, then its position in this case remains unchanged (the state of the channel is determined by the position of the divider and remains unchanged as well). If the divider was located at the leftside boundary then in this case B in the first well is exchanged for a particle A, which shifts the divider by one position to the right.

Complementing the set of equations (29) with the normalization condition

$$\sum_{n=0}^{L} p_n = 1 \tag{31}$$

for the steady-state case we obtain a closed system of linear equations with constant coefficients, the solution to which is:

$$p_0 = \frac{Z_B^+}{Z_A^- + Z_B^-}\gamma;\; p_L = \frac{Z_A^+}{Z_B^- + Z_A^+}\gamma (Z_B^+/Z_A^+)^L; \tag{32}$$

$$p_n = \gamma (Z_B^+/Z_A^+)^n, \tag{33}$$

where

$$\gamma^{-1} = \frac{Z_B^+}{Z_A^- + Z_B^+} + \frac{Z_A^+}{Z_B^- + Z_A^+}\left(\frac{Z_B^+}{Z_A^+}\right)^L + \frac{\frac{Z_B^+}{Z_A^+} - \left(\frac{Z_B^+}{Z_A^+}\right)^L}{1 - \frac{Z_B^+}{Z_A^+}}. \tag{34}$$

The unidirectional fluxes are:

$$\begin{aligned} j_A &= Z_B p_L \equiv (Z_B^+ + Z_B^-) p_L, \\ j_B &= Z_A p_0 \equiv (Z_A^+ + Z_A^-) p_0. \end{aligned} \tag{35}$$

The argumentation reported herein does not consider the character of motion of the holes: expressions (32)—(35) are thus valid for any arbitrary energy profile of the channel, and for external field and long-range particle interactions. The above consideration indicate that at high population, the calculation of unidirectional fluxes may be reduced to the calculation of values of Z. These values for unidirectional fluxes of holes are easy to calculate for homogenous channels (i.e. when the channel characteristics are determined by the channel length and boundary conditions) without any field. The motion of holes is quite similar to that of particles with the transition constants and correlation functions (in expression (3)) being replaced:

$$\begin{gathered} k_{1A}C_A \to k_{2A}, \quad k_{1B}C_B \to k_{2B}, \\ k_{2A} \quad \to k_{1A}C_A, \ k_{2B} \quad \to k_{1B}C_B, \\ \Theta \to 1 - \Theta, \\ F^{01}_{n,n+1} \to F^{10}_{n,n+1}, \ F^{10}_{n,n+1} \to F^{01}_{n,n+1} \end{gathered} \tag{36}$$

ζ^A_n and ζ^B_n denote the probabilities of the occurrence in the n-th well of holes that come from the left and the right solution, respectively. Considering that by virtue of (28) the nonlinear terms can be neglected, we get:

$$\begin{aligned} Z^+_A &= k_{1B}C_B\zeta^A_L, \quad Z^-_A = k_{1A}C_A\zeta^A_1, \quad Z_A = k_{2A}, \\ Z^+_B &= k_{1A}C_A\zeta^B_1, \quad Z^-_B = k_{1B}C_B\zeta^B_L, \quad Z_B = k_{2B}. \end{aligned} \tag{37}$$

and

$$\begin{aligned} \zeta^A_n - \zeta^A_{n+1} &= Z^+_A/\nu, \\ \zeta^B_{n+1} + \zeta^B_n &= Z^+_B/\nu. \end{aligned} \tag{38}$$

It is easy to see that expressions (38) are completely analogous to expressions (9) for low populations (without $F^{AB}_{n,n+1}$); all the characteristics of particle motion in (9) are replaced by respective characteristics of holes motion.

