Probabilities of Atomic Departures from the Slit System

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Abstract. The theoretical description of experimental data on transport in open systems has been of interest for more than a hundred years. Boltzmann proposed a new view of the transfer of matter. Now it is possible to describe the transfer processes from a microscopic point of view. The solution of the Boltzmann equation and the equations derived from it is a complex problem related to the mathematical problems of solving such equations. On the other hand, the complexity of the solution is related to the geometry of the system in which the transfer process takes place. Fundamental physical calculations are made for systems: flat, slotted, cylindrical, rectangular, etc. In the free molecular mode of gas flow, collisions of molecules occur mainly with the walls of systems. In this connection, there was a direction related to the calculation of the probabilities of atomic transport in the system. In this paper, we propose an approach for determining the probabilities of atomic outcomes from slit systems depending on the relative height of the walls of H systems. Exact formulas are obtained for calculating the probabilities of atomic departures from systems without colliding with walls, the distribution of atomic collisions over the height of the system wall, the probabilities of atoms entering the condensed phase after a single collision with the system walls, and the probabilities of atomic departures from systems after a single collision with walls. The accuracy of the obtained formulas was compared with the data obtained from computer experiments using the Monte Carlo method.

1 Introduction

The problems of heat and mass transfer in systems have been of interest to researchers for many decades. The approach from the molecular point of view allows us to obtain different results depending on the parameters and conditions used. Clausing, using a probabilistic approach, determined the flow of matter in the cylindrical and slit systems [1]. On the basis of probable reasoning, Knudsen, Smolukhovsky, and Dushman obtained formulas for a constant gas flow in a free-molecular flow regime in long and short cylindrical pipes. In the mid-60s, Waldman did a lot of work on non-equilibrium thermodynamics in the boundary layer [2]. Using the first approximation of the iterative procedure for solving the Boltzmann equation, Fustoss obtained a formula for the molecular flow as a function of the observation angle [3]. Thus, regularities were determined for a larger number of system parameters. All the works used certain approximations, but there are no exact solutions. With the development of computer technology, it became possible to use the Monte Carlo method for analyzing the flows of matter in systems [4]. The results of calculations were analyzed depending on the number of hours played.

Modeling the process of heat and mass transfer in open systems is an urgent task, both from the theoretical and practical point of view. The peculiarity of the description of the free-molecular transport ($Kn > 1$) of the gas phase flow is that the gas dynamics equations and the Boltzmann equation cannot be used because of large density fluctuations in the gas and the insignificant number of collisions of molecules in the gas phase. The almost complete absence of collisions of atoms or molecules in the gas phase allows us to calculate the trajectories of a large number of particles. We can assume that all collisions of atoms occur with the walls of systems. The trajectories of molecules represent straight lines from one surface to another.

An important factor is the presence of a potential barrier on the surface of the condensed phase and the walls of systems. The potential barrier on the surface of the condensed phase and the walls of the system is a filter that cuts off slow particles, changes the velocity component perpendicular to the surface, and, accordingly, the trajectory of the molecules. This also applies to atoms. In the limiting case, when the potential barrier value $U = 0$, the atoms flew out from the surface of the condensed phase equally likely in all directions. This means that the integrand included in all integrals presented in the paper is $\rho = 1$.

In the present paper, the obtained probabilities are compared with the results obtained by the Monte Carlo method. It was assumed that the particles are point-like, and the results of calculations depend only on the relative height of the wall of the system H. The relative wall height is defined as the ratio of the wall height to its width. The influence of the number of N atoms played on the probability of atomic departures was established. The masses of the played atoms are equal to

40 a.u.m., but this did not affect the results of calculations. The calculation results depend on the parameter $r = U / kT$, where T is the system temperature and k is the Boltzmann constant [5,6]. Since in our case $U = 0$, the parameter $r = 0$. At $r \to \infty$, the atoms fly off the surface according to the cosine law, and the integrand will be different.

