DIFFUSION IN GLASSY POLYMERS  
FROM RANDOM WALKS TO  
PARTIAL DIFFERENTIAL EQUATIONS*  

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(Received January 5, 2005)  

Dedicated, with admiration, to Professor Andrzej Fuliński on His jubilee

1D diffusion in glassy polymers with no stresses considered explicitly is studied. A class of different uncorrelated and correlated random walks (RW), described by suitable master equations, is presented. The limiting processes which lead to the set of partial differential equations (PDEs) of parabolic and hyperbolic types generating the “travelling waves” solutions are discussed. Finally, some numerical solutions addressed to diffusion in glassy polymers are discussed.

PACS numbers: 05.40.Fb, 05.10.Ge

1. Introduction

Diffusion in glassy polymers is known as non-fickian “case II diffusion” [1, 2]. In this work we would like to show the molecular basis of some of the equations used in the description of it. First of all, however, to provide some flavour of the process in question, let us comment on a few experimental facts which form a basis of classification of the process under consideration as “case II diffusion”. Namely, there are three such features (see Fig. 1):

• travelling waves form of probability density (concentration) profiles,
• S-shape of kinetic isotherm sorption curve \( \frac{M_t}{M_\infty} \rightarrow \sqrt{t} \),
• straight line form of \( \frac{M_t}{M_\infty} \rightarrow t \) for early times of the process.

* Presented at the XVII Marian Smoluchowski Symposium on Statistical Physics, Zakopane, Poland, September 4–9, 2004.  
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(1595)
Fig. 1. The characteristic features of case II diffusion.

So far there is no direct way of showing how to get from random walk process to partial differential equation generating the listed features of case II diffusion. Some guesses can be made however based on the first of the listed features i.e. travelling wave form of solution.

It is known that there are, at least, three classes of equations for which a suitable random walk process exists i.e.:

(i) Smoluchowski equation of the form

\[
\frac{\partial p}{\partial t} = -c \frac{\partial p}{\partial x} + D \frac{\partial^2 p}{\partial x^2},
\]

or

\[
\frac{\partial p}{\partial t} = -\frac{\partial}{\partial x}(c(x)p) + D \frac{\partial^2 p}{\partial x^2}.\]

(ii) Quasi-linear diffusion equation

\[
\frac{\partial p}{\partial t} = \frac{\partial}{\partial x} \left[ D(p) \frac{\partial p}{\partial x} \right].
\]

(iii) Damped wave equation (hyperbolic Smoluchowski equation)

\[
\frac{\partial p}{\partial t} + \tau \frac{\partial^2 p}{\partial t^2} = \frac{\partial}{\partial x} \left[ D(\cdot) \frac{\partial p}{\partial x} \right],
\]

where \( p \) is the probability density (or concentration of identical, non-interacting particles), and \( D(\cdot) \) stands for \( D, D(t) \) or \( D(x) \) possess the travelling, solitary wave solutions [3–5].
The analysis presented here is mainly applicable to 1D diffusion in glassy polymer membranes where a probability density (concentration) gradient arises within the membrane due to the boundary conditions. It can also be applied to the confined 1D geometries like nanopores. In higher dimensional space, in case there is a local equilibrium in transverse direction to the direction of the probability density gradient (i.e. direction of the diffusion flux) then the 2D/3D problem in confined geometries can be reduced to 1D diffusion problem with energetic and/or entropic barrier [6].

In the next section we shall provide a scheme of how to get from RW to the above mentioned PDEs with the emphasis on the physical “flavour” rather than the mathematical rigour.

2. From RW to PDE

2.1. Unrestricted 1D random walks with Smoluchowski equation as continuous limit

2.1.1. Constant jump probabilities of colliding molecules

The apparent randomness of the motion of molecule is characterised by assuming that each collision independently moves the particle to the right with probability \( \hat{p} \) or to the left with probability \( \hat{q} \), respectively, (where \( \hat{p} + \hat{q} = 1 \)).