Since

$$Z_A = Z^+_A + Z^-_A, \ Z_B = Z^+_B + Z^-_B, \tag{39}$$

for $Z^\pm_A$ and $Z^\pm_B$ we have:

$$\begin{aligned} Z^+_A &= \frac{1}{\Delta}k_{1B}C_Bk_{2A}; \quad Z^-_A = \frac{k_{2A}}{\Delta}\left(k_{1A}C_A + \frac{L-1}{\nu}k_{1A}C_Ak_{1B}C_B\right); \\ Z^+_B &= \frac{1}{\Delta}k_{1A}C_Ak_{2B}; \quad Z^-_B = \frac{k_{2B}}{\Delta}\left(k_{1B}C_B + \frac{L-1}{\nu}k_{1A}C_Ak_{1B}C_B\right). \end{aligned} \tag{40}$$

where

$$\Delta = k_{1A}C_A + k_{1B}C_B + \frac{L-1}{\nu}k_{1A}C_Ak_{1B}C_B. \tag{41}$$

At the same time for Z the following relations are valid:

$$Z_A = k_{2A}, \quad Z_B = k_{2B} \tag{42}$$

$$Z_B^+/Z_A^+ = \frac{k_{1B}C_Bk_{2A}}{k_{1A}C_Ak_{2B}} \tag{43}$$

The substitution of the obtained expressions into equations (32) and (35), yields a complete solution to the problem of unidirectional fluxes at high populations. It is evident from expressions (33) and (43) that the profiles for p_n or $F^{AB}_{n,n+1}$ (which in fact are the same) appear as exponents or (when $\Theta_1^A = \Theta_L^B$) constants. Now we obtain expressions for $F^{AB}_{n,n+1}$ and j_A, j_B for the case of "rapid" boundaries (12); for this case the obtained expressions cannot be used directly as the probability of the occurrence of more than one hole in the channel cannot be neglected*. However, by virtue of (12), it is possible to single out boundary wells as special ones (they start acting as solutions). Using transformations defined by Aityan and Portnov (1986) we get a model system with a number of wells less by two than in the initial system. Theoretical results for the distribution of the divider (correlation function $F^{AB}_{n,n+1}$), corresponding to the conditions of the computer experiment, assume the form:

$$p_0, p_L \ll 1/L;$$

$$p_1 = \frac{\gamma(1-\Theta_L^B)}{(1-\Theta_1^A)(L-2)+1-\Theta_L^B}; \quad p_n = \gamma\left(\frac{1-\Theta_L^B}{1-\Theta_1^A}\right)^n, \quad 1 < n < L-1;$$

$$p_{L-1} = \frac{\gamma(1-\Theta_1^A)}{(1-\Theta_L^B)(L-2)+1-\Theta_1^A}\left(\frac{1-\Theta_L^B}{1-\Theta_1^A}\right)^{L-2};$$

$$\gamma^{-1} = \frac{1-\Theta_L^B}{(1-\Theta_1^A)(L-2)+1-\Theta_L^B} + \frac{(1-\Theta_L^B)^{L-2}/(1-\Theta_1^A)^{L-3}}{(1-\Theta_L^B)(L-2)+1-\Theta_1^A} + \tag{44}$$

$$+[1-\Theta_L^B-(1-\Theta_1^A)((1-\Theta_L^B)/(1-\Theta_1^A))^{L-2}]/(\Theta_L^B-\Theta_1^A).$$

The substitution of the expressions obtained into equations (32) and (35), yields a complete solution to the problem

$$j_A = \gamma\frac{(1-\Theta_1^A)(1-\Theta_L^B)[(1-\Theta_L^B)/(1-\Theta_1^A)]^{L-2}}{(1-\Theta_L^B)(L-2)+1-\Theta_1^A};$$

$$j_B = \gamma\frac{(1-\Theta_1^A)(1-\Theta_L^B)}{(1-\Theta_1^A)(L-2)+1-\Theta_L^B}. \tag{45}$$

where

* This is due to the fact that for the case of "rapid" boundaries the condition of relative shortness of a hole life in a channel is not valid.

