Vol. 32 (2001) ACTA PHYSICA POLONICA B No 2

DIFFUSION IN A MEMBRANE SYSTEM*

Tadeusz Kosztołowicz

Institute of Physics, Pedagogical University
Konopnickiej 15, 25-406 Kielce, Poland
e-mail: tkoszt@pu.kielce.pl

(Received October 30, 2000)

Diffusion in a one-dimensional system with a thin membrane (which is treated as a partially permeable wall) for the discrete and continuous time and space variables is discussed. The internal structure of the membrane is not explicitly involved into consideration. Starting from microscopic models of diffusion we obtain the boundary condition at the membrane for macroscopic diffusion equation.

PACS numbers: 05.40.+j, 05.60.+w, 02.30.–f

1. Introduction

Diffusion in a system with the homogeneity being disturbed at one point (which corresponds to a system with a thin membrane) is important in various fields of physics, chemistry and biophysics (see *e.g.* [1], [2]). It is also interesting from the mathematical point of view. Since the concentration gradients are assumed to be only along the x-direction, the problem is effectively one-dimensional. Usually the diffusion in the membrane system is considered within the diffusion equation

$$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial x^2}\,, \tag{1}$$

where two boundary conditions at a thin membrane are needed (when the membrane is of finite thickness the number of the boundary conditions at the membrane increases to four). Assuming that the flux flowing through the membrane is continuous, we need a second boundary condition. The internal structure of the membrane is not explicitly involved into our considerations.

* Presented at the XXIV International School of Theoretical Physics "Transport Phenomena from Quantum to Classical Regimes", Ustroń, Poland, September 25–October 1, 2000.

Instead, we assume that the permeability of the membrane is described by the general permeability coefficient. For example, it can be defined as a ratio of the total surface of all holes to the membrane surface. There are two ways to determine the boundary conditions at the membrane from the microscopic models. In the first one, the random walk on the discrete lattice in terms of the discrete Master equations is considered [3, 4], while the second one is based on the diffusion in the phase-space [5]. The boundary conditions for the systems with fully reflecting, fully absorbing or partially absorbing walls have been considered previously [1–6]. In contrast to the membrane system, the diffusion is then investigated only in half-space bounded by the wall. We note that the diffusion in the membrane system is qualitatively different from that in the system with partially absorbing wall, because in the latter one the particle once absorbed has no chance to return to the system. Till now there is not satisfactory procedures of obtaining the boundary condition at the partially permeable wall form the microscopic models. In this paper we present new results of our investigations concerning this issue.

2. Diffusion in the discrete membrane system

We start from the following birth-death equations for the system with a thin membrane, which is placed between the N and $N+1$ sites:

$$\begin{aligned}
\frac{\partial P(m,t)}{\partial t} &= a\left[P(m-1,t)+P(m+1,t)-2P(m,t)\right],\ m\neq N,N+1\,,\\
\frac{\partial P(N,t)}{\partial t} &= bP(N+1,t)+aP(N-1,t)-(a+b)\,P(N,t)\ ,\\
\frac{\partial P(N+1,t)}{\partial t} &= aP(N+2,t)+bP(N,t)-(a+b)\,P(N+1,t)\ ,
\end{aligned}$$

where $b=(1-q)\,a$. To solve above equations we use the method of Montroll and Weiss [7]. The solutions are [8]

$$\begin{aligned}
P_{--}(m,t;m_0) &= \exp(-2at)\Big[I_{|m-m_0|}(2at)+qI_{2N-m-m_0+1}(2at)\\
&-2q(1-q)\sum_{k=0}^{\infty}(2q-1)^k I_{2N-m-m_0+k+2}(2at)\Big]\ ,\quad m,m_0\leq N\ ,
\end{aligned}\tag{2}$$

$$\begin{aligned}
P_{+-}(m,t;m_0) &= \exp(-2at)(1-q)\Big[I_{m-m_0(2at)}\\
&+2q\sum_{k=0}^{\infty}(2q-1)^k I_{m-m_0+k+1}(2at)\Big]\ ,\quad m\geq N+1,\, m_0\leq N\ ,
\end{aligned}\tag{3}$$

where m_0 is the initial position of the particle, I_m denotes the modified Bessel function. The indices $+$ and $-$ of Green's functions refer to the signs of $(m-N)$and (m_0-N), respectively. In the above equations we take into account only those terms where the lower arguments of the binomials are integer. The functions P_{++} and P_{-+} can be obtained from the functions (2) and (3) respectively, by "mirror reflection" of the space axis with respect to the membrane (when the terms $m-m_0$, $2N-m-m_0$ *etc.* change their sign). The series occurring in (2) and (3) are convergent, so we can approximate the full series by the finite one (which contain only several first terms). From physical point of view the omitting the terms with large k is justified. The term occurring in the series $exp\,(-2at)\, I_{2N-m-m_0+k+2}\,(2at)$ can be interpreted as a probability of finding the particle at site m under condition that initially it is at the site $2N-m_0+k+2$. This means that the particle must take at least $n=2N-m-m_0+k+2$ steps $(m, m_0 \le N)$ during the time interval t. Since the probability $\Psi_n\,(t)$ of take n steps in the time interval decreases with n according to the Poisson distribution [9]