When solving such problems, three problems arise: the correctness of the program algorithm, the correctness of the random number sensors, and the number of particles played N to obtain results with a given accuracy.

2 Calculations

In this part of the work, on the basis of the proposed approach, an exact analytical formula was obtained for the probability of an atom leaving the surface of a condensed phase without colliding with the walls of the $W1(0;0)$ system. The first index determines the number of collisions of atoms with the walls of systems, and the second - the value of the parameter $r = 0$. The results of theoretical calculations were compared with the results of computer experiments.

Fig. 1 shows a cross-section diagram of a slit system with a relative wall height H. The atom is located on the surface of the condensed phase ($z = 0$) at the point x. An atom from the surface of the condensed phase can fly out of the slit system at an angle that falls within the interval $\theta \in (\theta_{cr1}; \theta_{cr2})$. The value of the critical angle $\theta_{cr1} = arctg(x / H)$.

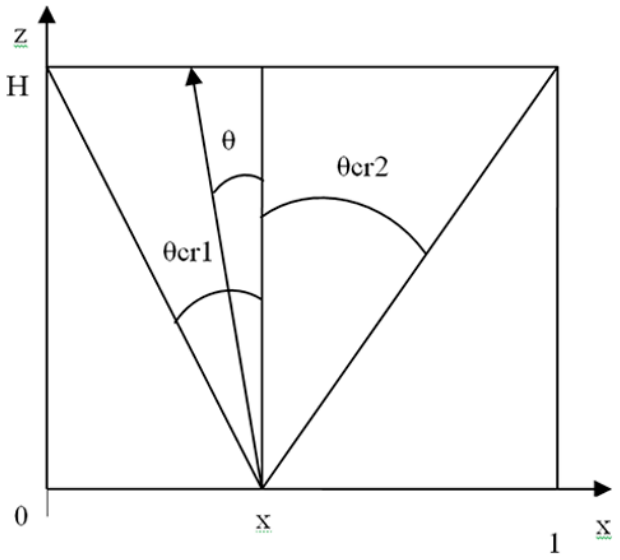

Fig. 1. The scheme of the slot system and the trajectory of departure from the system.

Find the probability of the atom's departure through the left part of the system. Due to the symmetry of the slit system, the probability of an atom flying through the right side of the system will be the same. Integrating the integral function with respect to the variable x from 0 to 1 and with respect to the variable θ from 0 to θ_{cr1}, taking into account the normalization of I, we obtain:

$$W1(0;0) = \frac{1}{I}\int_0^1 dx \int_0^{arctg\frac{x}{H}} d\theta, \qquad (1)$$

where

$$I = \int_0^1 dx \int_0^{\pi/2} d\theta. \qquad (2)$$

After calculating the double integrals, we obtain an exact formula for the probability of an atom leaving the slit system H without colliding with the walls of the system:

$$W1(0;0) = \frac{2}{\pi}\left(arctg\frac{1}{H} - \frac{H}{2}\ln\left(1+\frac{1}{H^2}\right)\right) \qquad (3)$$

When $H = 0$, we get that the probability of departure of atoms from such a system is 1. When $H \to \infty$ the probability of departure of atoms from a slit system tends to 0.

To compare the results of calculations obtained using this formula and the results obtained in computer experiments, computer experiments were performed with different numbers of N atoms. The calculation results are shown in table 1.

Table 1. The number of atoms ejected from the slot systems and the probability of atom departures.

