Boundary conditions at a thin membrane that generate non–Markovian normal diffusion

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We show that some boundary conditions assumed at a thin membrane may result in normal diffusion not being the stochastic Markov process. We consider boundary conditions defined in terms of the Laplace transform in which there is a linear relation between the probabilities of finding a particle on both membrane surfaces, with coefficient depending on the Laplace transform parameter; a similar assumption also applies to probability fluxes. Such boundary conditions (or boundary conditions equivalent to them) are most commonly used when considering the diffusion in a membrane system. There is derived the criterion to check whether the boundary conditions lead to fundamental solutions of diffusion equation satisfying the Bachelier-Smoluchowski-Chapmann-Kolmogorov (BSCK) equation. If this equation is not met, the Markov property is broken. In particular, it has been shown that the Markov property is broken for the system with one-sided fully permeable membrane and with a partially absorbing membrane. When a probability flux is continuous at the membrane, the general form of the boundary condition for which the fundamental solutions meet the BSCK equation is derived.

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I. INTRODUCTION

One of the most important features of a stochastic process is the Markov property. Although van Kampen mentioned that ‘non-Markov is the rule, Markov is the exception’ [1], it is very often assumed that a modelled process is Markovian, at least ‘approximately’. The Markov process is fully determined by both the conditional probability $P(x, t|x', t')$ of finding a system in a state $x$ at time $t$, provided that at time $t'$ it was in a state $x'$, and the probability $P(x, t)$. If the process is Markovian, then the conditional probability fulfills the Bachelier-Smoluchowski-Chapmann-Kolmogorov (BSCK) equation [2–6]

$$P(x, t|x_0, t_0) = \int_{-\infty}^{\infty} dx' P(x, t|x', t') P(x', t'|x_0, t_0).$$

Thus, if Eq. (1) is not met, there is a non-Markovian process and conditional probabilities $P(x, t|x_1', t_1'; \ldots ; x_n', t_n')$, $n \geq 2$, must be used to describe the process. However, if Eq. (1) is met, it is not obvious if the process is Markovian [1, 4, 5].

Normal diffusion in a system with constant diffusion coefficient $D$ is the Wiener, Markovian, process for which the conditional probability density of finding a diffusing particle at the point $x$ at time $t$ under condition that at the initial moment $t_0$ the particle was at the position $x_0$ depends on the time difference $\delta$ [2, 3]

$$P(x, t|x_0, t_0) \equiv P(x, t-t_0|x_0).$$

In further considerations we assume $t_0 = 0$. The process is described by the normal diffusion equation

$$\frac{\partial P(x, t|x_0)}{\partial t} = D \frac{\partial^2 P(x, t|x_0)}{\partial x^2},$$

the initial condition is $P(x, 0|x_0) = \delta(x - x_0)$. In an unbounded system the boundary conditions read $P(-\infty, t|x_0) = P(\infty, t|x_0) = 0$.

The problem of determining the boundary conditions at a thin membrane has been widely considered, see for example [2, 3] and the references cited therein. Boundary conditions (BCs) at a thin membrane are associated with a certain process of transporting the particle through the membrane. Such a process can be quite complex and cause a disturbance of Markov properties for diffusion of molecules located especially near the membrane. It has been shown [10] that the Riemann–Liouville fractional time derivative of the 1/2 order is involved in boundary conditions for a partially permeable wall for normal diffusion. The fractional time derivative is an integer operator with a ‘long memory’ kernel. Its presence in the subdiffusion equation makes the subdiffusion process non-Markovian [11]. This fact suggests that the presence of fractional time derivative in BC can spoil the Markov property for normal diffusion.

