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# MEMBRANE BOUNDARY CONDITION

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Using a microscopic phase-space model of the membrane system, the boundary condition at a membrane is derived. According to the condition, the substance flow across the membrane is proportional to the difference of the substance concentrations at the opposite membrane surfaces. The Green's function of the diffusion equation is found for the derived boundary condition and the exact solution of the equation is given.

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## 1. Introduction

The membrane systems play an important role in several fields of technology [1], where the membranes are used as filters, and biophysics [2], where the membrane transport is crucial for the cell physiology. The diffusion in the membrane system is also interesting by itself as a nontrivial stochastic problem. The process is usually described by means of the diffusion equation. Since the equation is of the second order one needs two boundary conditions at the membrane surfaces. One condition is provided by the conservation of diffusing substance but there is no obvious choice of the second condition. Although several proposals can be found in the literature [3,4] a systematic derivation of the boundary condition within a microscopic model of the process is missing.

While the problem of diffusion in a system with a partially permeable wall (the membrane) is not well explored, there is a vast literature devoted to the systems with (partially) reflecting or (partially) absorbing walls. Two classes of microscopic approaches have been repeatedly used to derive the boundary condition for these cases: the random walk on the discrete lattice, see *e.g.* [5–7], and the diffusion in the (continuous) phase-space, see *e.g.* [8,9]. The first approach starts with the death–birth equation while the second one usually utilizes the Fokker–Planck equation. The results for a membrane system cannot be obtained by a simple modification of those discussed in the literature in context of the (partially) reflecting or (partially) absorbing wall. In these cases, the analysis is performed only for a half-space bounded by the wall while the membrane system demands the full space considerations. Even the half-space membrane subsystem has not much to do with that of the reflecting or absorbing wall. From the microscopic point of view, the most important difference is that the brownian particle once annihilated by the absorbing wall never returns to the system while the particles can pass through the membrane back and forth.

In this note we refer to a simple phase-space model of the membrane system and, following [8, 9], we derive, for the first time to our best knowledge, the boundary condition for the diffusion equation. The condition appears to be rather natural — the substance flow across the membrane is proportional to the difference of the substance concentrations at the membrane. In the second part of our paper we find the Green's function of the diffusion equation which satisfies the derived boundary condition. The exact solution of the equation with a specific initial condition is also given. Finally, our considerations are critically discussed.

## 2. Derivation of boundary condition

Let us consider a system where the substance diffuses across the membrane which is assumed to be a zero width partially permeable wall. The typical thickness of manufactured membrane varies from, say, 0.1 mm to 0.01 mm [1]; the biological membranes are even much thiner [2]. Since, the size of the whole system is usually of order of 1 cm, it is natural to treat, at least as a first approximation, the membrane as infinitely thin. There is also a technical reason for such a treatment. When the membrane is of finite width, one needs to specify an initial substance concentration inside the membrane to solve the diffusion equation. However, the concentration is usually not experimentally accessible and consequently, the model with the finite width membrane is, in practice, not much better than that with the infinitely thin one.

The membrane is located at $x = 0$. Since the concentration gradients are assumed to be only along the $x-$direction the problem is effectively one dimensional. One can imagine the membrane as a reflecting wall with homogeneously distributed holes. Then, the substance particles are either reflected by the wall or pass through it without change of their momenta. We denote by $\alpha$ the ratio of the total surface of all holes to the membrane surface. Then, the probability to pass through the membrane just equals $\alpha$. The limiting case $\alpha = 0$ corresponds to the holeless, not permeable wall while $\alpha = 1$ to the fully permeable wall or to lack of membrane at all. The parameter $\alpha$ is, obviously, independent within our model of the particle velocity.