N/H	0,1	0,7	2	10
The number of atoms that escaped from systems without colliding with walls				
10^5	79225	36540	15295	3216
10^6	790366	363838	152738	31390
10^7	7897575	3637825	1531312	317319
10^8	78971615	36349497	15317031	3177349
The probability of departure of atoms W1(0;0)				
10^5	0,792251	0,365401	0,152958	0,032161
10^6	0,790366	0,363838	0,152738	0,031392
10^7	0,789758	0,363783	0,153131	0,031732
10^8	0,789716	0,363495	0,153170	0,031773
Relative error				
10^5	0,328814	0,547619	0,104609	1,187504
10^6	0,091224	0,120658	0,243554	1,236381
10^7	0,014245	0,105420	0,013844	0,145595
10^8	0,009012	0,026402	0,039374	0,014509

The probability $W1(0;0)$ was defined as the ratio of the number of atoms that flew out of the system without colliding with the walls to the number of atoms played. In fact, this ratio determines the arithmetic mean, but for very large N it tends to the corresponding probability. For clarity, the first part of the table shows the results of calculations of the number of atoms that

flew out of the system without colliding with the walls of the systems. It should be noted that the table shows the results of calculations of individual computer experiments. As the number of *N* atoms being played increases, the number of outgoing atoms increases, but the first digits practically do not change.

The results of flight probabilities obtained in computer experiments are shown in the middle part of the table.1. For comparison, the results of calculations obtained by the formula (3) are given. The last part of the table shows the corresponding relative errors of the results of computer experiments and theoretical calculations. We can note a tendency to decrease errors with an increase in the number of played *N* atoms. The dependence of the probability of atomic departures on the relative height of the walls of *H* systems is shown in Fig. 2.

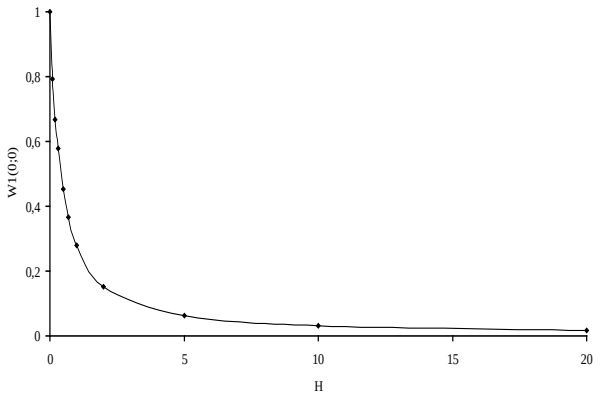

Fig. 2. Graph of the probability of departure from the systems without colliding with the walls.

Fig. 3 shows the dependences of relative errors ε as a percentage of the relative height of the walls of *H* systems. The relative errors obtained for large values of *H* have a large value, since the number of escaping atoms is less than for small slit systems. It can be noted that relative errors do not exceed 1.5%.

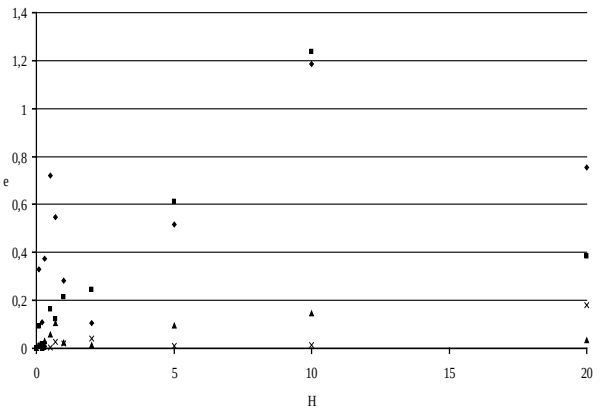

Fig. 3. Distributions of relative errors between theoretical values and computer experiments.

In another series of 12 computer experiments, data were obtained on the number of atoms that flew out of systems without colliding with the walls of systems to determine statistical deviations. The results of calculations are shown in table 2. The arithmetic mean of the corresponding data was calculated and divided by the number of played atoms $N = 10^7$. For comparison, the results of calculations using the formula (3) are presented. A comparison of the calculation results shows that the relative error of the average arithmetic probabilities of atomic departures and theoretical values does not exceed several hundredths of a percent.

Table 2. The number of atoms ejected from the slit systems, depending on the relative height of the walls of the systems.

