Chapter 7. The Relaxation Effect of Gradient Flows in Nanoporous Media

Abstract

This chapter is devoted to the process of diffusion of matter with a simple initial distribution. Unlike conventional ways of tackling non-zero relaxation times of diffusive flows are taken in account. That could be the case within a porous media. According to the hypothesis proposed the mechanism of striking a balance of current is believed to be its convolution with exponential kernel (see eq. (7-2)). Under the assumptions made, we derive the equation describing the process. To model the problem 2nd and 3rd kind boundary conditions are chosen. For the resulting equation to be numerically solved finite difference method is used.

KEYWORDS: *diffusive flow relaxation time; porous medium; finite difference method, 2nd and 3rd boundary conditions*

Nomenclature

α in section 7.1 is a spatial coordinate number, taking 1,2 or 3 as its value; whereas in all the other sections it is referred to proportionality factor in the «source term» of problem's equation (7-4)

β one more proportionality factor (see eq. (7-4))

Δt distance between two adjacent samples on the t-axis

Δx distance between two adjacent samples on the x-axis

ℓ geometrical size of 1D-problem

τ relaxation time of gradient flows

τ_{diff} $\sim \frac{\ell^2}{D}$ - characteristic diffusion time (time required for diffusion over the volume, twice of the original size)

ε magnitude of the last term in partial sum of Fourier series

J gradient flow magnitude

n concentration of matter

t time variable

x spatial coordinate

7.1 Model

Assuming the number of particles is preserving, we consider its continuity equation

$$\partial_t n + \partial_\alpha J^\alpha = 0 \tag{7-1}$$

In our model gradient flow is assumed to be as follows

$$J^\alpha = -K * \partial_\alpha n$$

Its expanded form

$$J^{\alpha} = -\int_0^t K(t-t')\partial_\alpha n(t')dt'$$

Here K is given as

$$K(t) = \frac{D}{\tau}\exp\left(-\frac{t}{\tau}\right) \tag{7-2}$$

Apply Fourier transform with respect to the time variable to (7-1)

$$-i\omega n_\omega - \partial_\alpha\partial_\alpha n_\omega \cdot \frac{D}{1-i\omega\tau} = 0$$

Re-arrange the terms

$$[1+\tau(-i\omega)](-i\omega n_\omega) - D\Delta n_\omega = 0$$

And make back transformation to the time domain in order to get the following result

$$(1+\tau\partial_t)\partial_t n - D\Delta n = 0 \tag{7-3}$$

7.2 Mathematical Statement

For the sake of simplicity we treat one-dimensional task

$$\begin{cases} \dfrac{\partial n}{\partial t} \ + \ \tau \dfrac{\partial^2 n}{\partial t^2} \ + \ \alpha(n - n^*) = \ D\dfrac{\partial^2 n}{\partial x^2} \\ n|_{t=0} = n(x), \qquad\qquad n_t|_{t=0} = 0 \\ (n_x - \beta n)|_{x=0} = 0, \ \ n_x|_{x=\ell} = 0 \end{cases} \tag{7-4}$$

We consider the system evolution within a volume of size ℓ. Initial distribution $n(x)$ (see figure 7-1) is chosen to be

$$n(x) = H(x) - H\left(x - \frac{\ell}{2}\right) \tag{7-5}$$

where $H(x)$ is the Heaviside step function

$$H(x) = \begin{cases} 1, \ \text{if } x > 0 \\ 0, \ \text{else} \end{cases} \tag{7-6}$$