The distribution function of the substance particles $f(p, x, t)$, where $p$ and $x$ are, respectively, the particle momentum and position at the time $t$, satisfies the relations

$$\begin{aligned} f(-p, 0^-, t) &= (1-\alpha) f(p, 0^-, t) + \alpha f(-p, 0^+, t)\,, && (1) \\ f(p, 0^+, t) &= (1-\alpha) f(-p, 0^+, t) + \alpha f(p, 0^-, t)\,. && (2) \end{aligned}$$

Defining the particle flow and the partial flows as

$$\begin{aligned} j(x,t) &\overset{\text{def}}{=} \int_{-\infty}^{+\infty} dp \frac{p}{m} f(p,x,t)\,, \\ j_+(x,t) &\overset{\text{def}}{=} \int_{0}^{+\infty} dp \frac{p}{m} f(p,x,t)\,, && (3) \\ j_-(x,t) &\overset{\text{def}}{=} -\int_{-\infty}^{0} dp \frac{p}{m} f(p,x,t) && (4) \end{aligned}$$

with $m$ being the particle mass, one rewrites the relations (1), (2) as

$$\begin{aligned} j_-(0^-, t) &= (1-\alpha) j_+(0^-, t) + \alpha j_-(0^+, t)\,, && (5) \\ j_+(0^+, t) &= (1-\alpha) j_-(0^+, t) + \alpha j_+(0^-, t)\,. && (6) \end{aligned}$$

One observes that adding Eqs. (5), (6) and using the formula $j(x,t) = j_+(x,t) - j_-(x,t)$ we get the conservation of the substance flow at the membrane *i.e.*

$$j(0^-, t) = j(0^+, t)\,. \qquad (7)$$

Now, we decompose the distribution function as

$$f(p,x,t) = f_0(p) + f_1(p,x,t)\,, \tag{8}$$

where $f_0(p)$ is the distribution function of local equilibrium *i.e.*

$$f_0(p,x,t) = \frac{n(x,t)}{\sqrt{2\pi m k_{\rm B}T}} \exp\left[-\frac{p^2}{2mk_{\rm B}T}\right]$$

with $T$ and $k_{\rm B}$ denoting the temperature and Boltzmann constant, respectively. In contrast to the equilibrium distribution function, which is even ($f_0(-p) = f_0(p)$), the function $f_1$ is assumed to be odd ($f_1(-p,x,t) = -f_1(p,x,t)$). The decomposition (8), which plays a crucial role in our considerations, can be justified in two closely related ways. One can assume that $f(p,x,t)$ satisfies the Fokker–Planck equation. Then, the decomposition (8) corresponds to the first two terms of the expansion of the distribution function in the large friction limit [9]. One can also refer here to a more general scheme of Chapman–Enskog expansion which is applicable not only to the Fokker–Planck equation. However, the function $f_1$ is not obligatory odd in this case. Nevertheless, this is the odd part of $f_1$ which really matters; the even part does not contribute to the particle flow while its contribution to the particle density can be neglected because $f_0 \gg |f_1|$. At the end of our paper we briefly discuss how our results would be modified if the decomposition (8) is not limited to the two terms.

Substituting the distribution function of the form (8) into Eqs. (3), (4) and applying the Fick law

$$j(x,t) = -D\frac{\partial n(x,t)}{\partial x}\,, \tag{9}$$

where $D$ is the diffusion constant, one finds

$$j_+(0^\pm,t) = \sqrt{\frac{k_{\rm B}T}{2\pi m}}n(0^\pm,t) - \frac{D}{2}\left.\frac{\partial n(x,t)}{\partial x}\right|_{x=0^\pm}\,, \tag{10}$$

$$j_-(0^\pm,t) = \sqrt{\frac{k_{\rm B}T}{2\pi m}}n(0^\pm,t) + \frac{D}{2}\left.\frac{\partial n(x,t)}{\partial x}\right|_{x=0^\pm}\,. \tag{11}$$

The relations (10), (11) allow one to convert Eqs. (5), (6) to the form

$$\begin{aligned}\alpha\sqrt{\frac{k_{\rm B}T}{2\pi m}}\Big(n(0^-,t) - n(0^+,t)\Big) &= -\frac{2-\alpha}{2}D\left.\frac{\partial n(x,t)}{\partial x}\right|_{x=0^-} \\ &\quad +\frac{\alpha}{2}D\left.\frac{\partial n(x,t)}{\partial x}\right|_{x=0^+}\,,\end{aligned} \tag{12}$$

$$\alpha\sqrt{\frac{k_{\mathrm{B}}T}{2\pi m}}\Big(n(0^+,t)-n(0^-,t)\Big) = +\frac{2-\alpha}{2}D\,\frac{\partial n(x,t)}{\partial x}\bigg|_{x=0^+} -\frac{\alpha}{2}D\,\frac{\partial n(x,t)}{\partial x}\bigg|_{x=0^-}\,. \tag{13}$$

