4
Stochastic Mathematical Modelling

Stochastic mathematical modelling is, together with transfer phenomena and statistical approaches, a powerful technique, which can be used in order to have a good knowledge of a process without much tedious experimental work. The principles for establishing models, which were described in the preceding chapter, are still valuable. However, they will be particularized for each example presented below.

4.1
Introduction to Stochastic Modelling

As analyzed in the preceding chapters concerning the description of a process evolution, stochastic modelling follows the identification of principles or laws related to the process evolution as well as the establishment of the best mathematical equations to characterize it.

The first approaches to compare stochastic models and chemical engineering were made in 1950, with the Higbie [4.1] and Dankwerts transfer models [4.2]. Until today, the development of stochastic modelling in chemical engineering has been remarkable. If we made an inventory of the chemical engineering modelling studies we could see that a stochastic solution exists or complements all the cases [4.3–4.8].

In many modelling studies, the model establishment is made in relation to the transfer and balance of a property (for instance see Chapter 3, Section 3.1). Nevertheless, a property evolution from the initial to the final state can vary randomly as a result of the stochastic combination of different elementary processes. This statement is in good agreement with the unitary concept of transfer phenomena [4.9–4.11] and was reported by Bratu [4.11] in the following assertion:

> *"Each transformation or phenomenon results from one or many elementary steps or processes. The equilibrium state results from similar but contrary transport fluxes."*

This statement can also be obtained when a transport process evolution is analyzed by the concept of Markov chains or completely connected chains. The math-

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ematical theory of completely connected chains [4.12–4.16] can be described with this condensed statement:

> *"The state of a system at time **n** is a random variable A_n with values in a finite space $(\mathrm{A}\ \underline{\mathbf{A}})$ (measurable). The state evolution at time n+1 results from the arrival of a B_{n+1} result, which is also a random variable with values in a finite space $(\mathrm{B}\ \underline{\mathbf{B}})$ (measurable). The arrival of a result signaling the state evolution can be represented considering a* $\mathbf{u}$ *application of* $\mathrm{A}\times\mathrm{B}$ *in* A *and introducing the following statement:* $\mathrm{A}_{n+1}=\mathbf{u}(\mathrm{A}_n,\mathrm{B}_{n+1})$ *for all* $n\geq 0$*. The* B_{n+1} *probability distribution is conditioned by* $\mathrm{B}_n,\mathrm{A}_n,\mathrm{B}_{n-1},\mathrm{A}_{n-1},\ldots\ldots\mathrm{B}_1,\mathrm{A}_1,\mathrm{A}_0$*, and symbolized as* $(\mathrm{P}(\mathrm{B}_{n+1}/\mathrm{B}_n,\mathrm{A}_n,\ldots))$*, it depends only on state* A_n*. The group* $[(\mathrm{A},\underline{\mathbf{A}}),(\mathrm{B},\underline{\mathbf{B}}),\mathbf{u}{:}\mathrm{A}\times\mathrm{B}\rightarrow\mathrm{A},\mathrm{P}]$ *defines a random system with complete connections."*

Some of the examples shown in the following paragraphs present the characteristics of a random system with complete connections. However, other examples do not concern a completely connected system but present only some Markov unitary processes [4.6, 4.17].

The stochastic modelling of the phenomena studied here can be described by one standard physical model (descriptive model) which can be defined by the following statement:

> *"The property carriers, such as elementary particles of fluids or molecules, evolve during their displacement through one or more elementary processes (called process components), their passage from one process to another is made by one stochastic process called connection or connection process."*

It is important to notice the similitude of this descriptive model to the complete definition of connections of a system given before. For chemical engineering processes, the model needs to be particularized and then the assertions written below have to be taken into account [4.4–4.7]:

- If one elementary particle is participating in a process of transport phenomena within a medium with random characteristics (granular medium, porous solid, etc.), the medium will be responsible for the random velocity changes of the particle. In this case, the transport process concerning the local velocity is the so-called "process component", whereas the transport process changes given by the random properties of the medium are called "connection process".
- The transport phenomenon occurs when the displacement of the carriers through different media ("process components") and the passage from one medium to another are realized by a random commutation process ("connection process").