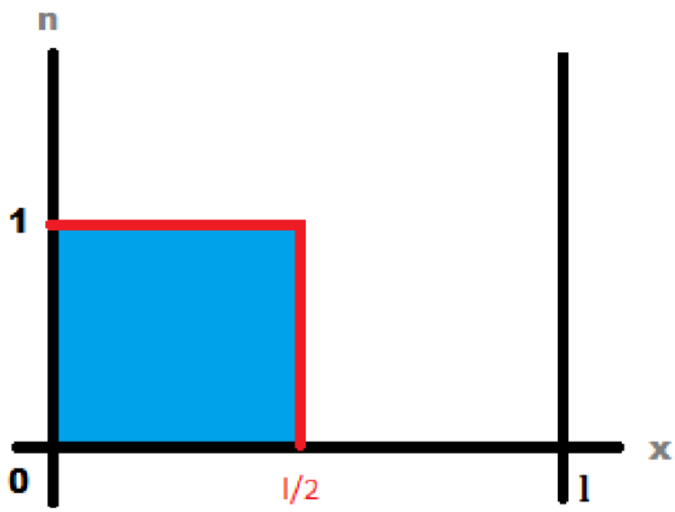

Figure 7-1: Initial matter distribution

The term $+\alpha(n - n^*)$, not presented in section 7.1, and which appears here in (7-4), stands for sources\sinks that might be in the volume defined.

As for boundary constraints, the Robin and the Dirichlet conditions are set on the left and right borders respectively.

7.3 Analytical Solution

We look for the solution of the following form

$$n(t,x) \sim \sum_k \theta_k(t) X_k(x) \tag{7-7}$$

In this way the problem (7-4) is divided into 2 parts

$$
\begin{cases}
X_k''(x) + \lambda_k X_k(x) = 0 \\
X_k'(0) - \beta X_k(0) = 0,\ X_k'(\ell) = 0 \\
X_k(x) \not\equiv 0
\end{cases}
\tag{7-8}
$$

$$
\begin{cases}
\theta_k''(t) + \frac{1}{\tau}\theta_k'(t) + \lambda_k \frac{D}{\tau}\theta_k(t) + \alpha\theta_k = B_k \\
\theta_k(0) = A_k,\ \theta_k'(0) = 0 \\
\theta \not\equiv 0
\end{cases}
\tag{7-9}
$$

$$
{}^{1}A_k = \frac{(n(x), X_k)}{(X_k, X_k)}, \quad B_k = \frac{(\alpha n^*, X_k)}{(X_k, X_k)}
$$

The first one, (7-8), which is also renown as a Sturm–Liouville problem, has the solution

$$
X_k(x) = \beta \sin \sqrt{\lambda_k} x + \sqrt{\lambda_k} \cos \sqrt{\lambda_k} x
$$

$$
\lambda_k = \left(\frac{z_k}{\ell}\right)^2
$$

where z_k is k-th (from the origin) root of the equation below

$$
z = \beta\ell \cot z
$$

The solution of the latter task (7-9) is a bit cumbrous since it de-

[1] $\langle \bullet, \bullet \rangle$ - an inner product given for any two elements f and g by

$$
\langle f, g \rangle = \int_0^\ell f(x) g(x) dx
$$

pends on the d_k's sign

$$
\begin{gathered}
d_k \equiv 1 - 4\tau\left(\alpha + \lambda_k D\right) \\
C_1 := A_k - \frac{B_k}{\alpha + \lambda_k D} \\
\lambda_0 = \frac{1}{2\tau}
\end{gathered}
$$

- $d_k = 0$

$$
\begin{gathered}
\theta_k(t) = (C_1 + C_2 t)\exp(-\lambda_0 t) \\
C_2 := \lambda_0 C_1
\end{gathered}
$$

- $d_k > 0$

$$
\begin{gathered}
\theta_k(t) = \exp(-\lambda_0 t)\left[C_1 \cosh \lambda_0 \sqrt{d_k} t + C_2 \sinh \lambda_0 \sqrt{d_k} t\right] \\
C_2 := C_1 / \sqrt{d_k}
\end{gathered}
$$

- $d_k < 0$

$$
\begin{gathered}
\theta_k(t) = \exp(-\lambda_0 t)\left[C_1 \cos \lambda_0 \sqrt{-d_k} t + C_2 \sin \lambda_0 \sqrt{-d_k} t\right] \\
C_2 := C_1 / \sqrt{-d_k}
\end{gathered}
$$