If we recall \( p(x,t) \) as a probability of a particle to be at position \( x \) at time \( t \) then we can easily accept that

\[
p(x,t + \tau) = \hat{p}p(x - \delta,t) + \hat{q}p(x + \delta,t),
\]

i.e. that the probability of a particle to be at \( x \) at the time \( t + \tau \) equals the probability that it was at the point \( x - \delta \) at the time \( t \) multiplied by the probability \( \hat{p} \) that it moved to the right in the following step plus the probability that the particle was at the point \( x + \delta \) at the time \( t \) multiplied by the probability \( \hat{q} \) that it moved to the left in the following step.

Fig. 2. An illustration of behaviour of jumping molecule to be found at position \( x \) and time \( t + \tau \) according to Eq. (5).
Expanding all terms of Eq. (5) in a Taylor series with the remainder we get
\[
\begin{align*}
    p(x,t + \tau) &= p(x,t) + \tau p_t(x,t) + O(\tau^2), \\
    p(x \pm \delta,t) &= p(x,t) \pm \delta p_x(x,t) + \frac{1}{2}\delta^2 p_{xx}(x,t) + O(\delta^3).
\end{align*}
\]  
(6)

Substituting (6) into (5) and taking the limits as \(\delta \to 0\) and \(\tau \to 0\) we readily obtain
\[
\frac{\partial p}{\partial t} = -c \frac{\partial p}{\partial x} + D \frac{\partial^2 p}{\partial x^2},
\]  
(7)
i.e. the desired Smoluchowski equation with \(D = \lim_{\delta \to 0}(\delta^2/2\tau)\) and \(c = \lim_{\delta \to 0}(\delta/\tau(\hat{p} - \hat{q}))\).

2.1.2. Position dependent jump probabilities

Extending the results of the previous section we shall consider the random walk process in which probability that a particle located at the point \(x\) moves to the right at the \(i\)-th step is
\[
P(x_i = \delta) = \hat{p}(x) = \frac{1}{2}[1 + b(x)\delta],
\]  
(8)
and the probability that it moves to the left is
\[
P(x_i = -\delta) = \hat{q}(x) = \frac{1}{2}[1 - b(x)\delta].
\]  
(9)

As can be seen from the above \(\hat{p}(x) + \hat{q}(x) = 1\) for any \(b(x)\). On the other hand the choice of \(b(x)\) should provide an obvious relation \(0 \leq \hat{p}, \hat{q} \leq 1\).

Hence, taking into consideration Eqs. (8) and (9) the relation (5) can be altered as follows
\[
p(x,t + \tau) = \hat{p}(x-\delta)p(x-\delta,t) + \hat{q}(x+\delta)p(x+\delta,t),
\]  
(10)
and using Taylor series expansion the final limiting partial differential equation can be obtained
\[
\frac{\partial p}{\partial t} = -\frac{\partial}{\partial x}D[b(x)p] + D\frac{\partial^2 p}{\partial x^2}.
\]  
(11)

Note that for constant \(b\) we get \(c = bD\). It is also worthy to notice that heterogeneous “drift term” provided by Eq. (11) reflects much better the activity of induced stresses in case II diffusion than the constant one (cf. Eq. (7)). Namely, some experimental evidences on shape and placement of the concentration profile can be taken into account in constructing the \(b(x)\) function (it should be given, anyway!) [7].
It is noteworthy that similar 1D Smoluchowski-type equation with position dependent coefficients arises from the reduction of some 2D/3D diffusion problems in confined geometries (e.g. diffusion in the nanopores of smoothly varying cross section area) [6]. In such case the dependence on position accounts for the local inhomogeneity of the membrane.

2.2. Unrestricted 1D random walk with nonlinear (quasi-linear) diffusion equation as continuous limit

As should be expected, in case of nonlinear diffusion equation, the probabilities of a random walker to go right ($\hat{p}$) or left ($\hat{q}$) are concentration (probability density) dependent. We will refer to two cases introduced by Montroll and West [4, 9].