- During their displacement, elementary particles are constantly encountering obstacles, other moving elements, oscillation states etc. The particle evolution is randomly chosen among the different presented possibilities (“process components”).
- A particle (molecule, group of molecules, turbulent group etc.) evolves in a medium which produces its own transformation. This means that the process exchange characterizes the particle evolution. The process occurring before and after the transformation is called the “process component”, whereas the transformation itself which represents the stochastic evolution is called the “connection process”.
- The elementary particles randomly pass from one compartment to another; the process of swapping compartments forms the “connection process” whereas the transformation realized in each compartment represents the “process components”.
- When phenomena result in the formation of various structures, the passage from one structure to another occurs randomly, in this case the structure formation is the “process component” and the transitory steps correspond to the “connection process”.

When a stochastic process takes place, the passage from one elementary process to another is caused by external effects. These effects are related to the medium by the process evolution itself. We can assert that a process can be adapted to stochastic modelling if we can identify the elementary “process components”. In addition, for the “connection process” the number of states has to be same as the “process components”. This very abstract introduction will be better explained in the next paragraph by including a practical example.

4.1.1
Mechanical Stirring of a Liquid

Studies of the mixing effectiveness of stirring devices are quite numerous; they generally analyze the effects produced by:
- the turn rate or frequency of the stirrer,
- the configuration and the distribution of the stirring paddles in the apparatus,
- the physicochemical properties of the medium,
- the position of the input and the output of the currents in the apparatus tank.

It has been very difficult to develop a general model able to describe the influence of all the different parameters on the mixing effectiveness [4.18–4.20]. However, many researchers have tried to develop models as complete as possible, among them a special mention has to be given to the research team who developed the first commercial program called *Visimix* 1999 [4.21, 4.22].

As an example, we analyze here, step by step, a continuous mixing apparatus provided with stirring paddles. The first step is to uniformly express the state of the currents, which characterize the different flow patterns inside the apparatus (see Section 3.3). The second step concerns the development of a stochastic model for characterizing the mixing. For this purpose, we will use the procedure of analysis initially developed by Kafarov [4.4], which has been completed and modified since by other authors [4.5, 4.6, 4.23]. The apparatus considered here is shown in Fig. 4.1. In this apparatus provided with stirring paddles, the main current of flow is radial and it separates into two different currents closed the walls. The size of these flow currents depends on the stirrer position, the number of turns of the stirrer and the medium properties. Indeed, we can consider that the stirrer divides the apparatus into two regions (the higher region and the lower region with respect to the paddles) with different and independent currents.

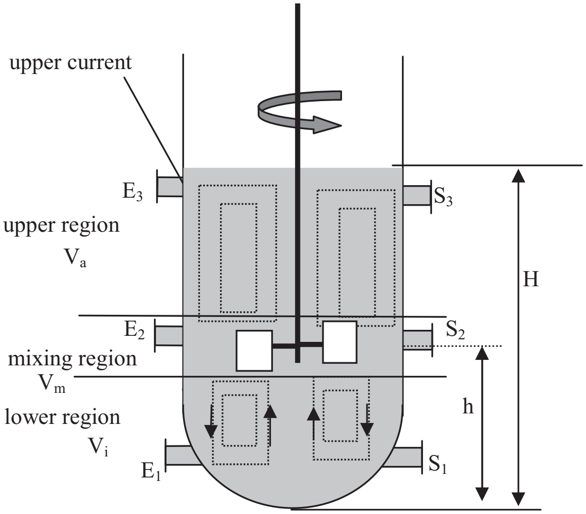


Figure 4.1 Schematic illustration of a stirring apparatus for liquid mixing.