7.4 Finite Difference Method

To model the problem (7-4) the explicit scheme with order $O(\Delta t^2, \Delta x^2)$ is used

$$\frac{f_i^{n+1} - f_i^{n-1}}{2\Delta t} \;+\; \tau \frac{f_i^{n+1} - 2f_i^n + f_i^{n-1}}{\Delta t^2} - \\ -\; D\frac{f_{i+1}^n - 2f_i^n + f_{i-1}^n}{\Delta x^2} \;+\; \alpha(f_i^n - n^*) = 0$$

Re-arranging the terms gives us

$$f_i^{n+1} = \frac{1}{1+\gamma}\big[(f_i^{n-1} \;+\; \gamma(2f_i^n - f_i^{n-1}) + \\ +\; \mu(f_{i+1}^n - 2f_i^n + f_{i-1}^n) \;+\; 2\kappa(f_i^n - n^*)\big] \tag{7-10}$$

with the notion imposed

$$\gamma \equiv 2\frac{\tau}{\Delta t} > 0, \quad \mu \equiv 2\frac{D\Delta t}{\Delta x^2} > 0, \quad \kappa \equiv \alpha\Delta t$$

The studies on the scheme sustainability carried out with the use of the spectral representation result in the following constraints

$$\begin{gathered} \kappa \geq 0 \\ \kappa + 2\mu \leq 2\gamma \end{gathered} \tag{7-11}$$

7.5 Results

Although the choice of such initial distribution has significantly simplified the problem of finding the analytical solution, it does not in any way make a modeling of the process somehow easier on the part of numerical aspect. According to Godunov's order barrier theorem, linear methods cannot provide non-oscillatory solutions higher than first order. For either problem where there is a steep gradient the monotonicity of exact solution is not preserved. Since $n(x)$ has a discontinuity (see figure 7-1 or eq. (7-5), (7-6)), the arising small[2] spurious oscillations take place on the graphs of numerical solution and cannot be reduced by grinding mesh sizes. The consideration of ways of their elimination is beyond the scope of this work. Also you may notice that some oscillations are present on the curves of analytical solution as well. The fact is that the convergence rate of Fourier coefficients of function directly depends on its smoothness. In particular the coefficients of the piecewise defined function $n(x)$ converge sublinearly. So, if desired, these oscillations can be completely eliminated with an appropriate decrease in the parameter ε, however the program execution may consume much more time.

To model the process two possible cases are chosen: with sources$\backslash$sinks and without them. For the former case we also consider the situations when the relaxation effect of current can be neglected and when it takes the dominant role - to make sure that everything goes on as it should. The results of all calculations are given below.