As seen, Eqs. (12), (13) provide again the flow conservation (7) and the desired boundary condition

$$j(0,t) = -\kappa\Big(n(0^+,t)-n(0^-,t)\Big)\,, \tag{14}$$

where

$$j(0,t) = j(0^+,t) = j(0^-,t)\,,$$

and the membrane permeability coefficients $\kappa$ is defined as

$$\kappa \equiv \frac{\alpha}{1-\alpha}\sqrt{\frac{k_{\mathrm{B}}T}{2\pi m}}\,. \tag{15}$$

One observes that the boundary condition at a membrane (14) is analogous to the Fick law with the permeability coefficient $\kappa$ (15) being an analogue of the diffusion constant $D$. Within the elementary theory of transport phenomena, see *e.g.* [11], one estimates $D$ as $\overline{v}l$ with $\overline{v}=\sqrt{3k_{\mathrm{B}}T/m}$ being the thermal velocity of the brownian particle and $l$ denoting its mean free path. Then, the diffusion current approximately equals the concentration difference at the mean free path multiplied by $\overline{v}$. Analogously, the diffusive current across the membrane (14) is proportional to the concentration difference at the membrane multiplied by $\overline{v}$. The current across the membrane is additionally modified, when compared to the usual diffusive one, by a factor which is equal, within our mechanical membrane model, to the ratio of the area of all the membrane holes to the area of the reflecting membrane surface. This factor goes to infinity when the reflecting surface vanishes and the membrane effectively disappears. In such a case, however, the concentration difference at the membrane vanishes and the product remains finite.

## 3. Solving the diffusion equation

In this section we are going to solve the diffusion equation

$$\frac{\partial n(x,t)}{\partial t} = D\frac{\partial^2 n(x,t)}{\partial x^2}\,, \tag{16}$$

with the boundary conditions (7), (14) and the initial one given as

$$n(x,0) = n_0(x)\,.$$

We introduce, as usually, the Green's function $G(x,x',t,t')$ which solves the equation

$$\frac{\partial}{\partial t}G(x,x',t,t') = D\frac{\partial^2}{\partial x^2}G(x,x',t,t')\,, \tag{17}$$

with the initial condition

$$\lim_{t\to t'} G(x,x',t,t') = \delta(x-x')\,, \tag{18}$$

and four boundary conditions: two, which are obtained from (7), (14) *i.e.*

$$\left.\frac{\partial}{\partial x}G(x,x',t,t')\right|_{x=0^-} = \left.\frac{\partial}{\partial x}G(x,x',t,t')\right|_{x=0^-} \tag{19}$$

$$-D\left.\frac{\partial}{\partial x}G(x,x',t,t')\right|_{x=0^-} = -\kappa[G(0^+,t;x',t') - G(0^-,t;x',t')]\,, \tag{20}$$

and

$$\lim_{x\to\pm\infty} G(x,x',t,t') = 0\,. \tag{21}$$

Having the Green's function, the solution of the equation (16) is given as

$$n(x,t) = \int dx' n_0(x')G(x,x',t,0)\,. \tag{22}$$

Further, we always put $t'=0$ and denote the Green's function as $G(x,x',t)$.

We find the Green's function applying the standard procedure [10] of the Laplace transformation which gives

$$\widetilde{G}(x,x',s) \overset{\text{def}}{=} \int_0^\infty dt \mathrm{e}^{-st}G(x,x',t)\,.$$

Transforming Eq. (17) and the initial condition (18) we get the equation

$$D\frac{d^2}{dx^2}\widetilde{G}(x,x',s) - s\widetilde{G}(x,x',s) = -\delta(x-x')\,. \tag{23}$$