We consider BCs for the probabilities describing diffusion of a single particle. Assuming that particles diffuse independently of one another, the same BCs can be used for concentrations of the particles. We do not consider BCs generating by processes which depend on the particles concentration, e.g. gradual clogging of membrane pores by particles. We consider boundary conditions defined in terms of the Laplace transform of membrane surfaces, with coefficient depending on the Laplace transform parameter; a similar assumption also applies to probability fluxes. Such
II. BACHELIER-SMOLUCHOWSKI-
CHAPMANN-KOLMOGOROV EQUATION IN
TERMS OF THE LAPLACE TRANSFORM

Modelling the diffusion process in a membrane system it is convenient to perform the considerations in terms of the Laplace transform \( \mathcal{L}[\frac{df(t)}{dt}] = \int_0^\infty e^{-st} f(t) dt = \hat{f}(s) \). The Laplace transform of diffusion equation Eq. (3) reads

\[
s\hat{P}(x,s|x_0) - P(x,0|x_0) = \frac{\partial^2 \hat{P}(x,s|x_0)}{\partial x^2}.
\]  

We express Eq. (1) in terms of the Laplace transform. Using the formula Eq. (2), integrating both side of Eq. (1) with respect to \( t' \) in the time interval \( (0,t) \) and putting \( t_0 = 0 \) we obtain

\[
t \hat{P}(x,t|x_0) = \int_{-\infty}^{t} dx' \int_{0}^{t} dt' \hat{P}(x,t-t'|x')P(x',t'|x_0). 
\]  

Thus, if the integral operator kernel in a boundary condition is time-dependent, i.e. it is not given as \( \Phi(t) = \kappa \delta(t) \) which provides \( J(0^-, t|x_0) = \kappa P(0^-, t|x_0) \), the BSCK equation is not met and the diffusion process is non-Markovian.

IV. DIFFUSION IN AN UNBOUNDED SYSTEM

WITH A THIN MEMBRANE

To solve Eq. (1) in both regions separated by the membrane one needs four boundary conditions. We assume that the system is unbounded. Two of the boundary conditions read \( \hat{P}(\infty, s|x_0) = \hat{P}(\infty, s|x_0) = 0 \) and two others are usually fixed at the membrane. In the following we mark the function \( P \) by the indexes \( i \) and \( j \) which indicate the location of the points \( x \) and \( x_0 \), respectively. Assuming that the thin membrane is placed at \( x = 0 \), the indexes \( i \) and \( j \) denote the signs of \( x \) and \( x_0 \), respectively.

The boundary conditions at an assymetrical membrane should be different depending on which part of the system the diffusing particle is located initially. In order to explain this statement let us consider diffusion of two particles \( A \) and \( B \) located symmetrically with respect to the membrane at the initial moment; their probability distributions are denoted as \( P_A(x,t|x_0) \) and \( P_B(x,t|x_0) \), respectively. The probabilities of finding the particle \( A \) in the region \( x < 0 \) and the particle \( B \) in the region \( x > 0 \) at time \( t > 0 \) cannot be equal when the membrane is assymetrical. \( \int_{-\infty}^{0} P_A(x,s|x_0) dx \neq \int_{0}^{\infty} P_B(x,s|x_0) dx \).

This condition is fulfilled only if at least one of the boundary conditions at the membrane is different for the particles \( A \) and \( B \). In the following, boundary conditions will be defined separately for the cases of \( x_0 < 0 \) and \( x_0 > 0 \).

We assume that the boundary conditions at the membrane in terms of the Laplace transform are as follows

\[
\hat{P}_+(0^+, s|x_0) = \hat{P}_1(s) \hat{P}_-(0^-, s|x_0),
\]

\[
\hat{J}_+(0^+, s|x_0) = \hat{\Xi}_1(s) J_-(0^-, s|x_0),
\]
for \( x_0 < 0 \) and
\[
\hat{P}_-(0^-, s|x_0) = \Phi_2(s)\hat{P}_+(0^+, s|x_0),
\]
(13)
\[
\hat{J}_-(0^-, s|x_0) = \hat{Z}_2(0^+, s|x_0),
\]
(14)
for \( x_0 > 0 \), where \( \dot{J}_j(x, s|x_0) = -D\partial_x \hat{P}_j(x, s|x_0)/\partial x \).
We also assume that \( 0 \leq \Phi_1(s), \hat{Z}_1(2) \).