[2]where the sharp slope is not being kept for a long time

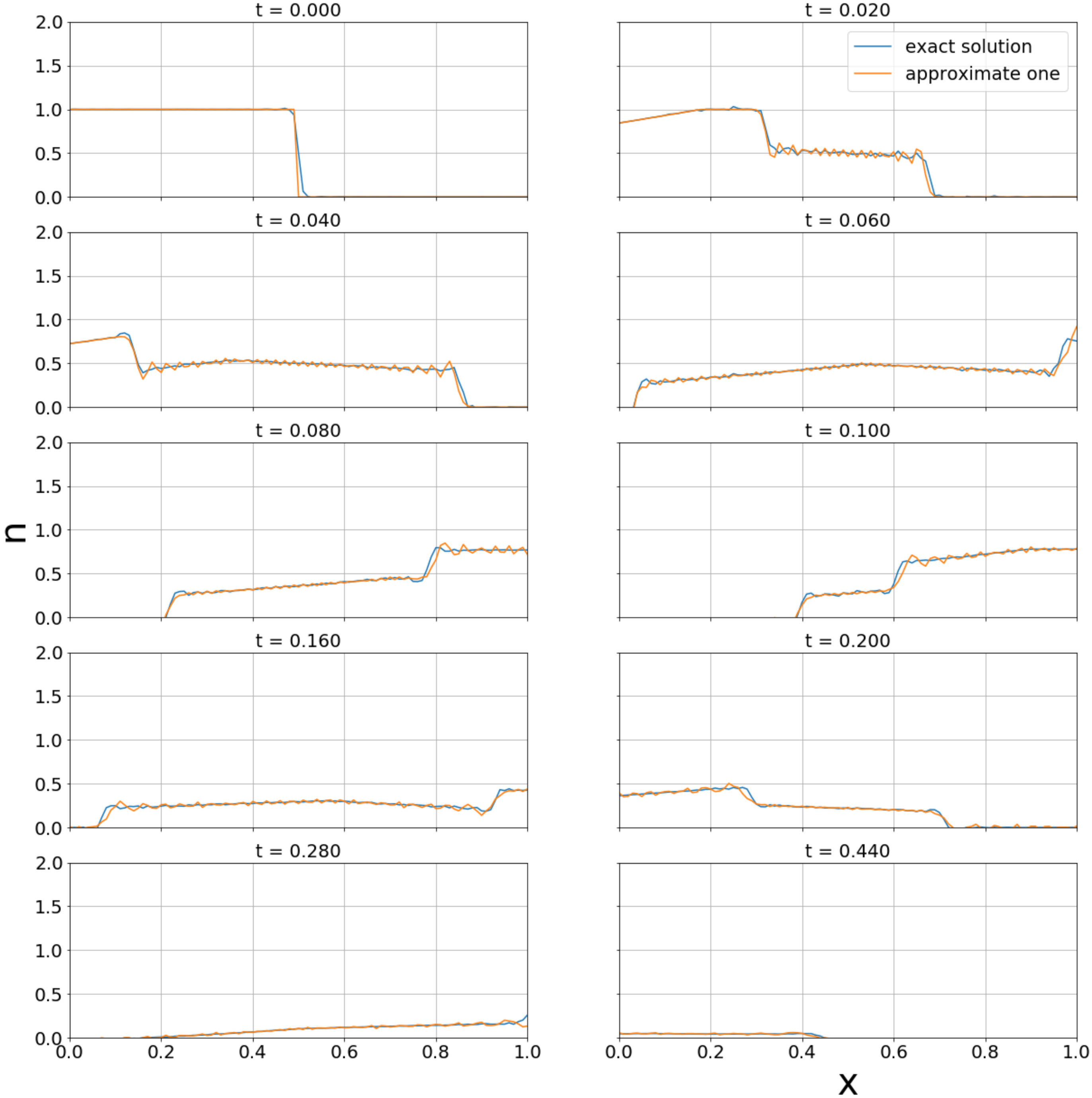

Figure 7-2: The graphs series above presents the course of the process in the absence of any sources ($\alpha = 0$). The calculations are made for the following set of parameters:
$\Delta x =$1E-2, $\Delta t =$1E-3, $\tau = 0.1$, $D = 8$, $\beta = 1$, $\varepsilon =$ 1E-6