$N=10^7$/H	0,1	2	10
1	7897575	1531312	317319
2	7896446	1530683	317484
3	7897084	1532382	316729
4	7896121	1533553	317127
5	7894780	1530533	317676
6	7895923	1531763	317572
7	7895626	1531524	318848
8	7897074	1532479	318318
9	7893911	1533045	318041
10	7894926	1529914	318632
11	7898377	1530485	316935
12	7896230	1530291	317641
Σ	94754073	18377964	3812322
$\overline{X}$	7896173	1531497	317693,5
$W1_{MC}$	0,789617	0,153149	0,031769
$W1_{theor}$	0,789645	0,15311	0,031778
ε%	0,003546	0,025472	0,028636

The analysis of the obtained results showed an excellent agreement between the data of computer experiments and the results obtained by formula (3).

We find formulas for determining the probability of an atom hitting the wall of the system and the density of the distribution of collisions of atoms with the wall after departure from the surface of the condensed phase. Fig. 4 shows a cross-section diagram of a slit system with a relative wall height *H*. The atom is located on the surface of the condensed phase ($z = 0$) at the point *x*.

An atom that has escaped from the surface of the condensed phase can hit the wall of the slit system at an angle that belongs to the interval $\theta \in (\theta_{cr1}; \pi/2)$. The value of the critical angle $\theta_{cr1} = arctg(x/H)$.

Find the probability of an atom hitting the left wall of the system. Due to the symmetry of the slit system, the probability of an atom hitting the right wall of the system will be the same.

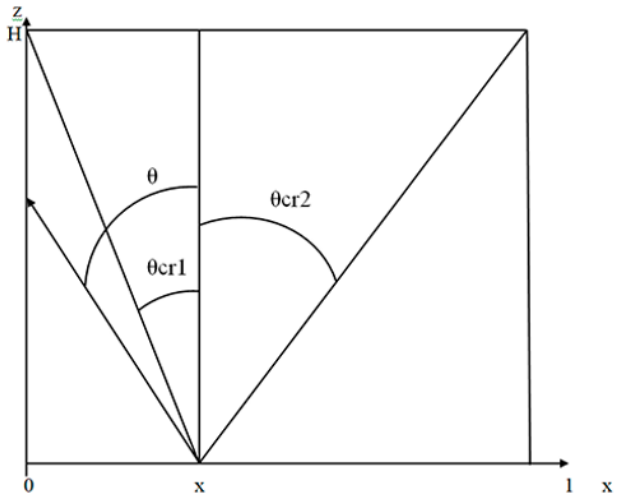

Fig. 4. Scheme of atom departure from the surface of the condensed phase and hit the wall of the system.

Integrating the integrand function with respect to the variable x from 0 to 1 and with respect to the variable θ from θ_{cr1} to $\pi/2$, taking into account the normalization of I, we obtain:

$$W2(0;0) = \frac{1}{I}\int_0^1 dx \int_{arctg\frac{x}{H}}^{\frac{\pi}{2}} d\theta, \qquad (4)$$

where

$$I = \int_0^1 dx \int_0^{\pi/2} d\theta. \qquad (5)$$

After calculating the double integrals, we obtain an exact formula for the probability of an atom hitting the walls of the slit system after leaving the surface of the condensed phase:

$$W2(0;0) = 1 - \frac{2}{\pi}\left(arctg\frac{1}{H} - \frac{H}{2}\ln\left(1+\frac{1}{H^2}\right)\right). \qquad (6)$$

This formula could be obtained from the condition:

$$W1(0;0) + W2(0;0) = 1. \qquad (7)$$

The density of the probability distribution of collisions of atoms along the wall height is determined as the first derivative of the probability of atoms hitting the wall of the system after departure from the surface of the condensed phase. Replacing H with z in formula (6) and taking the derivative with respect to z, we obtain:

$$p2(0;0) = \frac{dW2(0;0)}{dz} = \frac{1}{2\pi}\ln\left(\frac{z^2+1}{z^2}\right). \qquad (8)$$

An exact formula is obtained for calculating the density of the probability distribution of collisions of atoms with one wall of a slit system after departure from the surface of the condensed phase. In the limiting case for $z \to 0$, we get that $p2(0;0) \to \infty$. In another limiting case, for $z \to \infty$ $p2(0;0) \to 0$.