The fundamental solutions to Eq. (4) for the boundary conditions Eqs. (11)–(14) are
\[
\hat{P}_-(x, s|x_0) = \frac{1}{\sqrt{DS}} e^{-|x-x_0|\sqrt{\frac{D}{s}}},
\]
(15)
\[
\hat{P}_+(x, s|x_0) = \frac{\hat{\Phi}_1(s)\hat{\Xi}_1(s)}{\hat{\Phi}_1(s) + \hat{\Xi}_1(s)} \frac{1}{\sqrt{DS}} e^{-|x-x_0|\sqrt{\frac{D}{s}}},
\]
(16)
\[
\hat{P}_+(x, s|x_0) = \frac{\hat{\Phi}_2(s)\hat{\Xi}_2(s)}{\hat{\Phi}_2(s) + \hat{\Xi}_2(s)} \frac{1}{\sqrt{DS}} e^{-(x-x_0)\sqrt{\frac{D}{s}}},
\]
(17)
\[
\hat{P}_+(x, s|x_0) = \frac{1}{\sqrt{DS}} e^{-|x-x_0|\sqrt{\frac{D}{s}}},
\]
(18)
Using the notation of fundamental solutions defined in this paper, Eq. (4) takes the following form
\[
-\frac{d\hat{P}_{ij}(x, s|x_0)}{ds} = \int_{-\infty}^{0} dx'\hat{P}_{-i}(x, s|x')\hat{P}_{-j}(x', s|x_0)
+ \int_{0}^{\infty} dx'\hat{P}_{+i}(x, s|x')\hat{P}_{+j}(x', s|x_0),
\]
(19)
i, j \in \{+, -\}. We define the function \( R_{ij}(x, t|x_0) \) by means of its Laplace transform
\[
\hat{R}_{ij}(x, s|x_0) = -\frac{d\hat{P}_{ij}(x, s|x_0)}{ds}
\]
(20)
From Eqs. (15)–(18) and (20) we get
\[
\hat{R}_{-i}(x, s|x_0) = \frac{1}{2\sqrt{DS}} e^{(x+x_0)\sqrt{\frac{D}{s}}}
\]
\[
\left[ \frac{\hat{\Phi}_1(s)\hat{\Xi}_1(s)}{\hat{\Phi}_1(s) + \hat{\Xi}_1(s)} \left( \frac{\hat{\Phi}_1(s) - \hat{\Xi}_1(s)}{\hat{\Phi}_1(s) + \hat{\Xi}_1(s)} - \frac{\hat{\Xi}_2(s)}{\hat{\Phi}_1(s) + \hat{\Xi}_2(s)} \right)
+ 2s\frac{\hat{\Phi}_1(s)\hat{\Xi}_1(s) - \hat{\Phi}_1(s)\hat{\Xi}_1(s)}{(\hat{\Phi}_1(s) + \hat{\Xi}_1(s))^2} \right].
\]
(21)
\[
\hat{R}_{+i}(x, s|x_0) = \frac{1}{2\sqrt{DS}} e^{-(x-x_0)\sqrt{\frac{D}{s}}}
\]
\[
\left[ \frac{\hat{\Phi}_2(s)\hat{\Xi}_2(s)}{\hat{\Phi}_2(s) + \hat{\Xi}_2(s)} \left( \frac{\hat{\Phi}_2(s) - \hat{\Xi}_2(s)}{\hat{\Phi}_2(s) + \hat{\Xi}_2(s)} - \frac{\hat{\Xi}_1(s)}{\hat{\Phi}_2(s) + \hat{\Xi}_1(s)} \right)
- 2s\frac{\hat{\Phi}_2(s)\hat{\Xi}_2(s) - \hat{\Phi}_2(s)\hat{\Xi}_2(s)}{(\hat{\Phi}_2(s) + \hat{\Xi}_2(s))^2} \right].
\]
(22)
\[
\hat{R}_{++}(x, s|x_0) = \frac{1}{2\sqrt{DS}} e^{-(x-x_0)\sqrt{\frac{D}{s}}}
\]
\[
\left[ \frac{\hat{\Phi}_2(s)\hat{\Xi}_2(s)}{\hat{\Phi}_2(s) + \hat{\Xi}_2(s)} \left( \frac{\hat{\Phi}_2(s) - \hat{\Xi}_2(s)}{\hat{\Phi}_2(s) + \hat{\Xi}_2(s)} - \frac{\hat{\Xi}_1(s)}{\hat{\Phi}_2(s) + \hat{\Xi}_1(s)} \right)
+ 2s\frac{\hat{\Phi}_2(s)\hat{\Xi}_2(s) - \hat{\Phi}_2(s)\hat{\Xi}_2(s)}{(\hat{\Phi}_2(s) + \hat{\Xi}_2(s))^2} \right].
\]
(23)
where \( \hat{\Phi}_1'(s) = d\hat{\Phi}_1(s)/ds \) and \( \hat{\Xi}_1'(s) = d\hat{\Xi}_1(s)/ds \).