2.2.1. Clannish random walk

Suppose we have a population of two species of random walkers $A$ and $B$ who perform a concurrent 1D random walk characterised by the intensification of the clannishness of the members of one species as the concentration of the other increases. The walk is performed on a horizontal line divided into a number of cells, each of the length $a$, and it is assumed that the density of both species combined is $\rho$, which remains constant. The total numbers of walkers in each cell is $N = \rho a$ (see details in [10]).

A clannishness bias, characterised by a parameter $\alpha$ is introduced such that from a cell of concentration $p$ of $A$’s the probability of an $A$ making its next step to the right is

$$\hat{p} + \alpha(1 - p),$$

while that to the left is

$$\hat{q} - \alpha(1 - p),$$

and, obviously, $\hat{p} + \hat{q} = 1$.

Following the treatment in [10] we finally get

$$\frac{\partial p}{\partial t} = -\frac{\partial}{\partial x} \left[ D \frac{\partial p}{\partial x} - Pp - \psi p(1 - p) \right],$$

(14)

where $D = \text{lim}_{\delta \to 0} (a^2/2\tau)$, $P = \text{lim}_{\delta \to 0} (a(2\hat{p} - 1)/\tau)$, $\psi = \text{lim}_{\delta \to 0} (2\alpha a/\tau)$.

By suitable “rescaling” Eq. (14) can be put in a slightly simpler form. Namely, if

$$\phi = P + \psi \quad \text{and} \quad r = \frac{p\phi}{\psi},$$
then we get
\[
\frac{\partial r}{\partial t} = - \frac{\partial}{\partial x} \left[ D \frac{\partial r}{\partial x} - \psi r(1 - r) \right],
\]
(15)
as an alternative form of the clannish random walk equation.

The clannish random walk resulting in an arbitrary functional drift, was discussed in [8].

2.2.2. Quasi-linear random walk

Very similar arguments lead to the following, quasi-linear diffusion equation as a continuous limit of concentration dependent random walk [9].

\[
\frac{\partial p}{\partial t} = D \frac{\partial^2 p}{\partial x^2} - 2\psi \frac{\partial}{\partial x} \left[ g(p)p \frac{\partial p}{\partial x} \right],
\]
(16)
or
\[
\frac{\partial p}{\partial t} = \frac{\partial}{\partial x} \left[ \hat{D} \frac{\partial p}{\partial x} \right],
\]
(17)
where \( D = a^2/(2\tau) \), \( \psi = (\mu a^2)/\tau \), \( \hat{D} = D - 2\psi g(p)p \), \( g \) is a weighting function, \( \mu \) is a coupling parameter.

As can be seen from the form of diffusion coefficient \( \hat{D} \) there are some possibilities to get the step function like relationship for \( \hat{D}(p) \) needed to reflect the situation in case II diffusion (see Fig. 3). This can be done by a suitable choice of a coupling parameter \( \mu \), negative in this situation.

\[\text{Fig. 3. Concentration profiles for quasi-linear diffusion equation. Early time solution to Eq. (16) for } p(x,0) = 0, p(0,t) = 1 \text{ and } D(p) = 50.5 + 49.5 \tanh((p - 0.8)/0.05).\]
2.3. Unrestricted 1D random walk with hyperbolic Smoluchowski equation as continuous limit

In this section we will consider the correlated random walk i.e. when
\[ \langle x_i x_j \rangle \neq 0 \quad \text{for any} \quad i, j \quad (18) \]
holds, and the correlation coefficient reads
\[ \rho(x_i, x_j) = \frac{\langle (x_i - \langle x_i \rangle)(x_j - \langle x_j \rangle) \rangle}{[V(x_i)V(x_j)]^{\frac{1}{2}}} \quad (19) \]

Assuming partial correlations between two non-adjacent random variables \( x_i \) and \( x_j \) (i.e. \( |j - i| > 1 \)) are equal to zero, and identical distribution of random variables, we have
\[ \rho(x_i, x_{i+1}) = \rho \quad (20) \]
and consequently
\[ \rho(x_i, x_{i+k}) = \rho^k \quad (21) \]