The results of calculations obtained by formula (8) were compared with the results obtained in computer experiments. Computer experiments were carried out with different numbers of N atoms and systems with wall heights H = 0.5 and H = 5. The height of the wall of the system was divided into 20 intervals, and the number of atoms trapped in this cell was determined. The results of calculations for a slit system with H = 0.5 are shown in table 3. The density of atoms was determined as the ratio of the number of atoms trapped in a given cell to the number of atoms played and the length of the cell. The results of calculations of individual experiments are presented. The relative error ε was less than one percent. The largest deviation of the theoretical values from the results of computer experiments is observed in the first two cells near the surface of the condensed phase. This can be explained by the fact that the point z = 0 is the break point of the function (8).

Table 3. Densities of probability distributions of collisions of atoms over the height of the system wall.

z	0,0125	0,0625	0,1125	0,1625
М-К	1,49194	0,88363	0,69661	0,58422
теор	1,39487	0,88316	0,69744	0,58254
e,%	6,95907	0,05355	0,11986	0,28804
z	0,2625	0,3125	0,3625	0,4125
М-К	0,43518	0,38606	0,34160	0,30709
теор	0,43634	0,38507	0,34264	0,30687
e,%	0,26630	0,25709	0,30351	0,0701

Table 4. Densities of probability distributions of collisions of atoms over the height of the system wall.

z	0,125	0,625	1,125	1,625	2,125
М-К	0,7627	0,2046	0,0932	0,0513	0,0319
теор	0,6643	0,2020	0,0926	0,0511	0,0318
e,%	14,804	1,2687	0,5784	0,4863	0,3831
z	2,625	3,125	3,625	4,125	4,625
М-К	0,0216	0,0155	0,0116	0,0091	0,0072
теор	0,0215	0,0155	0,0116	0,0091	0,0072
e,%	0,1664	0,2642	0,2253	0,7798	0,3565

Table 4 shows the results of calculations for determining the densities of atomic probability distributions along the system wall for H = 5. The same regularities are established as for the system with H = 0.5. Table 3 shows the results of calculations for the same system with H = 5, but with an order of magnitude greater number of played atoms. The absolute error gets better for some z values, but the relative error, if any, improves only slightly.

Fig. 5 shows the density of the probability distribution of atoms over the height of the slit system wall with H = 0.5.

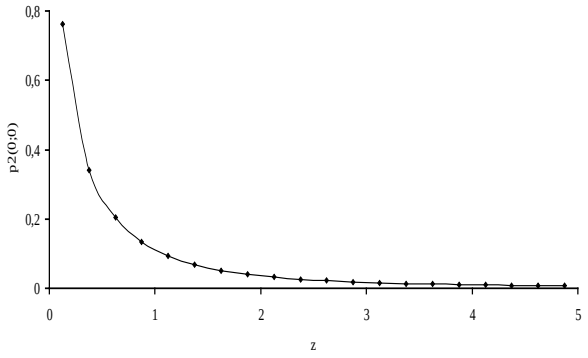

Fig. 5. Density of the probability distribution of collisions of atoms with the system wall. $H = 5$.

The distribution graphs obtained using the Monte Carlo method and the formula (8) practically do not differ from each other.

Analysis of the calculation results showed a good agreement between the data of computer experiments and the results obtained by formula (8). The obtained data can be used for comparison with the data obtained in real experiments on sputtering on glass plates.

We find the probability of atoms entering the condensed phase after leaving the system wall. In previous calculations, it was found that the density of the distribution of the collision of atoms over the height of the wall of the slit system is determined by the exact formula (8).