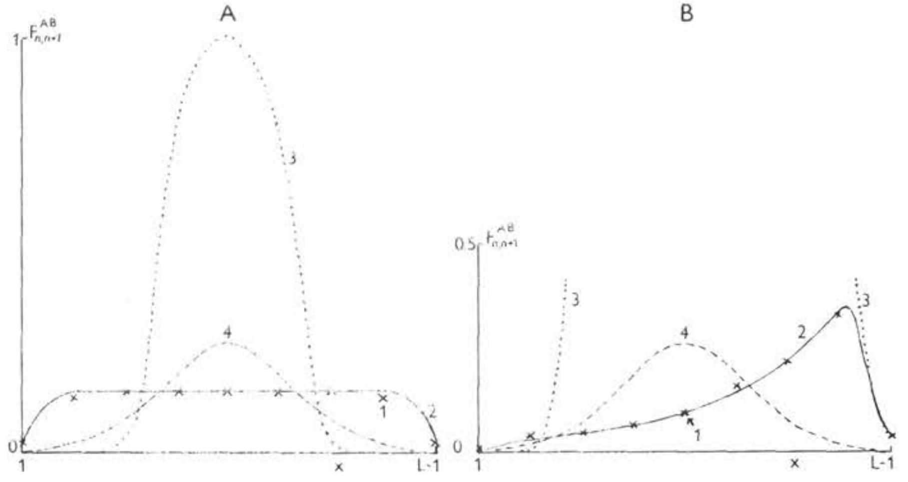

Fig. 4. Profile of the pair correlation function $F^{AB}_{n,n+1}$ for high populations, (1) — computer experiment, (2) — the divider method approximation, (3) — "discrete" superposition approximation (the present paper), (4) — "continuous" superposition approximation, $L = 10$. a) — $\Theta_1^A = 0.9901$, $\Theta_L^B = 0.9901$. b) — $\Theta_1^A = 0.9990$, $\Theta_L^B = 0.9985$.

$$1 - \Theta_1^A \equiv \frac{k_{2A}}{k_{1A}C_A}, \quad 1 - \Theta_L^B \equiv \frac{k_{2B}}{k_{1B}C_B} \tag{46}$$

and if $k_{1A} = k_{1B}$, $k_{2A} = k_{2B}$ the unidirectional fluxes ratio is

$$j_A/j_B = \frac{(L-2)C_B + C_A}{(L-2)C_A + C_B}\left(\frac{C_A}{C_B}\right)^{L-2} \tag{47}$$

Results of calculations of $F^{AB}_{n,n+1}$ as compared to the computer experiment are given in Fig. 4*a*, *b*. Fig. 4 (*a* — symmetrical case, *b* — asymmetrical case) shows that the curve $F^{AB}_{n,n+1}$ calculated by expression (44) practically coincides with the results of the computer experiment (curve 2 and points 1). Results for unidirectional fluxes are given in Table, (Nos 14—17, 22, 28). It is easy to see that expressions (44) and (45) are in very good agreement with the computer experiment at extremely high populations. The accuracy of these expressions decreases exponentially with the populations becoming smaller.

For medium populations the divider method gives inaccurate results (Fig. 5, curve 2). Inaccurate results are obtained at low populations for $F^{AB}_{n,n+1}$ (Fig. 2, curve 2) and due to negligible $F^{AB}_{n,n+1}$ the divider method gives almost correct result for populations Θ_n^A, Θ_n^B and fluxes j_A, j_B.

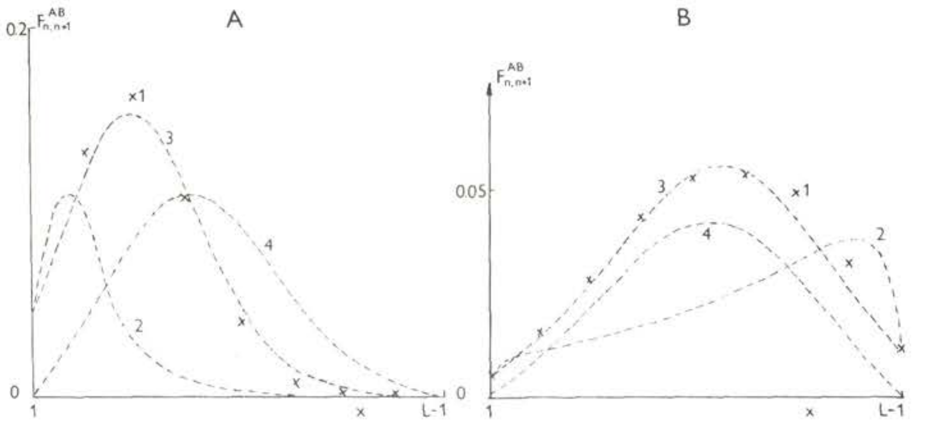

Fig. 5. Profile of the pair correlation function $F^{AB}_{n,n+1}$ for medium populations. (1) — computer experiment. (2) — the divider method approximation. (3) — "discrete" superposition approximation (the present study). (4) — "continuous" superposition approximation. $L = 10$ a) — $\Theta_1^A = 0.5$, $\Theta_L^B = 0.9091$. b) — $\Theta_1^A = 0.5$, $\Theta_1^B = 0.3333$.