The functions \( \hat{\Phi}_{1,2} \) and \( \hat{\Xi}_{1,2} \) provide the fundamental solutions which fulfill the BSCK equation Eq. (19) if
\[
\hat{R}_{ij}(x, s|x_0) = 0,
\]
(25)
for all values of \( i \) and \( j \). Combining the equations \( \hat{R}_{-i}(x, s|x_0) = 0 \) and \( \hat{R}_{+i}(x, s|x_0) = 0 \) we get
\[
\hat{\Phi}_1(s)\hat{\Xi}_1(s) \left( \hat{\Phi}_1(s)\hat{\Phi}_2(s) - 1 \right) = 2s\hat{\Phi}_1'(s),
\]
(26)
\[
\hat{\Phi}_2(s)\hat{\Xi}_1(s) \left( \hat{\Phi}_1(s) + \hat{\Xi}_1(s) \right) \left( 1 - \hat{\Xi}_1(s)\hat{\Xi}_2(s) \right) \left( \hat{\Phi}_2(s) + \hat{\Xi}_2(s) \right) \left( 1 + \hat{\Xi}_1(s) \right)
= 2s\hat{\Xi}_1'(s),
\]
(27)
and from the equations \( \hat{R}_{-+}(x, s|x_0) = 0 \) and \( \hat{R}_{++}(x, s|x_0) = 0 \) we obtain

\[
\hat{\Phi}_2(s)\hat{\Xi}_1(s) \left( \hat{\Phi}_1(s)\hat{\Phi}_2(s) - 1 \right) = 2s\hat{\Phi}_2'(s), \tag{28}
\]

\[
\hat{\Phi}_1(s)\hat{\Sigma}_2(s) \left( \hat{\Phi}_2(s) + \hat{\Xi}_2(s) \right) \left( 1 - \hat{\Xi}_1(s)\hat{\Sigma}_2(s) \right) \left( \hat{\Phi}_1(s) + \hat{\Sigma}_1(s) \right) \left( 1 + \hat{\Xi}_2(s) \right) = 2s\hat{\Sigma}_2'(s). \tag{29}
\]

Solutions to Eqs. \((26)\)–\((29)\) can be found for some special cases only. These equations should be treated as the criterion whether the boundary conditions at the thin membrane Eqs. \((11)\)–\((14)\) lead to the fundamental solutions which fulfill the BSCK equation. Below we consider three specific cases of boundary conditions at the membrane.

1. **Continuous flux at the membrane**

We get the continuous flux at the membrane supposing \( \hat{\Sigma}_1(s) = \hat{\Sigma}_2(s) = 1 \). Then, Eqs. \((26)\) and \((28)\) read

\[
\hat{\Phi}_1(s) \left( \hat{\Phi}_1(s)\hat{\Phi}_2(s) - 1 \right) = 2s\hat{\Phi}_1'(s), \tag{30}
\]

\[
\hat{\Phi}_2(s) \left( \hat{\Phi}_1(s)\hat{\Phi}_2(s) - 1 \right) = 2s\hat{\Phi}_2'(s). \tag{31}
\]

The solutions to Eqs. \((30)\) and \((31)\) are

\[
\hat{\Phi}_1(s) = \frac{1}{\alpha + \eta\sqrt{s}}, \tag{32}
\]

\[
\hat{\Phi}_2(s) = \frac{1}{\alpha + \alpha\eta\sqrt{s}}, \tag{33}
\]

where \( \alpha \) and \( \eta \) are constants, \( \alpha > 0 \). The inverse Laplace transform of Eqs. \((32)\) and \((33)\) for \( \eta \neq 0 \) are

\[
\Phi_1(t) = \frac{1}{\eta} \int_0^\infty \frac{1}{\alpha} e^{-\alpha\tau} \text{erfc} \left( \frac{\sqrt{t}}{\alpha\eta} \right) d\tau, \tag{34}
\]