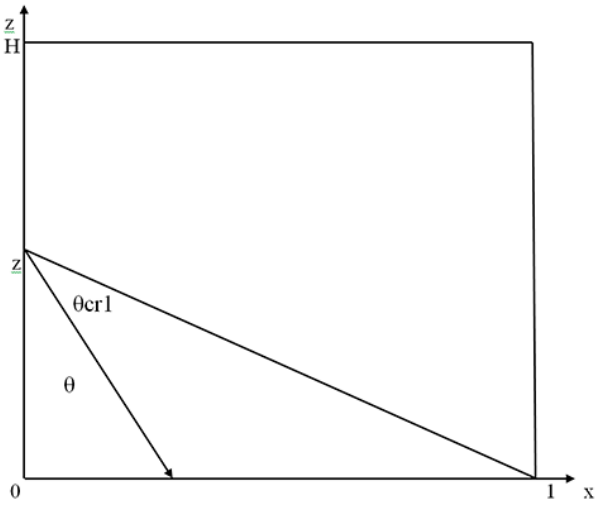

Fig. 6. Diagram of an atom entering the condensed phase after a collision with a wall.

An atom that has escaped from the wall surface can enter the condensed phase at an angle corresponding to the interval $\theta \in (0;\theta_{cr1})$. The value of the critical angle $\theta_{cr1} = arctg(1/z)$. Due to the symmetry of the slit system, the probability of an atom entering the condensed phase from the right wall of the system will be the same. Integrating the integrand (8) over the variable z from 0 to H and over the variable θ from 0 to θ_{cr1}, taking into account the normalization of I, we obtain the double integral:

$$W3(1;0) = \frac{1}{2\pi I}\int_0^H dz \ln\left(\frac{z^2+1}{z^2}\right)\int_0^{arctg\frac{1}{z}} d\theta =$$

$$= \frac{1}{2\pi I}\int_0^H dz \ln\left(\frac{z^2+1}{z^2}\right) arctg\frac{1}{z} \qquad (9)$$

where

$$I = \frac{\pi}{2}. \qquad (10)$$

The integral over the variable z can be expressed in terms of special functions, but it is advisable to solve it by numerical method.

The calculation results obtained by formula (9) were compared with the results obtained in computer experiments. Computer experiments were carried out with different numbers of N atoms and systems with several heights of H walls. The results of calculations for slit systems are shown in table 5. This table shows the results of calculations of individual computer experiments. The third part of the table shows the corresponding relative errors ε.

Table 5. The probability of atoms entering the condensed phase W3(1; 0).

H	0,1	2	5
Number of atoms trapped in the condensed phase			
$N=10^5$	10171	32235	32964
$N=10^6$	102054	321949	331802
$N=10^7$	1022759	3217659	3314116
$N=10^8$	10230987	32178188	33130734
Probabilities W3(1;0)			
$N=10^5$	0,10171	0,32235	0,32964
$N=10^6$	0,10205	0,32194	0,33180
$N=10^7$	0,10227	0,32176	0,33141
$N=10^8$	0,10231	0,32178	0,33130
Teop.	0,10233	0,32182	0,33134
Relative errors			
$N=10^5$	0,61462	0,16188	0,51306
$N=10^6$	0,27848	0,03728	0,13943
$N=10^7$	0,06165	0,01960	0,02160
$N=10^8$	0,02846	0,01464	0,00985

For the number of played atoms $N = 10^6$, the relative error does not exceed one percent. as the number of atoms played increases, the relative error decreases. for the case $N = 10^8$, the relative error does not exceed a few tenths of a percent.

Fig. 7 shows the probability distribution of atoms entering the condensed phase $W3$ (1;0) after departure from the surfaces of the walls of systems, depending on N.