5. The case of the superposition approximation for the correlation function

We analyzed two limiting population cases and followed the dependences of the main characteristics of the process on Θ, L at $\Theta \ll 1/L$ and $1 - \Theta \ll 1/L$. Aityan and Chizmadzhev (1981) and Aityan (1985) described an approach based on superposition approximation for the pair correlation function $F^{AB}_{n,n+1}$:

$$F^{AB}_{n,n+1} \approx \Theta^A_n \cdot \Theta^B_{n+1} \tag{48}$$

It was assumed for this case that the number of wells is large and that all the characteristics have a smooth dependence on the coordinate (i.e. on the well number), and thus

$$\begin{gathered} \Theta^A_n - \Theta^A_{n+1} \simeq -\frac{\partial \Theta^A_n}{\partial n}, \\ F^{AB}_{n,n+1} \approx \Theta^A_n \Theta^B_{n+1} \approx \Theta^A_n \Theta^B_n . \end{gathered} \tag{49}$$

The solution of Eq. (9) under these assumptions gave qualitatively correct dependences for Θ^A_n, $F^{AB}_{n,n+1}$, j_A (Fig. 5, curve 4, Fig. 6, curves 6 and 11). However, the range of validity of approximations (48) and (49) was not strictly defined. Let us show that the superposition approximation (48) is valid at least for the case when populations Θ^A_n, Θ^B_n have sufficiently nonsmooth profiles.

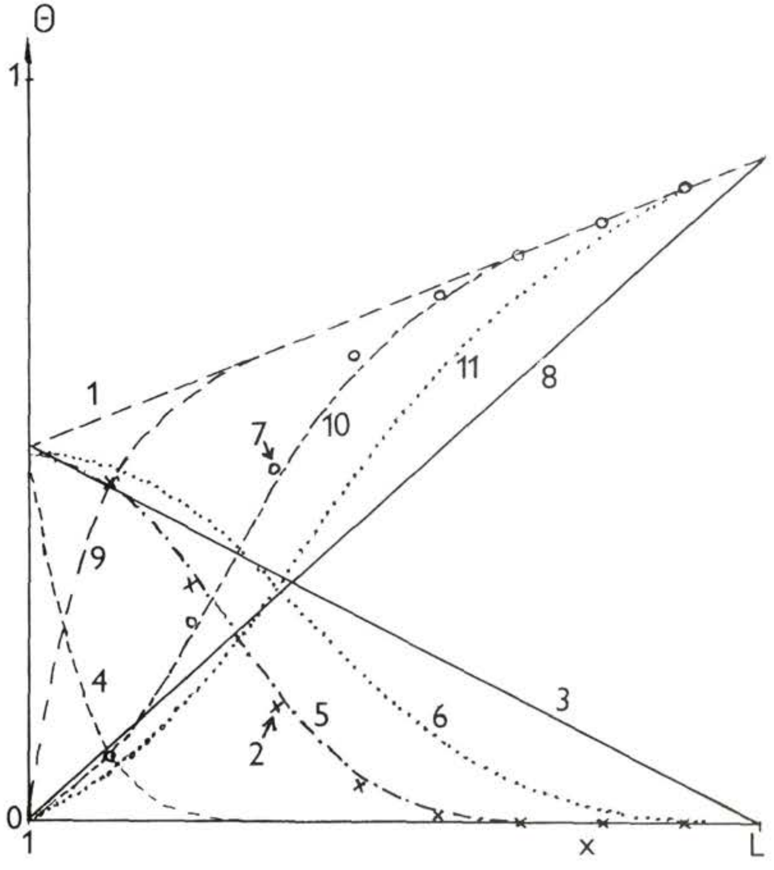

Fig. 6. Population profiles for $\Theta_1^A = 0.5$, $\Theta_L^B = 0.9091$. (1) — Θ_n, (2)–(6) — Θ_n^A, (7)–(11) — Θ_n^B, (2), (7) — computer experiment; (3), (8) — the linear approximation; (4), (9) — the divider method approximation; (5), (10) — "discrete" superposition approximation (the present study); (6), (11) — "continuous" superposition approximation, $L = 10$.