\[
\Phi_2(t) = \frac{1}{\alpha\eta} \int_0^\infty \frac{1}{\sqrt{Dt}} e^{-\eta^2\tau^2} \text{erfc} \left( \frac{\sqrt{t}}{\eta} \right) d\tau. \tag{35}
\]

where \( \text{erfc}(u) = (2/\sqrt{\pi}) \int_u^\infty e^{-\tau^2} d\tau \) is the complementary error function. Calculating the inverse Laplace transform of Eqs. \((11)\) and \((13)\) we obtain the following boundary conditions in the time domain

\[
P_{--}(0^-, t|x_0) = \int_0^t \Phi_1(t - t')P_{--}(0^-, t'|x_0)dt', \tag{37}
\]

with the kernels of integral operators given by Eqs. \((34)\) and \((35)\). For \( \eta = 0 \) we get \( \Phi_1(t) = \alpha t/\delta(t) \) and \( \Phi_2(t) = \delta(t)/\alpha \).

Boundary conditions Eqs. \((30)\) and \((31)\) may be presented in different forms. Combining Eqs. \((11)\), \((13)\), \((30)\), \((31)\), and using the relation \( \mathcal{L} \left[ \frac{d^\beta f(t)}{dt^\beta} \right] = s^\beta \hat{f}(s) \), \( 0 < \beta < 1 \), where

\[
\frac{d^\beta f(t)}{dt^\beta} = \frac{1}{\Gamma(1 - \beta)} \frac{d}{dt} \int_0^t dt' \frac{f(t')}{(t - t')^\beta} \tag{38}
\]

is the Riemann–Liouville fractional derivative, we get

\[
P_{--}(0^-, t|x_0) = \frac{1}{\alpha} P_{--}(0^+, t|x_0) + \eta \frac{\partial^{1/2} P_{--}(0^+, t|x_0)}{\partial t^{1/2}}, \tag{39}
\]

\[
P_{++}(0^+, t|x_0) = \alpha P_{--}(0^-, t|x_0) + \alpha \eta \frac{\partial^{1/2} P_{--}(0^-, t|x_0)}{\partial t^{1/2}}. \tag{40}
\]

The boundary conditions Eqs. \((39)\) and \((40)\) may be presented in the form not containing a fractional derivative. For \( x_0 < 0 \) the fundamental solutions to the diffusion equations obtained for the boundary condition is the same as for the following boundary conditions: \( J_{--}(0^-, t|x_0) = J_{++}(0^+, t|x_0) \equiv J(0, t|x_0) \) and

\[
J(0, t|x_0) = \lambda_1 P_{--}(0^-, t|x_0) - \lambda_2 P_{--}(0^+, t|x_0), \tag{41}
\]

where \( \lambda_1 = \sqrt{D}/\eta \) and \( \lambda_2 = \sqrt{D}/\alpha \eta \), see \((3)\).

The boundary conditions Eqs. \((39)\), \((39)\), and \((41)\) are equivalent to one another. We have shown that the presence of the time fractional derivative in a boundary condition does not mean that Markov property is disturbed.

2. **One-sided fully permeable**

We consider a thin membrane that is fully permeable to particles diffusing from the region \( x < 0 \) to the region \( x > 0 \) and partially permeable to particles moving in the opposite direction. Then, we suppose that \( \hat{\Xi}_2(s) \equiv \hat{\Phi}_1(s) \equiv 1 \). From Eqs. \((26)\)–\((29)\) we get \( \hat{\Phi}_2(s) = 0 \) or \( \hat{\Phi}_2(s) = 1 \) and \( \hat{\Xi}_2(s) = 0 \) or \( \hat{\Xi}_2(s) = 1 \). This result means that the BSCK equation is fulfilled if the membrane is fully permeable, fully reflecting or fully absorbing for particles diffusing from the right–hand part to left–hand part of the system. If the membrane is one-sided partially permeable we have \( \hat{\Phi}_2(s) \neq 0 \), \( \hat{\Phi}_2(s) \neq 1 \) or/and \( \hat{\Xi}_2(s) \neq 0 \), \( \hat{\Xi}_2(s) \neq 1 \), then Eqs. \((26)\)–\((29)\) are not met and the process is non–Markovian.