According to this topology, the flow in the apparatus is described by two circuits (the upper and the lower region), each of which contains a variable number of ideal mixed cells but meets in the mixing region (near the paddles). This region constitutes a cell with ideal mixing.

Figure 4.1 also shows the position of the input flow (E_1, E_2, E_3) which has to be coupled with the positions of the output flow (positions S_1, S_2, S_3) and the general current of circulation inside the vessel. We can observe from Fig. 4.1 that the volumes placed in the higher and lower regions depend on H and h (thus on the position of the stirrer paddle in the apparatus) as well as on the size of the stirring region. Indeed, the corresponding volumes can be described as follows:

$$V_a = \frac{\pi D^2}{4}(H - h) - \frac{V_m}{2} \tag{4.1}$$

$$V_a = \frac{\pi D^2}{4} h - \frac{V_m}{2} = V_u - V_s - \frac{V_m}{2} \tag{4.2}$$

We can expect the volume in the pumping region to depend on the dimensions of the stirrer paddle (diameter d, height of the pallet b) and on the dimensions of the tank:

$$V_m = \frac{\pi b}{60}\left(D^2 + \frac{Dd}{5} + \frac{d^2}{5}\right) \tag{4.3}$$

According to the topological description, we can consider a cell with ideal mixing in the stirring region; other cells can be considered in the upper region (with number: n_a) and in the lower region (with number: n_i). The respective number of cells in the regions can be calculated by the following algorithm:

1. The starting conditions are established.
2. V_a, V_m, V_i are calculated with Eqs. (4.1)–(4.3).
3. If $V_a > V_i$ then $r = V_a/V_i$; for the reverse case $r = V_i/V_a$.
4. The number of cells is chosen in the smaller region; (this consideration is frequently used) then, $n_i = n_{ch} = 1$ if the lower region is the smaller one, when the upper region is the smaller one we have $n_a = n_{ch} = 1$.
5. If $h/H = 0.5$ we can consider $n_i = n_a = n_{ch}$; if $h/H > 0.5$, which is equivalent to $V_i > V_a$ we can write $n_a = n_{ch}$ and $n_i = r^* n_{ch}$; however, if $h/H < 0.5$ and $V_a > V_i$ we can consider $n_i = n_{ch}$ and $n_a = r^* n_{ch}$

Once the topology has been established, it must be supplemented with the flows of the currents, which convey between the cells. Many solutions have been suggested to solve this problem. They differ by the mode of calculation of the main current produced by the stirrer. It is a function of the geometry, the number of the turns of the stirrer and the properties of the medium (density, viscosity). For the stirrer considered here, the flow rate of the main current and the flows in the higher and lower regions are calculated with the assistance of relations (4.4) and (4.5). Here f (ρ, η) expresses a function depending on the density and viscosity of the mixed medium:

$$Q = Q_1 + Q_2 = 10.5 d^2 b.n.f(\rho, \eta) \tag{4.4}$$

$$\frac{Q_1}{Q_2} = \frac{h}{H - h} \quad \text{for} \quad h/H > 0.5 \quad \text{or} \quad h/H = 0.5 \tag{4.5}$$

Now, the system contains N – 1 cells with ideal mixing, each one with a known volume; the cells are connected by the different currents. Here, N corresponds to the system exit, V_k is the volume of a k cell and Q_{kj} is the current (flow rate) from the k cell to the j cell.

If we consider a marked particle placed inside of our cellular system, then we can define this by the vector $E(n) = [e_0(n), e_1(n); e_2(n) \ldots e_k(n) \ldots e_{N-1}(n), e_N(n)]$

where e_k (n) expresses the probability of occurrence of the marked particle in the k cell after time n. Because the incidence of the marked particle inside a system is an undoubted event, we can write:

$$\sum_{k=1}^{N} e_k(n) = 1 \qquad \forall\ n = 0, 1, 2, \ldots \tag{4.6}$$

In the elementary processes (components), we establish that, in the small interval of time $\Delta\tau$, the particle can either pass to another cell or remain within its cell. The $\Delta\tau$ interval must be chosen in such a way that the particle can pass into a close cell during this interval, but not through it. Moreover, this passage can be regarded as instantaneous.