$$\Psi_n\,(t) = \frac{1}{n!}\left(\frac{t}{\tau}\right)^n \exp\left(-\frac{t}{\tau}\right),$$

the terms with large k can be rejected from the series occurring in (2) and (3). Thus, in the following considerations we take the discrete Green's functions in the form:

$$P_{--}\,(m,t;m_0) = \exp\,(-2at)\Big[I_{|m-m_0|}\,(2at) + qI_{2N-m-m_0+1}\,(2at)$$
$$-2q\,(1-q)\sum_{k=0}^{p}(2q-1)^k\, I_{2N-m-m_0+k+2}\,(2at)\Big], \quad m,\, m_0 \le N\,,$$

$$P_{+-}\,(m,t;m_0) = \exp\,(-2at)\,(1-q)\Big[I_{m-m_0}\,(2at)$$
$$+2q\sum_{k=0}^{p}(2q-1)^k\, I_{m-m_0+k+1}\,(2at)\Big], \quad m \ge N+1,\, m_0 \le N\,.$$

3. From discrete to continuous space variable

To pass from discrete to continuous space variable we take the standard procedure, where the following relations are assumed [2, 6, 10]

$$x = n\varepsilon\,,$$

$$D = a\varepsilon^2\,,$$

the parameter ε is interpreted as a distance between discrete sites, D is the diffusion coefficient. The Green's functions for the continuous system are obtained in the limit of small ε

$$\lim_{\varepsilon\to 0}\frac{1}{\varepsilon}P\left(m,t;m_0\right)=G\left(x,t;x_0\right)\ . \tag{4}$$

For the homogeneous system the Green's function is

$$P_0\left(m,t;m_0\right)=\exp\left(-2at\right)I_{|m-m_0|}\left(2at\right)\ ,$$

and obeys the limit

$$\lim_{\varepsilon\to 0}\frac{1}{\varepsilon}P_0\left(m,t;m_0\right)=G_0\left(x,t;x_0\right)\ .$$

where $G_0\left(x,t;x_0\right)=\frac{1}{2\sqrt{\pi Dt}}\exp\left(-\frac{(x-x_0)^2}{4Dt}\right)$ is the Green's function for the continuous system without the membrane . To calculate the limit of small ε for the discrete Green's functions, we need to consider the following problem: does the reflecting coefficient q depend on the parameter ε (and what is the function $q=q\left(\varepsilon\right)$)? To obtain the answer we keep our attention for a moment on the system with partially absorbing wall, where the Green's functions and boundary conditions at the wall are well-known for the discrete [4, 6, 11] as well as for the continuous system [5]. For the discrete system the Green's function, which fulfills the following microscopic boundary condition at the partially absorbing wall placed between N and $N+1$ states (here $m_0\leq N$)

$$P\left(N+1,t;m_0\right)=\alpha P\left(N,t;m_0\right)$$

is

$$P\left(m,t;m_0\right)=\exp\left(-2at\right)\left[I_{|m-m_0|}\left(2at\right)+\alpha I_{2N-m-m_0+1}\left(2at\right)\right.$$
$$\left.-\left(1-\alpha^2\right)\sum_{k=0}^{\infty}\alpha^k I_{2N-m-m_0+k+2}\left(2at\right)\right]\ , \tag{5}$$

where α is the absorbing parameter of the wall, $\alpha\in[0,1]$. The boundary condition at the wall for the continuous system is

$$J\left(x_N,t;x_0\right)=\lambda G\left(x_N,t;x_0\right)\ ,$$

where $J=-D\frac{\partial G}{\partial x}$ is the diffusive flux, λ is the "macroscopic" absorbing parameter of the wall. In this case the Green's function reads

$$G_{--}\left(x,t;x_0\right)=\frac{1}{2\sqrt{\pi Dt}}\left[\exp\left(-\frac{(x-x_0)^2}{4Dt}\right)+\exp\left(-\frac{\left(2x_N-x-x_0\right)^2}{4Dt}\right)\right]$$
$$-\frac{\lambda}{D}\exp\left(\frac{\lambda\left(2x_N-x-x_0+\lambda t\right)}{D}\right)\operatorname{erfc}\left(\frac{2x_N-x-x_0+2\lambda t}{2\sqrt{Dt}}\right)\ . \tag{6}$$