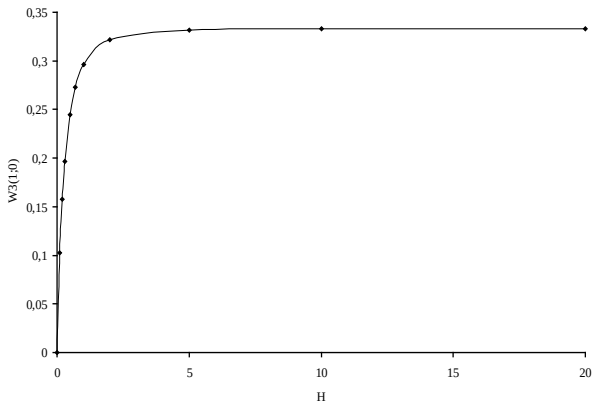

Fig. 7. The probability of atoms entering the condensed phase after a single collision with the walls.

The distribution graphs obtained using the Monte Carlo method and the formula (9) practically do not differ from each other, as can be seen from table 5. Analysis of the probability graph *W*3 (1; 0) allowed us to establish that up to the value $H = 2$ there is a rapid growth, which is replaced by a slight increase in this value. It can be assumed that the curve approaches the asymptotic value, which is equal to 1/3. Relative errors are related both to the number of atoms played *N*, and to the accuracy of calculating a certain integral.

Using the previously obtained formula for the density distribution of collisions of atoms with the system wall (8), we find the probability of the atoms leaving the slit system after one collision with the system wall. The scheme of the atom's departure is shown in Fig. 8.

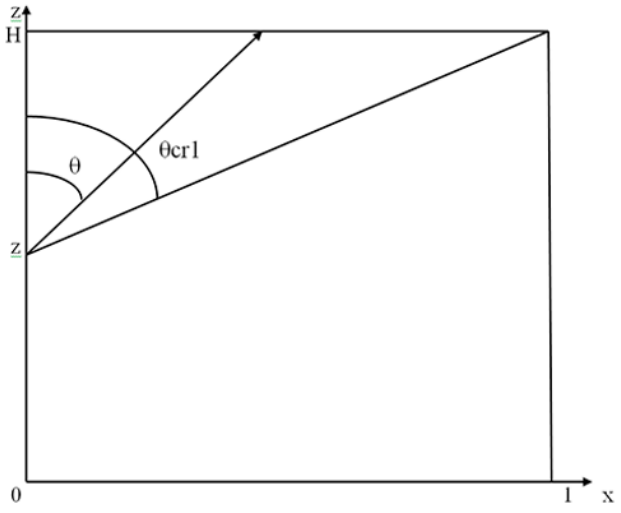

Fig. 8. Scheme of atom departure from the system after colliding with the wall.

An atom that has escaped from the wall surface can escape from the system at an angle that belongs to the interval $\theta \in (0;\theta_{cr1})$. The value of the critical angle $\theta_{cr1} = arctg(1/(H-z))$. Due to the symmetry of the slit system, the probability of an atom flying out of the system from the right wall of the system will be the same. By integrating the integrand (8) over the variable *z* from 0 to *H* and over the variable θ from 0 to θ_{cr1}, taking into account the normalization of *I*, we obtain the double integral:

$$W1(1;0) = \frac{1}{2\pi I}\int_0^H dz \ln\left(\frac{z^2+1}{z^2}\right)^{arctg\frac{1}{H-z}}\int_0^{} d\theta = \frac{1}{2\pi I}\int_0^H dz \ln\left(\frac{z^2+1}{z^2}\right) arctg\frac{1}{H-z} \qquad (11)$$

where

$$I = \frac{\pi}{2}. \qquad (12)$$

The calculation of the integral with respect to the variable θ is not difficult, but the integration with respect to the variable *z* is quite complex and its solution for various values of *H* is obtained numerically. The results of the calculations are shown in the second part of table 6.

Table 6. Probabilities of atomic departures from slit systems W1(1; 0).