Following [11] we can write
\[ \langle x^2 \rangle = \left( \frac{\delta^2}{\tau} \right) \left[ 1 + \rho \tau t - \frac{2\rho(1 - \rho^\frac{1}{2})\tau^2}{(1 - \rho)^2} \right] \quad (22) \]
where \( \delta \) is the particle jump within time \( \tau \) and they both tend to zero. Assuming further that \( \lim(\delta/\tau) = \gamma \) is finite (the particle velocity) we get
\[ \lim_{\tau \rightarrow 0} \left( \frac{\tau}{1 - \rho} \right) = \frac{1}{2\lambda} \quad \lambda > 0 \quad (23) \]
to provide, a finite non-zero limit for Eq. (22). Following Ornstein and Uhlenbeck [12] we also have
\[ \lim_{\tau \rightarrow 0} \left( \rho^\frac{1}{2} \right) = e^{-2\lambda t} \quad (24) \]
so, finally, Eq. (22) tends to
\[ \langle x^2 \rangle = \frac{\gamma^2}{\lambda} \left[ t - \frac{1}{2\lambda} \left( 1 - e^{-2\lambda t} \right) \right] \quad (25) \]
Let us observe that equation (25) gives
\[ \langle x^2 \rangle = Dt \quad (26) \]
where $D = \gamma^2/\lambda$ for large values of time i.e. the result from Section 2.1.1, and for small times, on expanding $e^{-2\lambda t}$ in a Maclaurin series Eq. (25) gives

$$\frac{\sqrt{\langle x^2 \rangle}}{t} \approx \gamma,$$

which says that the motion of the particle is nearly uniform with speed $\gamma$. Following the approach of [11] we shall show how to construct the set of “master equations” and their limiting PDE that characterises the correlated RW described.

Let $\alpha(x, t)$ be the probability that a particle is at point $x$ at time $t$ and arrived there from the left, whereas $\beta(x, t)$ is the probability that a particle is at $x$, and arrived there from the right. Let also define probability that the particle persists in its direction after completing a stop by $\hat{p}$, and by $\hat{q}$ the probability that the particle reverses its direction. Probabilities $\hat{p}$ and $\hat{q}$ are constant and their sum equals 1. With step $\delta$ occurring in time $\tau$ we get (see Fig. 4)

$$\alpha(x, t + \tau) = \alpha(x - \delta, t)\hat{p} + \beta(x - \delta, t)\hat{q},$$

$$\beta(x, t + \tau) = \beta(x + \delta, t)\hat{p} + \alpha(x + \delta, t)\hat{q}.$$  

Fig. 4. An illustration of behaviour of jumping molecule to be found at position $x$ and time $t + \tau$ according to Eqs. (28), (29).

Following [3,11] one can get from Eqs. (28) and (29) the coupled system of first order PDEs

$$\frac{\partial \alpha}{\partial t} = -\gamma \frac{\partial \alpha}{\partial x} - \lambda \alpha + \lambda \beta,$$

$$\frac{\partial \beta}{\partial t} = \gamma \frac{\partial \beta}{\partial x} + \lambda \alpha - \lambda \beta,$$

describing probability density functions for right and left moving particles, respectively.
2.3.1. Constant particle velocity, $\gamma = \text{const.}$

This case, by the postulate $\gamma = \text{const.}$, refers to homogeneous space within which the molecule walks randomly. As we already have seen from Fig. 4 the probability density distribution of a moving particle $p(x, t)$ is a sum of $\alpha$ and $\beta$

$$p(x, t) = \alpha(x, t) + \beta(x, t).$$  \hspace{1cm} (32)

The system (30) and (31) along with the proper initial conditions constitute an initial value problem (IVP) that can be solved directly. However, to compare our results with those of the previous sections we need to get the suitable PDE of second order. To do that we simply follow [3], to get finally

$$\frac{\partial p}{\partial t} + \tau \frac{\partial^2 p}{\partial t^2} = D \frac{\partial^2 p}{\partial x^2},$$  \hspace{1cm} (33)

i.e. hyperbolic diffusion equation where $\tau = 1/(2\lambda)$ and $D = \gamma^2/(2\lambda)$.