The function (5) become the function (6) in the limit (4) if the following relation is taken

$$\alpha\left(\varepsilon\right)=\exp\left(-\frac{\varepsilon\lambda}{D}\right)\ .$$

For the system of partially permeable wall let us assume a more general form of the function $q=q\left(\varepsilon\right)$

$$q\left(\varepsilon\right)=q_0\exp\left(-\frac{\varepsilon\eta}{D}\right)\ . \tag{7}$$

Since $q\left(\varepsilon\right)\in(0,1]$, then $q_0\in(0,1]$ and $\eta\geq 0$ (we exclude here the trivial case of $q_0=0$). The parameters q_0 and η control the permeability of the membrane. In the following we consider two cases which give the results not equivalent to each other. In the limit of small ε the result depends on the parameter q_0. After the calculations we obtain the following Green's functions for the continuous membrane system [8] (here $x_N=\varepsilon N$ is the location of the membrane, $x_0=\varepsilon m_0$).

For $q_0=1$

$$G_{--}\left(x,t;x_0\right)=\frac{1}{2\sqrt{\pi Dt}}\left[\exp\left(-\frac{\left(x-x_0\right)^2}{4Dt}\right)+\exp\left(-\frac{\left(2x_N-x-x_0\right)^2}{4Dt}\right)\right]$$
$$-\frac{\eta}{D}\exp\left(\frac{2\eta\left(2x_N-x-x_0+2\eta t\right)}{D}\right)\text{erfc}\left(\frac{2x_N-x-x_0+4\eta t}{2\sqrt{Dt}}\right)$$
$$G_{+-}\left(x,t;x_0\right)=\frac{\eta}{D}\exp\left(\frac{2\eta\left(x-x_0+2\eta t\right)}{D}\right)\text{erfc}\left(\frac{x-x_0+4\eta t}{2\sqrt{Dt}}\right)\ .$$

These functions fulfill the boundary conditions

$$J_{--}\left(x_N^-,t;x_0\right)=\eta\left[G_{--}\left(x_N^-,t;x_0\right)-G_{+-}\left(x_N^+,t;x_0\right)\right]\ , \tag{8}$$
$$J_{+-}\left(x_N^+,t;x_0\right)=\eta\left[G_{--}\left(x_N^-,t;x_0\right)-G_{+-}\left(x_N^+,t;x_0\right)\right]\ , \tag{9}$$

where $J_{ij}\left(x,t;x_0\right)=-D\frac{\partial G_{ij}\left(x,t;x_0\right)}{\partial x}$. Let us note that from (8) and (9) we immediately obtain that the flux is continuous at the membrane

$$J_{--}\left(x_N^-,t;x_0\right)=J_{+-}\left(x_N^+,t;x_0\right)\ .$$

For $q_0<1$

$$G_{--}\left(x,t;x_0\right)=\frac{1}{2\sqrt{\pi Dt}}\left[\exp\left(-\frac{\left(x-x_0\right)^2}{4Dt}\right)\right.$$
$$\left.+\delta\exp\left(-\frac{\left(2x_N-x-x_0\right)^2}{4Dt}\right)\right]\ ,\ x,\,x_0<x_N\,, \tag{10}$$

$$G_{+-}\left(x,t;x_0\right)=\frac{\left(1-\delta\right)}{2\sqrt{\pi Dt}}\exp\left(-\frac{\left(x-x_0\right)^2}{4Dt}\right)\ ,\ x>x_N,\,x_0<x_N\ , \tag{11}$$

where the parameter $\delta = q\,(2q-1)^p$ (which does not depend on time) controls the membrane permeability. This parameter is interpreted as a conditional probability of finding the particle in the region $x > x_N$ under the condition that after removing the wall it is found in this region [10]. The Green's functions (10) and (11) satisfy the continuity of the diffusive fluxes at the membrane. Furthermore they generate the second boundary condition which can be formulated in the following two equivalent forms.

1. The ratio of concentrations at the both sides of the membrane is independent of time

$$\frac{G_{+-}\left(x_N^-, t; x_0\right)}{G_{--}\left(x_N^+, t; x_0\right)} = \frac{1-\delta}{1+\delta}\,. \tag{12}$$

2. The flux flowing through the membrane is proportional to the analogous flux flowing in the system with removed membrane

$$J\left(x_N, t; x_0\right) = (1-\delta)\, J_0\left(x_N, t; x_0\right)\,,$$

where $J_0 = -D\frac{\partial G_0}{\partial x}$ is the flux flowing in the system with removed membrane. Equivalence of these boundary conditions means that the solutions of the diffusion equation (1) with these conditions are the same. The boundary condition generated by the functions (10) and (11) can be also formulated in more heuristic form [10]: if during a given time interval some particles reach the membrane placed at point x_N, the fraction δ of them will be stopped while $(1-\delta)$ will go through.