As far as the behaviour of the particle in such a system respects the rules of the Markov process, it will be controlled by a Markov connection. This means that the probability of the particle occurrence within the k cell after n + 1 time (i.e. $\tau = n.\Delta\tau$) is given only by its probability of occurrence in the j cell after time n and by its probability of transfer from the j cell to the k cell denoted p_{jk}. Now we can write:

$$e_k(n+1) = \sum_{j=1}^{N} e_j(n) p_{jk} \tag{4.7}$$

For j = 1,N and k = 1,N the probability p_{jk} is denoted as a matrix P which is called the stochastic matrix of the process, the matrix of passing or "the stochastic one":

$$P = \begin{bmatrix} p_{11} & p_{12} & p_{13} & \cdot & p_{1N} \\ p_{21} & p_{22} & p_{23} & \cdot & p_{2N} \\ \cdot & \cdot & \cdot & \cdot & \cdot \\ p_{N-11} & p_{N-12} & \cdot & \cdot & p_{N-1N} \\ p_{N1} & p_{N2} & p_{N3} & \cdot & p_{NN} \end{bmatrix} \tag{4.8}$$

During the building of the stochastic matrix, it is necessary to make sure that $\sum_{j=1}^{N} p_{ij} = 1$ (the total of the probabilities according to one line equals one) and if $\sum_{i=1}^{N} p_{ij} = 1$ (the total of the probabilities according to a column equals one). However, it should be specified that $\sum_{i=1}^{N} p_{ij}$ is not always one. Before going any further, it should be specified that:

- p_{ii} represents the probability for the marked particle to be and to remain in cell i in the interval $\Delta\tau$
- p_{ij} represents the probability for the marked particle to be in cell i and to go into cell j in the time interval $\Delta\tau$.

Concerning the last line of matrix P, if $p_{NN} = 1$ (the particle that leaves the system cannot come back), all other probabilities (p_{Nk} where $k \neq N$) have to be considered as zero.

If the initial state of the system is E(0), then, by means of matrix P we can write:

$$E(1) = E(0) * P \tag{4.9}$$

By analogy:

$$E(2) = E(1) * P\ E(3) = E(2) * P \ldots E(n+1) = E(n) * P \tag{4.10}$$

The last equations prove that the Markov chains [4.6] are able to predict the evolution of a system with only the data of the current state (without taking into account the system history). In this case, where the system presents perfect mixing cells, probabilities p_{ii} and p_{ij} are described with the same equations as those applied to describe a unique perfectly stirred cell. Here, the exponential function of the residence time distribution (p_{ii} in this case, see Section 3.3) defines the probability of exit from this cell. In addition, the computation of this probability is coupled with the knowledge of the flows conveyed between the cells. For the time interval $\Delta\tau$ and for i = 1,2,3, ...N and j = 1,2,3,......N – 1 we can write:

$$p_{ii} = \exp\left(- \frac{\sum\limits_{i=1, i \neq j}^{N} Q_{ji}}{V_i} \Delta\tau \right) \tag{4.11}$$

$$p_{ij} = \frac{Q_{ji}}{\sum\limits_{i=1, i \neq j}^{N} Q_{ji}} \left[1 - \exp\left(- \frac{\sum\limits_{i=1, i \neq j}^{N} Q_{ji}}{V_i} \Delta\tau \right) \right] \tag{4.12}$$

When matrix P is filled, vector E(0) is known, the calculation for E(1), E(2), E(3)... E(n)... can be easily carried out. At this time, we can formulate the following question which is also valid in almost all chemical engineering cases: *What information is produced with the assistance of this stochastic model?* The answer to this question shows that the model is frequently used for:

1. calculating the system reaction to one disturbance impulse:

$$F(\tau) = e_N(n) = \sum_{n=0}^{\infty} e_{N-1}(n)\Delta n \quad , \quad \tau = n\Delta\tau \tag{4.13}$$

2. precisely estimating the mean residence time and the residence time variance around the mean residence time:

$$\tau_m = \sum_{n=0}^{\infty} (1 - e_N(\tau))\Delta\tau \tag{4.14}$$

$$\sigma^2 = 2\sum_{n=0}^{\infty} (1 - e_N(\tau))n\Delta\tau - \left| \sum_{n=0}^{\infty} (1 - e_N(n))\Delta\tau \right|^2 \tag{4.15}$$

3. appreciating the evolution with time of the function (λ) that shows the stirring intensity for our topological cell assembly:

$$\lambda(n) = \frac{e_{N-1}(n)}{1 - e_N(\tau)} \tag{4.16}$$

We can observe that, with the help of simulation software, we can produce the numerical results which give the effect of the stirrer's number of turns, the position of the stirrer in the tank, the effect of the dimension of the stirring paddles, etc., on the model exits mentioned above.

4.1.2
Numerical Application

An elliptic-based cylindrical apparatus (D = 1 m, H = 1 m) contains a solution stirred with a 6-paddled stirrer (d = 0.4 m and b = 0.1 m). The stirrer is placed in the tank in such a position as to get the ratio h/H = 0.2 (see Fig. 4.1) and to work at n = 0.1, 0.3, 0.5, 0.7, 0.9, 1.1, 1.3, 1.5 revolutions/s. A compound with the same physical properties as the solution is fed close to the liquid surface. The obtained mixture is flushed out through a pipe placed near the base of the apparatus. The entry and the exit flows are identical (Q_{ex} = 0.0048 m^3/s). Now the question is to obtain the dependences of the parameters characterizing this mixing case according to the number of revolutions of the stirrer.

Before developing the algorithm of calculation, we have to deduce the mixture topology. Then: $r = \frac{h/H}{1 - h/H} = 0.2/0.8 = 1/4$; because h/H<0.5, we can assert that the stirrer is placed in the lower part of the tank and then with n_{ch} = 1 we have n_i = 1, $n_a = n_{ch} / r = 4$. So the tank contains six elemental mixing cells: one in the lower region, one in the mixing region and four in the higher region; If $Q_1 + Q_2 = Q$ and $Q_2 / Q_1 = h/(H - h)$; then $Q_1 = 4/5\ Q$ and $Q_2 = 1/5\ Q$. With these simple calculations, we can establish the flow topology shown in Fig. 4.2.

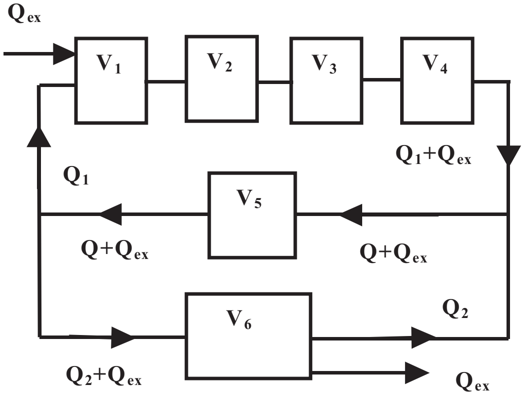


Figure 4.2 Topology of the numerical application 4.1.2.