2.3.2. Position dependent particle velocity, $\gamma = \gamma(x)$

This case refers to spatially inhomogeneous, correlated random walk problem. Assuming $\lambda = \text{const.}$ and $\gamma = \gamma(x)$ we get

$$\frac{\partial \alpha}{\partial t} = -\gamma(x) \frac{\partial \alpha}{\partial x} - \lambda \alpha + \lambda \beta,$$

$$\frac{\partial \beta}{\partial t} = \gamma(x) \frac{\partial \beta}{\partial x} + \lambda \alpha - \lambda \beta.$$  \hspace{1cm} (34, 35)

Following essentially the same procedure we arrived at the “Smoluchowski type” hyperbolic diffusion equation

$$\frac{\partial p}{\partial t} + \tau \frac{\partial^2 p}{\partial t^2} = D(x) \frac{\partial^2 p}{\partial x^2} + \frac{1}{2} D'(x) \frac{\partial p}{\partial x},$$  \hspace{1cm} (36)

where prime indicates differentiation with respect to $x$. Please, note that the form of $D(x)$ function provides modelling of both: attractive forces when $D(x)$ is an increasing function of $x$ and repulsive forces otherwise.

2.3.3. Time dependent particle velocity, $\gamma = \gamma(t)$

This case describes the particle movement under the force which does not follow the Stokes law [13], like in the case of $\gamma = \text{const.}$, but offers the diffusion in the time dependent potential. Assuming $\lambda = \text{const.}$ and $\gamma = \gamma(t)$ we get

$$\frac{\partial \alpha}{\partial t} = -\gamma(t) \frac{\partial \alpha}{\partial x} - \lambda \alpha + \lambda \beta,$$

$$\frac{\partial \beta}{\partial t} = \gamma(t) \frac{\partial \beta}{\partial x} + \lambda \alpha - \lambda \beta.$$  \hspace{1cm} (37, 38)
Also in this case the procedure from the previous section holds \textit{i.e.} adding Eqs. (37) and (38) and next subtracting one from another, and differentiation with respect to \( t \) and \( x \), respectively, yields the following equation

\[
\frac{\partial p}{\partial t} + \tau \frac{\partial^2 p}{\partial t^2} = D(t) \frac{\partial^2 p}{\partial x^2} + \frac{1}{2} D'(t) \frac{\partial p}{\partial x},
\]  

(39)

where prime indicates differentiation with respect to time. Also here both types of forces can be modelled, \textit{i.e.} attractive and repulsive.

As we have seen from the above there are quite a few possibilities of providing a molecular view of travelling wave behaviour of a probability density. In the next paragraph we shall show how it looks like on a phenomenological level \textit{i.e.} we shall present some numerical solutions of the aforementioned PDEs\textsuperscript{1}.

### 3. Results and discussion of numerical solutions

We shall restrict our analysis to one initial and boundary value problem (IBVP) \textit{i.e.} to unsymmetrical sorption which formulation can be presented in the following form

\[
\begin{cases}
\hat{A} p = 0, & \quad x \in (0,l), \quad t \in \mathbb{R}^+ \\
p(x,0) = 0, & \\
p(0,t) = p_0, & \\
\text{flux } |_{x=l} = 0, & 
\end{cases}
\]

(40)

where \( \hat{A} \) stands for differential operator which takes the form of Eqs. (1)–(4).

#### 3.1. The simplest Smoluchowski equation

In this case the \( \hat{A} \) takes the form

\[
\hat{A} \equiv \frac{\partial}{\partial t} + c \frac{\partial}{\partial x} - D \frac{\partial^2}{\partial x^2}.
\]

(41)

Our intention is to demonstrate that Eq. (1) can reproduce the main features of case II diffusion (\textit{cf.} Fig. 1) for a suitably chosen drift constant \( c \) (see Fig. 5)

Note, that the value of drift coefficient represents the constant force (the negative derivative of linear potential field) supporting the diffusional movement of a Brownian particle.