4. Diffusion in the phase-space

To derive the boundary condition at the membrane from the considerations performed in the phase-space, we assume that the distribution function of the diffusing particles $f\,(x, v, t)$ (where x and v are, respectively, the particle position and velocity at the time t), satisfies the relations [12]

$$f\left(x_N^-, -v, t\right) = (1-\beta)\, f\left(x_N^-, v, t\right) + \beta f\left(x_N^+, -v, t\right)\,, \tag{13}$$

$$f\left(x_N^+, v, t\right) = (1-\beta)\, f\left(x_N^+, -v, t\right) + \beta f\left(x_N^-, v, t\right)\,. \tag{14}$$

The terms proportional to $(1-\beta)$ correspond to the reflected particles and those proportional to β to the particles which go through the membrane (β can be treated as a ratio of the total surface of all holes to the membrane surface). Defining the particle flow as $J\,(x,t) = J_+\,(x,t) - J_-\,(x,t)$ with

$$J_+\,(x,t) = \int_0^\infty v f\,(x, v, t)\, dv\,,$$

$$J_-(x,t) = -\int_{-\infty}^{0} vf(x,v,t)\,dv\,,$$

one rewrites the relations (13) and (14) as

$$J_-\left(x_N^-,t\right) = (1-\beta)\,J_+\left(x_N^-,t\right) + \beta J_-\left(x_N^+,t\right)\,,$$

$$J_+\left(x_N^+,t\right) = (1-\beta)\,J_-\left(x_N^+,t\right) + \beta J_+\left(x_N^-,t\right)\,.$$

One observes that adding the partial fluxes we get the conservation of the substance flow at the membrane *i.e.*

$$J\left(x_N^-,t\right) = J\left(x_N^+,t\right)\,.$$

We can decompose the distribution function as [5]

$$f(x,v,t) = f_0(x,v,t) + f_1(x,v,t)\,,$$

where f_0 is the equilibrium distribution function *i.e.*

$$f_0(x,v,t) = \frac{C(x,t)}{\sqrt{2\pi m k_{\mathrm{B}} T}}\exp\left(-\frac{mv^2}{2k_{\mathrm{B}}T}\right)\,,$$

with C, T and k_{B} denoting the concentration of the diffusing particles, temperature and Boltzmann constant, respectively. In contrast to the equilibrium distribution function, which is even ($f_0(x,-v,t) = f_0(x,v,t)$), the function f_1 is assumed to be odd ($f_1(x,-v,t) = -f_1(x,v,t)$). From above relations, after simple calculations we obtain following boundary condition at the membrane

$$J(x_N,t) = -\kappa\left(C\left(x_N^+,t\right) - C\left(x_N^-,t\right)\right)\,, \tag{15}$$

where $J(x_N,t) = J\left(x_N^+,t\right) = J\left(x_N^-,t\right)$, and the membrane permeability coefficient κ is defined as

$$\kappa = \frac{\beta}{1-\beta}\sqrt{\frac{k_{\mathrm{B}}T}{2\pi m}}\,.$$

5. Final remarks

Finding of the boundary condition at the membrane for the case of continuous system appears as a nontrivial problem. The procedure of passing from discrete to continuous system gives two qualitatively different results. We note that within presented formalism there is no possibility to obtain different boundary condition than the ones (8) and (9) (or (15)) and (12). In the paper [13] the time evolution of near-membrane layer has been investigated. The near-membrane layer is a region where the concentration of the substance transported across the membrane is significantly decreased. Its thickness is defined as a length over which the concentration drops γ times with respect to the concentration given at the membrane surface (γ is arbitrary large number). It is shown that within the experimental errors the thickness of the near-membrane layers μ grows in time for any γ as $\rho\sqrt{t}$ with the coefficient ρ being independent of the membrane permeability. From theoretical point of view such a result is obtained on the basis of Green's functions (10) and (11).

For interpretation of the cases considered in Sec. 3, we add that the functions (10) and (11) is also obtained when we put $\eta = 0$ (with $q_0 < 1$) in (7). Then the parameter q does not depend on the ε. Such a situation is possible when the discrete sites N and $N+1$ lay on the membrane surfaces when $\varepsilon \to 0$, so any additional discrete sites between these sites and the membrane surfaces do not appear in this limit. In opposite situation (when $q_0 = 1$), there appear the additional sites between the sites N (and $N+1$) and the membrane surfaces and their number goes to infinity proportionally to $\frac{1}{\varepsilon}$. So, the boundary conditions (8) and (9) rather correspond to the points which are not placed at the membrane surfaces.

The author wishes to express his thanks to Stanisław Mrówczyński for the fruitful discussions and critical comments on the manuscript. This paper was partially supported by the Polish State Committee for Scientific Research (KBN) under Grant No. 2 P03B 129 16.

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