One trivially finds the general solution of the homogenous equation (23) while the inhomogenous equation is easily solved by means of the Fourier transformation. In this way we get

$$\widetilde{G}(x,x',s) = \frac{1}{2Dq}\mathrm{e}^{-q|x-x'|} + A\mathrm{e}^{qx} + B\mathrm{e}^{-qx}\,,$$

where $q^2 \equiv s/D$ while the constants $A$ and $B$ are determined by the boundary conditions (19), (20), (21). To calculate the constants one has to distinguish four cases related to the signs of $x$ and $x'$. We denote as $G_{++}$ the Green's function which corresponds to $x > 0$ and $x' > 0$; as $G_{+-}$ that one for the case of $x > 0$ and $x' < 0$, *etc.* After inverting the Laplace transform we get

$$\begin{aligned}
G_{+-}(x,x',t) &= G_{-+}(x,x',t) \\
&= \frac{\kappa}{D}\exp\left(\frac{2\kappa(|x-x'|+2\kappa t)}{D}\right)\operatorname{erfc}\left(\frac{|x-x'|+4\kappa t}{2\sqrt{Dt}}\right), \quad (24) \\
G_{++}(x,x',t) &= G_{--}(x,x',t) \\
&= \frac{1}{2\sqrt{\pi D t}}\left[\exp\left(-\frac{(x-x')^2}{4Dt}\right)+\exp\left(-\frac{(x+x')^2}{4Dt}\right)\right] \\
&\quad -\frac{\kappa}{D}\exp\left(\frac{2\kappa(|x+x'|+2\kappa t)}{D}\right)\operatorname{erfc}\left(\frac{|x+x'|+4\kappa t}{2\sqrt{Dt}}\right), \quad (25)
\end{aligned}$$

with erfc($x$) being the complementary error function *i.e.*

$$\operatorname{erfc}(x) = \frac{2}{\sqrt{\pi}}\int_x^\infty dt\, \mathrm{e}^{-t^2} .$$

As an application of the Green's functions (24), (25) we consider the time evolution of the concentration of the substance which is initially homogeneously distributed in the left half-space *i.e.* the initial condition reads

$$n(x,0) = n_0 \Theta(-x) .$$

Then, Eq. (22) provides

$$\begin{aligned}
n_+(x,t) &= n_0 \int_{-\infty}^{0} dx' G_{+-}(x,x',t) \\
&= \frac{n_0}{2}\left[\operatorname{erfc}\left(\frac{x}{2\sqrt{Dt}}\right) - \exp\left(\frac{2\kappa(x+2\kappa t)}{D}\right)\operatorname{erfc}\left(\frac{x+4\kappa t}{2\sqrt{Dt}}\right)\right], \quad (26) \\
n_-(x,t) &= n_0 \int_{-\infty}^{0} dx' G_{--}(x,x',t) \\
&= \frac{n_0}{2}\left[2 - \operatorname{erfc}\left(\frac{-x}{2\sqrt{Dt}}\right) + \exp\left(\frac{2\kappa(-x+2\kappa t)}{D}\right)\operatorname{erfc}\left(\frac{-x+4\kappa t}{2\sqrt{Dt}}\right)\right], \\
& \quad (27)
\end{aligned}$$

where $n_+(x,t) \equiv n(x,t)$ for $x > 0$ and $n_-(x,t) \equiv n(x,t)$ for $x < 0$.

Let us briefly discuss the solution (26), (27). One observes that when $\kappa=0$, which corresponds to the fully reflecting wall, we get from (26), (27) an expected result *i.e.* $n_+(x,t)=0$ and $n_-(x,t)=n_0$. In the opposite limit $\kappa\to\infty$ corresponding to the lack of any membrane, we find the well known formulas:

$$\begin{aligned} n_+(x,t) &= \frac{n_0}{2}\mathrm{erfc}\left(\frac{x}{2\sqrt{Dt}}\right), \\ n_-(x,t) &= \frac{n_0}{2}\left[2-\mathrm{erfc}\left(\frac{-x}{2\sqrt{Dt}}\right)\right]. \end{aligned}$$

Finally, one observes that for $\sqrt{Dt}\gg|x|$ and $\kappa t\gg|x|$ the solution (26), (27) provides

$$n_\pm(x,t)\cong\frac{n_0}{2}\left[1\mp\frac{1}{2\kappa}\sqrt{\frac{\pi D}{t}}\right].$$

Thus, $n_\pm(x,t)=n_0/2$ for $t\to\infty$.