\textsuperscript{1} The divergence form of Eqs. (36), (39) will be discussed in Appendix.
3.2. Smoluchowski equation with position dependent drift term

Let us observe that operator (42) offers description with inhomogeneous drift i.e. the force under which the Brownian molecule moves depends upon position [7]. In Fig. 6 we present the family of solutions of the problem (40) with $\hat{A}$ given by Eq. (42) for different $b(x) = \{1 + \varepsilon x^2\}$ where $\varepsilon$ is a constant. The choice of particular relation for $b(x)$ depends on “physical” analysis of the situation in question. For example $b(x)$ as a negative function on $x$ describes Brownian motion with a particle subjected to an elastic “restoring” force.

$$\hat{A} \equiv \frac{\partial}{\partial t} + c \frac{\partial}{\partial x} Db(x) - D \frac{\partial^2}{\partial x^2}.$$

(42)

It is quite evident that in case of $x$-dependent drift we can have diffusion enhanced by a drift (positive sign) or drift acting opposite to diffusion (negative sign).
3.3. Hyperbolic diffusion with constant $D$

This equation is known to eliminate the infinite speed of a particle in Brownian motion by the usual parabolic equation, that is definitely not realistic [14]. This is also well known that this equation, known as damped wave equation, generates the "travelling wave solution" or d’Alembert solution [15]. Therefore, the features shown in Fig. 7 are quite expected provided the relaxation time $\tau$ is sufficiently large, usually in the order of minutes.

It should be noticed that case II diffusion features are reproduced only for $\tau \geq 1$.

3.4. Hyperbolic diffusion with $x$ dependent $D$

The process represented by Eq. (36) is, in fact, hyperbolic inhomogeneous diffusion with inhomogeneous drift. As can be seen from Fig. 8 the manifestation of the spatial inhomogeneity takes place for sufficiently large $x$.

The choice of $D(x)$ dependence should depend on the case in question, and has to be verified by experimental data.

Fig. 6. Case II diffusion features reproduced by Smoluchowski equation with $x$-dep drift. Time evolution of $p(x, t)$ profiles for $\varepsilon = -9$; comparison of $p(x, t)$ profiles for different values of $\varepsilon$, where $b(x) = 1 + \varepsilon x^2$ and mass uptake as a function of time and square root of time.
Fig. 7. Case II diffusion features reproduced by hyperbolic diffusion with constant $D$ and different relaxation times $\tau$, according to Eq. (33).

Fig. 8. Case II diffusion features reproduced by hyperbolic diffusion with position dependent $D$, according to Eq. (36), where $\varepsilon$ is a parameter in expression on $D(x) = 1 + \varepsilon x$ and $\tau = 0.1$.
3.5. Hyperbolic diffusion with time dependent $D$

The case is, almost by definition, addressed to glassy polymers where the time dependent (relaxation) phenomena are the generic features [1, 16–18]. Like previously, the process of transport represented in this case by Eq. (39) is of Smoluchowski type i.e. it contains also the drift term.

As can be seen from Fig. 9 the influence of $t$-dependent coefficients in the set of plots is mild but significant. It is also quite visible that heterogeneity i.e. $x$-dependence is a more sensitive property than the time dependence.

4. Concluding remarks

In this paper we have extended an analysis of microscopic view of diffusion in a potential field (stresses). We have shown how to get from random walk to partial differential equation of second order for cases where jump probability depends upon position, time or presence of other particles. One of the main points in our analysis was an observation that stress field induced by the diffusing molecules is a potential field at least in Hooke’s law regime. That gave a solid basis for Smoluchowski type equations which have been used throughout the paper, supporting the existence of a “drift
term” i.e. deterministic part of a mass transport operator in question. On the other hand we have provided quite a few ways of expressing correlation (i.e. an active way of taking into account the presence of other molecules). Namely, in a standard way by assuming (18), we have arrived at the hyperbolic Smoluchowski equation. By letting the probability of randomly walking molecules to be $x, t$ or concentration dependent, we have been able to generate the class of PDEs as continuous limits of correlated (in a more general sense) random walk.