3. **Partially absorbing membrane**

When a particle can be absorbed with a certain probability at the membrane, then \( \hat{\Xi}_1(s) = \beta_1 \) and/or \( \hat{\Xi}_2(s) = \beta_2 \).
\( \beta_2 \), where \( \beta_1 \) and \( \beta_2 \) are the absorption probabilities, \( 0 < \beta_1, < 1 \). Assuming additionally that the membrane is not fully absorbing, \( \Phi_{1,2} \neq 0 \), we find that Eqs. (27) and (29) are not met in this case.

V. FINAL REMARKS

We have considered the normal diffusion equation with membrane boundary conditions Eqs. (11)–(14). We have shown that the fundamental solution \( P(x, t|x_0) \) to the diffusion equation fulfills the BSCK equation only if the Laplace transforms of the functions \( \Xi_{1,2} \) and \( \Phi_{1,2} \), that determine the boundary conditions at a thin membrane, fulfill the equations (26)–(28). If the BSCK equation is not met, the stochastic process is not Markovian. It seems that a good measure of how far the diffusion process is from Markov property is the factor

\[
R(x, t|x_0) = \mathcal{L}^{-1}\left[ \sum_{i,j \in (+,-)} |\hat{R}_{ij}(x, s|x_0)| \right]. \tag{42}
\]

Since the functions \( \hat{R}_{ij} \) are controlled by a factor \( e^{-\sqrt{2s}|x_0|+|x_0|} \), the function \( R \) is close to zero when the initial or final position of the particle is far from the membrane. In this case, the effect of the membrane on the 'deterioration of the Markov property' is negligible.

Boundary conditions at the membrane are often assumed without analyzing the process of penetration of a particle through the membrane. However, the boundary conditions are related to a certain process of a particle transport through the membrane, although such a process is not always explicitly defined. If the boundary conditions do not meet Eqs. (26)–(29), this process surely spoils the Markov property.

The Markovian process is described by a conditional probability \( P(x, t|x', t') = P(x, t|x', t')/\int dx' P(x, t|x', t') \), where \( P(x, t|x', t') \) is a two–points probability. In [3] it has been shown that instead of BSCK equation, one can use the relation which involves the normalized correlation functions. To experimentally check whether the BSCK equation is met, a very large number of elements of the four-dimensional matrix \( (x, t; x', t') \) should be determined \( [6] \). However, making such measurements for the diffusion process is very difficult. In [10] there is shown the procedure of experimental derivation of boundary conditions at a thin membrane directly from experimentally obtained concentration profiles of the diffusing substance. Making such measurements is relatively easy to do. Measurements that determine whether the diffusion process under study is Markovian require high precision. It is not obvious if the determination of boundary conditions from experimental data fulfills this condition. It seems reasonable to say that the process for which the experimentally determined functions \( \Phi_{1,2}(s) \) and \( \Xi_{1,2}(s) \) meet Eqs. (26)–(29) can be well approximated by a Markov process.

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[1] N.G. van Kampen, Braz. J Phys. 28, 90 (1998).
[2] C.W. Gardiner, Handbook of stochastic methods for physics, chemistry and the natural sciences, Springer, Berlin (2004).
[3] H. Risken, The Fokker–Planck equation. Methods of solution and applications., Springer, Berlin (1989).
[4] N.G. van Kampen, Stochastic processes in physics and chemistry, North–Holland, Amsterdam (1992).
[5] A. Fuliński, EPL 118, 60002 (2017).
[6] A. Fuliński, J. Phys. A: Math. Theor. 50, 054002 (2017).
[7] W. Feller, Ann. Math. Statist. 30, 1252 (1959).
[8] A. Bobrowski, Convergence of one–parameter operator semigroups in models of mathematical biology and elsewhere, Cambridge UP (2016).
[9] T. Kosztolowicz, Phys. Rev. E 99, 022127 (2019).
[10] T. Kosztolowicz, S. Wąsik, and K.D. Lewandowska, Phys. Rev. E 96, 010101(R) (2017).
[11] R. Metzler and J. Klafter, Phys. Rep. 339, 1 (2000).