## 4. Discussion

The decomposition (8), which, as already mentioned, plays a key role in the boundary condition derivation, includes only two terms. Since the solution of the Fokker–Planck equation can be systematically expanded in the powers of the inverse friction coefficient, one can easily supplement, following [9], the decomposition (8) by a next order term. Assuming that the Fick law (9) still holds, we again get the current conservation (7) while the equation analogous to (14) reads:

$$\begin{aligned} j(0,t) &+\frac{\alpha}{1-\alpha}\frac{D}{4\sqrt{\pi}\gamma}\left(\left.\frac{\partial^2 n(x,t)}{\partial x^2}\right|_{x=0^+}-\left.\frac{\partial^2 n(x,t)}{\partial x^2}\right|_{x=0^-}\right) \\ &=-\kappa\Big(n(0^+,t)-n(0^-,t)\Big), \end{aligned} \tag{28}$$

where $\gamma$ is the friction coefficient from the Fokker–Planck equation. If, following [8], one treats LHS of Eq. (28) as first two terms of the Taylor expansion of the current at a finite $x$, the boundary condition (28) can be manipulated to the form

$$(1-k)j\Big(-\frac{x_0}{1-k},t\Big)+kj\Big(\frac{x_0}{k},t\Big)=-\kappa\Big(n(0^+,t)-n(0^-,t)\Big), \tag{29}$$

where $k$ is an arbitrary number while $x_0$ denotes the thickness of the kinetic near membrane layer equal

$$x_0=\frac{\alpha}{4\sqrt{\pi}(1-\alpha)\gamma}.$$

Unfortunately, we can not see a way to remove the arbitrarness of $k$ which appears when, due to Eq. (7), we express $j(0,t)$ as $(1-k)j(0^+,t)+kj(0^-,t)$. Such a problem is absent in the formula analogous to (29) for the case of absorbing wall [8]. The results (28), (29) are interesting by themselves but they do not seem to be very useful as membrane boundary conditions. As well known, the diffusion equation provides a reliable description if the Chapman–Enskog expansion converges fast. Then, the third term is not needed in the decomposition (8) and one should use the boundary condition (14). However, the distribution function can significantly deviate from the equilibrium form in the near membrane layer as it happens in the vicinity of the absorbing wall [12]. Then, the boundary condition (29) seems to be natural but the diffusion equation should be combined with the Fokker–Planck for a correct description of the kinetic layer and the whole approach appears to be very cumbersome.

The formula of the membrane permeability coefficient (15) suggests that the permeability grows proportionally to $\sqrt{T}$. However, one should remember that this dependence has been obtained within a highly simplified mechanical model of the membrane which is treated as an infinitely thin reflecting wall with homogeneously distributed holes. Then, the substance particles are either reflected by the wall or pass through it without change of their momenta. In reality, the membrane structure is much more complicated and the parameter $\alpha$ should be treated as an effective probability to pass through the membrane. Consequently, $\alpha$ might be temperature dependent and then $\kappa$ is no longer proportional to $\sqrt{T}$.

In the series of papers of one of us [4], the boundary condition different than (14) has been advocated. Namely, using the symmetry arguments of the Green's function, there has been found instead of (14) the relation:

$$j(0,t) = (1-\delta)j_0(0,t)\,, \tag{30}$$

where $\delta$ is a dimensionless membrane permeability coefficient and $j_0$ is the substance flow in the system with the removed membrane. As discussed in [4], there is a transparent probabilistic interpretation of the relation (30). The solution of the diffusion equation, which satisfies the condition (30) [4], is qualitatively different than that found here. According to the solution, there is a finite flow across the membrane at infinite time while Eqs. (26), (27) give the vanishing flow in this limit.

We hope that an experiment will help to chose a right boundary condition and we plan to perform such an analysis in collaboration with experimentalists. However, one should remember that there is a whole variety of the mechanisms of the substance transport across the membrane [1]. If the boundary condition depends on the actual mechanism the problem does not have a unique solution.

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