Indeed, it is natural to assume that not only $F_{n,n+1}^{AB}$ but all the correlation functions, as well as $F_{n,n+1}^{BA}$, can be represented by superposition approximation. In order to simultaneously satisfy the single-file condition (8) the inequality

$$\Theta_n^A \Theta_{n+1}^B \gg \Theta_n^B \Theta_{n+1}^A \tag{50}$$

must hold at least as far as maximum of the function $F_{n,n+1}^{AB}$ is concerned. In this case the approximate equality

$$\tilde{F}_{n,n+1}^{BA} \approx 0 \tag{51}$$

will be satisfied for the correlation function $\tilde{F}_{n,n+1}^{BA} = \Theta_n^B \Theta_{n+1}^A$.

Inequality (50) can be satisfied only at the very strong difference between $\Theta^{A,B}_{n+1}$ and $\Theta^{A,B}_{n}$ in the range of $F^{AB}_{n,n+1}$ maximum. That is why the "continuous" superposition approximation (Aiyan 1985) (48) and (49) is less accurate than the approach based on "discrete" superposition (48) given below.

Substituting (48) into (9) we obtain:

$$\begin{aligned}\Theta^{A}_{n+1} &= \frac{(1-\Theta_{n+1})\Theta^{A}_{n} - j_A/v}{1-\Theta^{A}_{n}},\\ \Theta^{B}_{n-1} &= \frac{(1-\Theta_{n-1})\Theta^{B}_{n} - j_B/v}{1-\Theta^{B}_{n}}\end{aligned} \tag{52}$$

In the general case these equations do not have any analytical solution (as, incidentally, do not the equation with derivatives, obtained by Aityan (1985)). However, in the symmetrical case which is important for the understanding of the single-file character of transport

$$\Theta_n = \Theta = \text{const} \tag{53}$$

the exact solution to equations (52) can be found; it has the form (for Θ^{B}_{n} the solution is quite analogous because the conditions are symmetrical):

$$\Theta^{A}_{n} = (1-\lambda_1)\lambda_1^{n} + \mu(1-\lambda_2)\lambda_2^{n}, \tag{54}$$

where

$$\lambda_{1,2} = 1 - \frac{\Theta}{2} \pm \sqrt{\frac{\Theta^2}{4} + \frac{j_A}{v}} \tag{55}$$

Substituting (54) and (55) into equations (4) and solving them, we can find the two unknown variables μ and j_A. Assuming that the population is not too low, i.e.

$$\Theta \gtrsim 1/L \tag{56}$$

and that the channel contains a large number of wells

$$L \gg 1 \tag{57}$$

we have

$$\lambda_1 = 1 + j_A/v\Theta, \quad \lambda_2 = 1 + \Theta, \tag{58}$$

$$\Theta^{A}_{n} = \frac{-j_A/v\Theta + \mu\Theta(1-\Theta)^{n}}{1+\mu(1-\Theta)^{n}}, \tag{59}$$

where μ is obtained from the boundary conditions. For the case of "rapid" boundaries

$$\mu = -(1 - \Theta)^{-L-1}, \tag{60}$$

$$j_A = \nu\Theta^2(1 - \Theta)^L, \tag{61}$$

$$F^{AB}_{n,n+1} = \frac{\left(-\frac{j_A}{\nu\Theta} + \mu\Theta(1 - \Theta)^n\right)\left(-\frac{j_A}{\nu\Theta} + \mu\Theta(1 - \Theta)^{L-n}\right)}{(1 + \mu 1 - \Theta)^n)(1 + \mu(1 - \Theta)^{L-n})}. \tag{62}$$