H	0,1	0,7	2	5
Number of atoms ejected from the system				
$N=10^5$	9955	23122	16544	7524
$N=10^6$	100874	231482	166827	75363
$N=10^7$	1012771	2322137	1670716	753142
$N=10^8$	10130587	23239929	16697251	7529611
The probability of departure of atoms *W*1(1; 0)				
$N=10^5$	0,09955	0,23122	0,16544	0,07524
$N=10^6$	0,10087	0,23148	0,16682	0,07536
$N=10^7$	0,10127	0,23221	0,16707	0,07531
$N=10^8$	0,10130	0,23239	0,16697	0,07529
Teop.	0,10133	0,23247	0,16697	0,07532
Relative errors				
$N=10^5$	1,75760	0,53770	0,91811	0,10621
$N=10^6$	0,45099	0,42500	0,08743	0,05709
$N=10^7$	0,05319	0,11025	0,05905	0,0077
$N=10^8$	0,0248	0,03041	0,00029	0,03171

For comparison with theoretical calculations, the results of calculations of computer experiments carried out using the Monte Carlo method are presented. Computer experiments were carried out with different numbers of *N* atoms and systems with several heights of *H* walls. In this table, the results of calculations of individual computer experiments are presented. The third part of the table shows the corresponding relative errors ε. For the number of atoms played $N = 10^6$, the relative error exceeded one percent in only two cases due to the small number of atoms that flew out. As the number of atoms played increases, the relative error decreases. For

the case $N = 10^8$, the relative error does not exceed a few hundredths of a percent.

Fig. 9 shows the probability distributions of atomic departures from slit systems without colliding with the walls $W1(0; 0)$ and after one collision with the walls $W1(1; 0)$, depending on the relative height of the walls of systems H. The distribution graphs obtained using the Monte Carlo method and the formula (2) practically do not differ from each other, as can be seen from table 6. Analysis of the probability distribution graphs allowed us to establish qualitatively different types of dependencies. For atoms emerging from systems without collisions with the system walls, the distribution is monotonically decreasing. The graph of the probability distribution of atomic departures from systems after a single collision with walls has a maximum. The presence of the maximum can be explained by the fact that with an increase in the relative height of the walls of H systems, the probability of falling on them of atoms that have escaped from the surface of the concentrated phase increases, but at the same time the probability of departure after a collision with the walls of the system decreases. Relative errors are related both to the number of atoms played N, and to the accuracy of calculating a certain integral. Similar distributions of the probabilities of atomic departures from slit systems have been established for a larger number of collisions of atoms with the walls of systems. There was a decrease in the magnitude of the maxima and a slight shift of the maxima to the right.

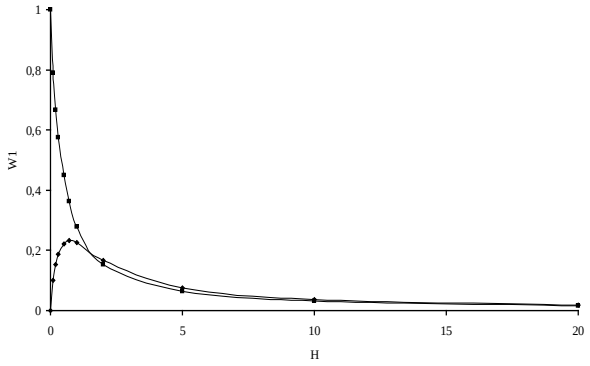

Fig. 9. The probability of atomic departures from the slit systems without collisions with the walls and after a single collision with the walls. ■ - $W1(0;0)$, ♦ - $W1(1;0)$.

Analysis of the calculation results showed an excellent match between the data of computer experiments and the results of calculations obtained by formula (11).

3 Conclusion

An approach is proposed for obtaining precise formulas for determining the probabilities of atomic outcomes from slit systems. The results of computer experiments confirmed the data obtained by the formulas with high accuracy. This indicates both the correctness of the approach for obtaining theoretical probabilities of outcomes, and the correctness of the developed computer program, the correct operation of random number sensors, and the optimal number of atoms played.

The obtained formulas can be used for testing newly developed random number sensors. This indicates the correct operation of the developed program and the correct operation of the random variable sensors.

The obtained theoretical probabilities of outcomes and the results of computer experiments can be used for comparison with the data obtained in real experiments**.**

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