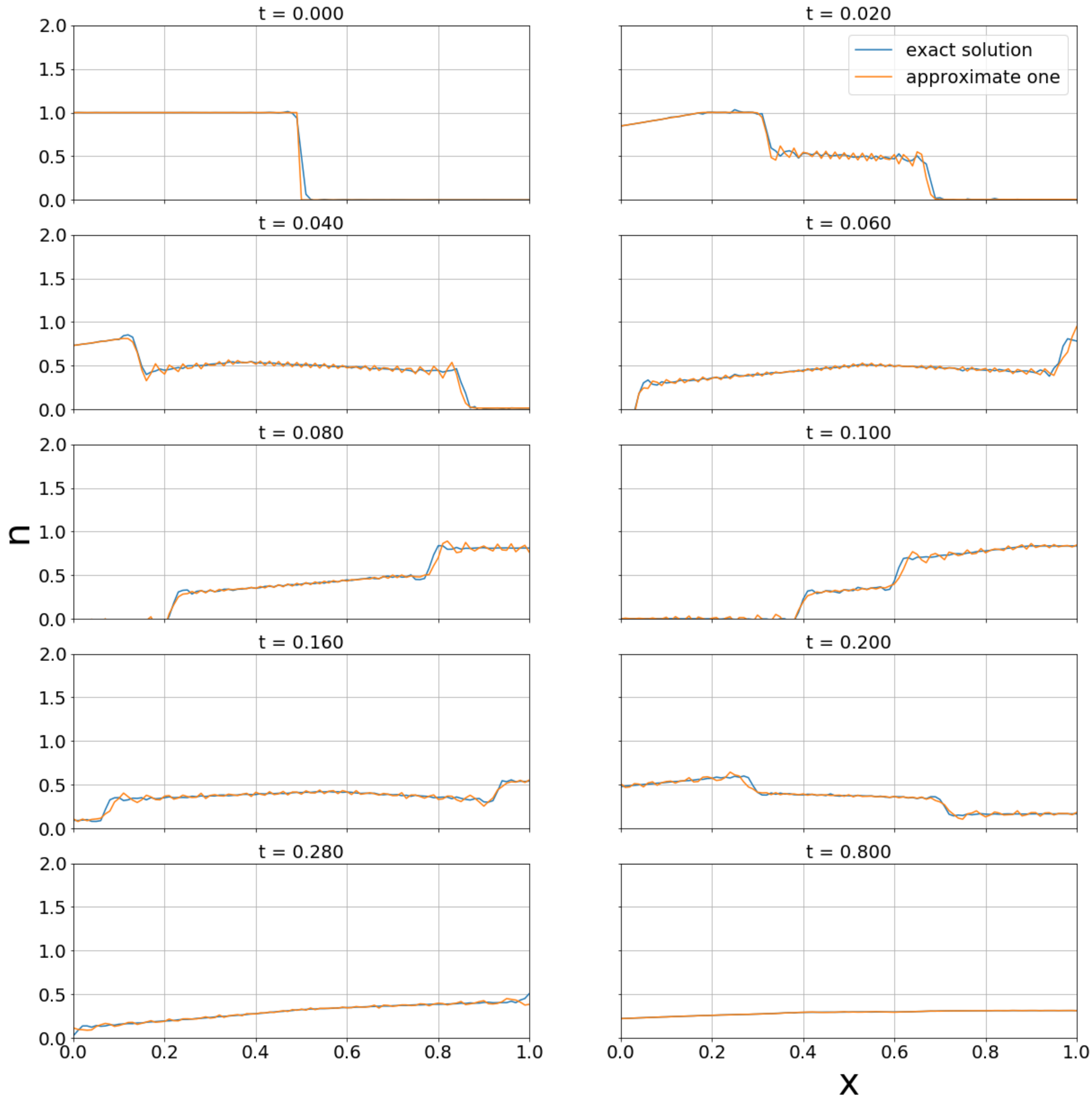

Figure 7-3: These graphs show the course of the process with sources\sinks present in the system $\alpha = 1,\ n^* = 2$. Unlike the previous case, the substance does not flow entirely outside the volume under consideration, being established at some level after a certain time.
The same set of parameters is used:
Δx =1E-2, Δt =1E-3, $\tau = 0.1,\ D = 8,\ \beta = 1,\ \varepsilon =$ 1E-6