The main purpose of our analysis, however, was to provide an explanation of case II diffusion. As can be clearly seen from Fig. 3 the quasi-linear RW gives the travelling waves form of concentration profiles. Decreasing velocity of these waves provides, however, no possibility of reproducing the two other features of case II [1, 2]. The full reproduction is provided by the set of parabolic Smoluchowski equations (Eqs. (41), (42)) as well as by hyperbolic type of diffusion equations (Eqs. (33), (36), (39)).

It is worthy to realize that both approaches are applicable to glassy polymers below their glass transition temperatures $T_g$ (or for penetrant concentration below critical value $c^*$). A very interesting approach to diffusion through nanopores in glassy polymers below their $T_g$ was presented only recently [19, 20]. Above $T_g$ the polymer changes itself to elastic state in which stresses relax (almost) instantaneously. Hence no stress field can exist there for prolonged periods of time. We claim, however, that even for polymers undergoing glass transition induced by diffusing particles our approach is still valid for layers of glassy polymer ahead of the case II diffusive front. Strong stresses there have been confirmed experimentally (resulting in cracks and crazes in the polymer) supporting the approach presented in this paper.

This work was partially supported by Silesian University of Technology grant number BW-422/RCh4/2004.

Appendix A

As it is well known the condition for mass conservation i.e. the continuity equation, reads

$$ \frac{\partial p}{\partial t} = -\frac{\partial J}{\partial x}, \quad (A.1) $$

where $p(x,t)$ is the probability density (concentration), and $J(x,t)$ is the flux.
All equations discussed in this paper fulfil this condition although not in all cases it is obvious. For the hyperbolic diffusion equation it reads

\[
\frac{\partial p}{\partial t} = -\frac{\partial}{\partial x} \left( -D \frac{\partial p}{\partial x} - \tau \frac{\partial J}{\partial t} \right)
\]  \hspace{1cm} (A.2)

and

\[
\frac{\partial p}{\partial t} = D \frac{\partial^2 p}{\partial x^2} + \tau \frac{\partial^2 J}{\partial t \partial x}.
\]  \hspace{1cm} (A.3)

Taking into account equation (A.1), we can get

\[
\frac{\partial^2 J}{\partial t \partial x} = -\frac{\partial^2 p}{\partial t^2},
\]  \hspace{1cm} (A.4)

what finally gives

\[
\frac{\partial p}{\partial t} + \tau \frac{\partial^2 p}{\partial t^2} = D \frac{\partial^2 p}{\partial x^2}.
\]  \hspace{1cm} (A.5)

In case of Smoluchowski hyperbolic diffusion equations \(i.e.\) with drift, the flux is given by the equation

\[
J(x,t) = -D(t) \frac{\partial p}{\partial x} + k(t)p - \tau \frac{\partial J}{\partial t},
\]  \hspace{1cm} (A.6)

where \(k(t) = 1/2D'(t)\).

For position dependent case we have to write

\[
J(x,t) = -D(x) \frac{\partial p}{\partial x} + kp - \tau \frac{\partial J}{\partial t},
\]  \hspace{1cm} (A.7)

where \(k\) is a constant drift coefficient. This allows only linear dependence of \(D\) upon \(x\) \(i.e.\) \(D(x) = D_0(1 + \varepsilon x)\). This assumption leads to

\[
\frac{\partial p}{\partial t} + \tau \frac{\partial^2 p}{\partial t^2} = \frac{\partial}{\partial x} \left[ D(x) \frac{\partial p}{\partial x} - \frac{1}{2} D'(x)p \right],
\]  \hspace{1cm} (A.8)

\(i.e.\) \(k = 1/2D'(x) = 1/2\varepsilon D_0\).

Note: In numerical calculations \(D_0 = 1\).

It is noteworthy that a general method to show that a diffusion equation fulfils the mass conservation law (\(i.e.\) is in agreement with the continuity equation) requires a proof that the diffusion flux \(J\) in the equation is exactly the same as the flux entering the dissipation or the entropy production of the particular diffusion process [21].
REFERENCES