Expressions for $F^{AB}_{n,n+1}$ are in good agreement with the computer experiment for medium populations (Fig. 5, curve 3; *5a corresponds to larger populations, 5b* to lower populations). It is clear that "continuous" superposition approximation gives only qualitatively correct results (curve 4); the divider method is completely invalid here (curve 2). It could be actually proven that in symmetrical case unidirectional fluxes are maximal at medium populations. Then, the population profile has a shape of an arctangens profile with an inflection point in the middle of the channel; the pair correlation function $F^{AB}_{n,n+1}$ has a non-monotonous profile with the maximum in the middle of the channel. Expression (52) for Θ and j_A gives the right result at medium as well as at low populations (Fig. 1, 6, Table: lines 1—12, 18—20, 23—25). From Fig. 6 it is clear that at medium populations approximation (52) gives a quantitatively correct result (curves 5 and 10). The linear approximation (curves 3 and 8) and the divider method (curves 4 and 9) do not agree with the computer experiment. The "continuous" superposition approximation (curves 6 and 11) gives qualitatively (but not quantitatively) correct results. Calculations associated with superposition approximation of correlation function $F^{AB}_{n,n+1}$ incorrectly describe its behaviour at extremely high populations (Fig. 4), while "continuous" approximation (Aityan 1985) (curve 4) gives correct results at least for the value order (that is why this approximation gave qualitatively correct results for unidirectional fluxes). "Discrete" superposition approximation gives entirely nonphysical results for extremely high polulations; normalization of the correlation function $F^{AB}_{n,n+1}$ (curve 3) yields values several times higher than unity.

Strictly speaking, superposition approximation cannot be used at extremely low populations because the normalization condition for the pair correlation functions is not valid. The function $F^{AB}_{n,n+1}$ calculated by this approximation is about half the exact correlation function, calculted using the random-walk method (Fig. 2, curves 3 and 4).

Discussion

Our investigations of the process of single-file transport allowed adequate description of this process for any population. Particular attention was paid to the pair correlation function $F^{AB}_{n,n+1}$ which plays the principial role in the single-file transport process (Aityan 1985). Three ranges of populations for which different approximations are valid have been found. At low populations, the transport is accomplished by independent motion of particles, which is described by the free diffusion equations. The pair correlation function $F^{AB}_{n,n+1}$ in zero approximation (9) can be neglected. To define corrections of the next order of smallness of populations, the function $F^{AB}_{n,n+1}$ had to be determined. This was done by the two particles random-walk method and turned out to be about two times larger than when determined by superposition approximation (48). The nonlinearity in the expressions for unidirectonal fluxes also turned out to be about two times larger as compared to superposition approximation values. The fact that superposition approximation, seemingly natural at low populations, does not work, and that the pair correlation function has the form $F^{AB}_{n,n+1} \approx 2\Theta^{A}_{n}\Theta^{B}_{n+1}$, can be explained quite easily: while substituting the expressions in superposition approximation of the pair correlation functions into equations (4) and (6), it is necessary to substitute the superposition approximation of the pair correlation function $F^{BA}_{n,n+1}$, which is approximately equal to the correlation function $F^{AB}_{n,n+1}$. Since $F^{BA}_{n,n+1} \equiv 0$, to save the normalization equation it is natural to assume that the doubled expression for the superposition approximation will be correct for $F^{AB}_{n,n+1}$.

At high populations single-file transport is described by the divider diffusion method. This method means that a rather complex and difficult problem of the pair correlation function comes to just two problems of unary functions solved in succession, i.e. for channel population marked by the holes (ζ^{A}_{n}, ζ^{N}_{n}) and for the unary function of the divider distribution showing the coordinate of the interface between two types of traced particles in the channel. This method gives good results at high populations when there are practically no vacant places (holes in the channel). The results described with high populations have a wider range of applications exceeding the framework of assumptions of particle motion in a channel as defined herein. In particular, it allows the solution of single-file transport within a channel with an external field applied as well as within nonhomogeneous channel.

The investigation of the limits of applicability of the superposition approximation has shown that the latter can be used with population profiles changing abruptly. This is the case with highly nonhomogeneous channel populations (the concentration of particles in the solution sharply differs from that in the other solution), as well as with medium populations.

Thus, the solution to the transport problem of single-file is provided for all levels of population — low, high and medium. The analytical calculations made in the study have been confirmed by a computer experiment carried out using an ES-1060 computer (Aityan and Portnov 1986).

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