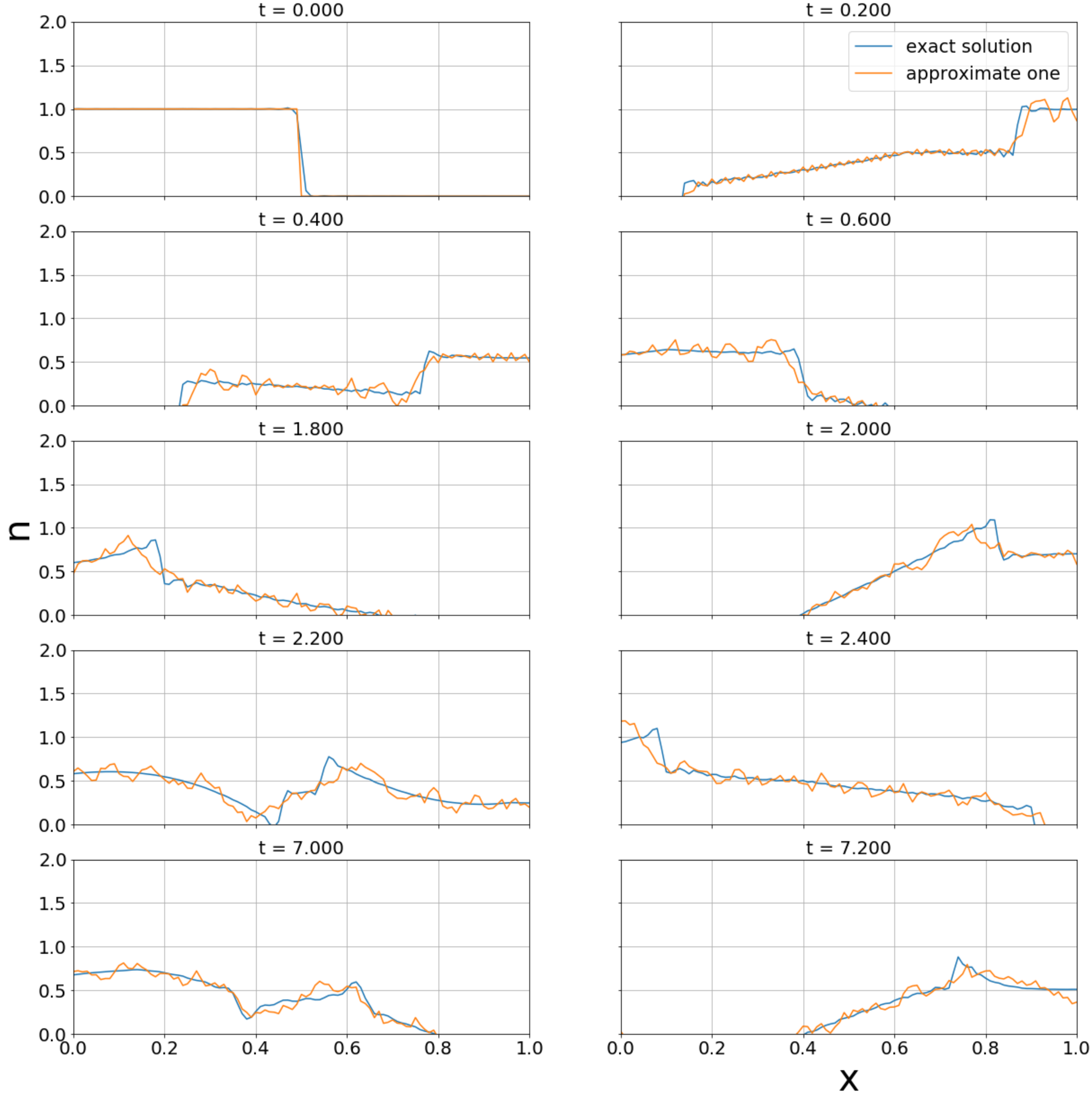

Figure 7-4: The case $\tau \gg \tau_{diff}$ for the set of parameters: $\alpha = 1,\ n^* = 2,\ \Delta x =$1E-2, $\Delta t =$1E-3, $\tau = 10,\ D = 100,\ \beta = 1,\ \varepsilon =$ 1E-6

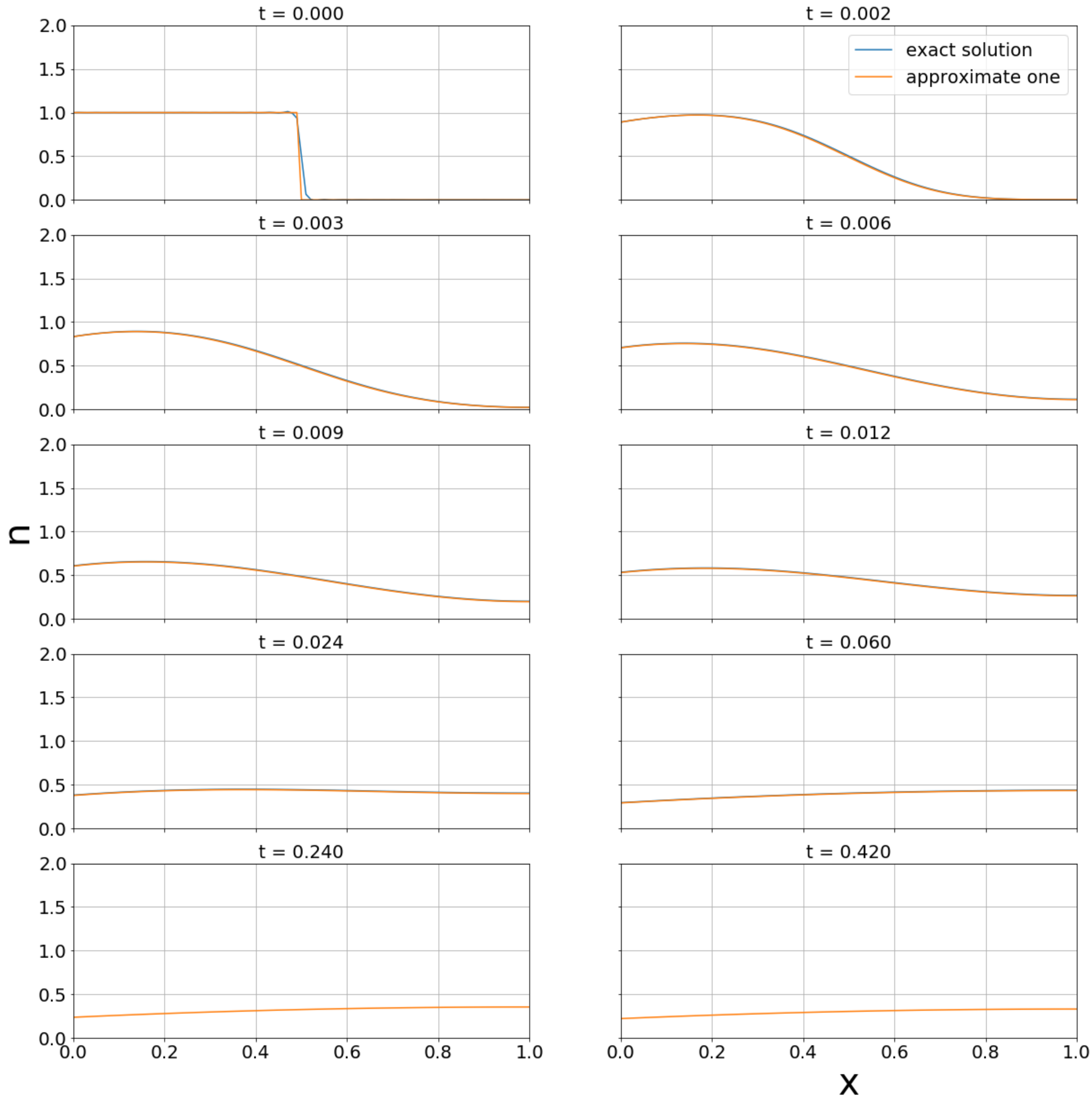

Figure 7-5: The case $\tau \ll \tau_{diff}$ for the set of parameters: $\alpha = 1$, $n^* = 2$, $\Delta x =$1E-2, $\Delta t =$3E-5, $\tau =$ 1E-4, $D = 8$, $\beta = 1$, $\varepsilon =$ 1E-6

7.6 Conclusions

1. The PDE describing the model (7-3) has been derived.

2. For the process modelling 2nd order scheme (7-10) has been constructed.

3. For the simple initial distribution of substance the obtained analytical solution decently approximates the experimental data - what can be seen from figures 7-2, 7-3 and etc. Also the limiting cases have been considered - figures 7-4, 7-5.

4. Analysis of the scheme sustainability has been carried out. The obtained restrictions on its application expressed in (7-11).