According to Eqs. (4.11) and (4.12) and in agreement with Fig. 4.2 we can conclude that among the 49 probabilities only the following ones are not null:

$$p_{11} = \exp\left(-\frac{Q_1 + Q_{ex}}{V_1}\Delta\tau\right), \; p_{22} = \exp\left(-\frac{Q_1 + Q_{ex}}{V_2}\Delta\tau\right),$$

$$p_{33} = \exp\left(-\frac{Q_1 + Q_{ex}}{V_3}\Delta\tau\right), \; p_{44} = \exp\left(-\tfrac{Q_1 + Q_{ex}}{V_4}\Delta\tau\right),$$

$$p_{55} = \exp\left(-\frac{Q + Q_{ex}}{V_5}\Delta\tau\right), \; p_{66} = \exp\left(-\frac{Q_2 + Q_{ex}}{V_6}\Delta\tau\right),$$

$$p_{77} = 1, \; p_{12} = 1 - \exp\left(-\frac{Q_1 + Q_{ex}}{V_1}\Delta\tau\right), \; p_{23} = 1 - \exp\left(-\frac{Q_1 + Q_{ex}}{V_2}\Delta\tau\right),$$

$$p_{34} = 1 - \exp\left(-\frac{Q_1 + Q_{ex}}{V_3}\Delta\tau\right), \; p_{45} = 1 - \exp\left(-\frac{Q_1 + Q_{ex}}{V_4}\Delta\tau\right)$$

$$p_{51} = \frac{Q_1}{Q + Q_{ex}}\left(1 - \exp\left(-\frac{Q + Q_{ex}}{V_5}\Delta\tau\right)\right),$$

$$p_{56} = \frac{Q_2 + Q_{ex}}{Q + Q_{ex}}\left(1 - \exp\left(-\frac{Q + Q_{ex}}{V_5}\Delta\tau\right)\right)$$

$$p_{65} = \frac{Q_2}{Q_2 + Q_{ex}}\left(1 - \exp\left(-\frac{Q_2 + Q_{ex}}{V_6}\Delta\tau\right)\right),$$

$$p_{67} = \frac{Q_{ex}}{Q_2 + Q_{ex}}\left(1 - \exp\left(-\frac{Q_2 + Q_{ex}}{V_6}\Delta\tau\right)\right)$$

With these probabilities, the passing matrix can be written. For brevity, we use the following notations: $\alpha k = (Q_1 + Q_{ex})/V_k$ for $k = 1,....4$; $\alpha k = (Q + Q_{ex})/V_k$ for $k = 5$; $\alpha k = (Q_2 + Q_{ex})/V_k$ for $k = 6$; $\beta = Q_1/(Q + Q_{ex})$; $\gamma = Q_2/(Q + Q_{ex})$; $\delta = Q_2/(Q_2 + Q_{ex})$; $\varepsilon = Q_{ex}/(Q_2 + Q_{ex})$. The macro-relation (4.17) expresses our matrix of the transition probabilities:

$$P = \begin{vmatrix} e^{-\alpha 1 \Delta\tau} & 1 - e^{-\alpha 1 \Delta\tau} & 0 & 0 & 0 & 0 \\ 0 & 0 & e^{-\alpha 2 \Delta\tau} & 1 - e^{-\alpha 2 \Delta\tau} & 0 & 0 \\ 0 & 0 & 0 & 0 & e^{-\alpha 3 \Delta\tau} & 1 - e^{-\alpha 3 \Delta\tau} \\ 0 & 0 & 0 & 0 & 0 & 0 \\ e^{-\alpha 4 \Delta\tau} & 1\, e^{-\alpha 4 \Delta\tau} & 0 & 0 & \beta(1 - e^{-\alpha 5 \Delta\tau}) & 0 \\ 0 & 0 & e^{-\alpha 5 \Delta\tau} & \gamma(1 - e^{-\alpha 5 \Delta\tau}) & 0 & 0 \\ 0 & 0 & 0 & \delta(1 - e^{-\alpha 6 \Delta\tau}) & e^{-\alpha 6 \Delta\tau} & \varepsilon(1 e^{-\alpha 6 \Delta\tau}) \\ 0 & 0 & 0 & 0 & 0 & 1 \end{vmatrix} \tag{4.17}$$

The numerical text of the calculation, shown in Fig. 4.3, leads to the program given in Fig. 4.4 and has the graphic interface (Fig. 4.5) associated with this program. A description of the graphic interface is given below:

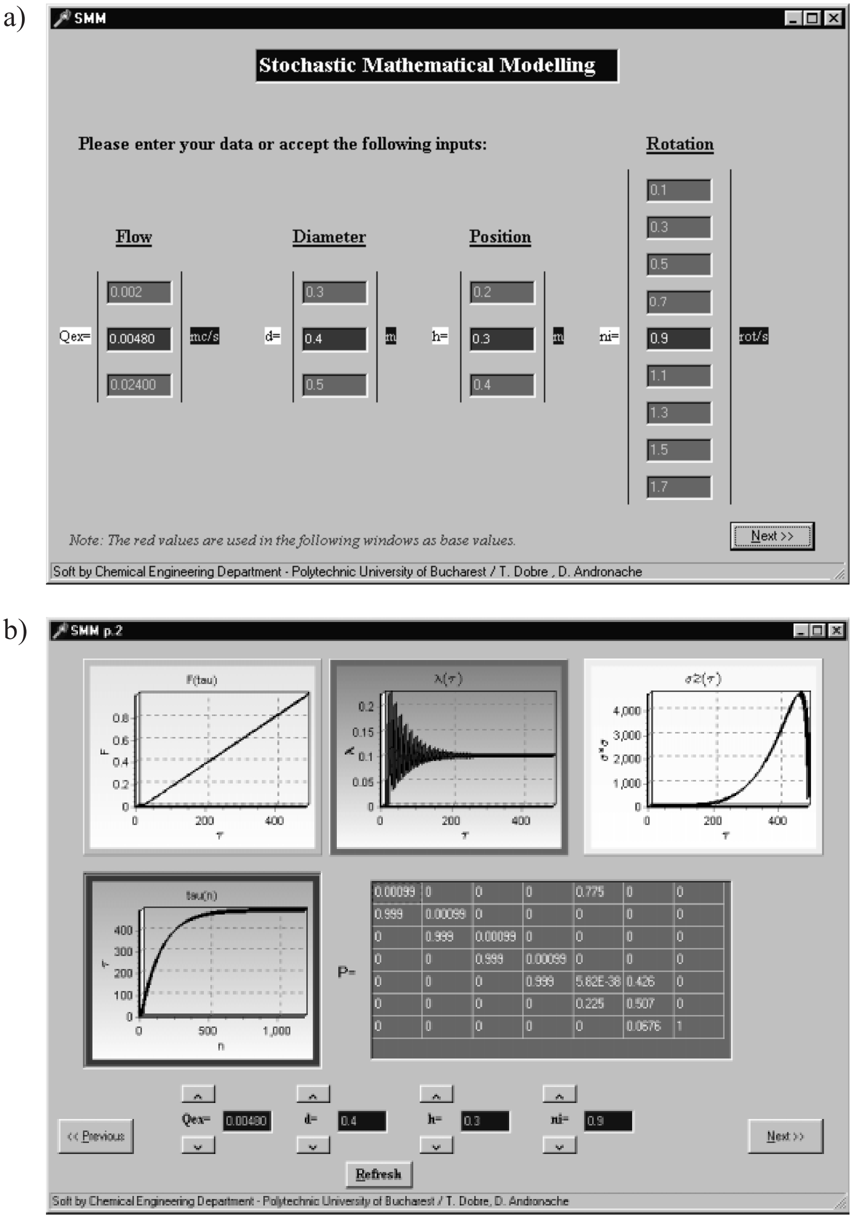
- *the first window* (SMM1) is used for the introduction of the set of values which will be used for the simulation considered in the last window (SMM3) where the parameters are fixed in such a way as to have constant values by pair.
- in *the second window* (SMM2) with keys "∧" and "∨", the user moves among the values of vectors considered in the first window (Q_{ex}, d, h, n_i). Each press on the key leads to the calculation of the chosen situation. If the user supplements the fields with values that are not among those previously fixed, then pressing the button "Refresh" leads to the calculation of $F(\tau)$ vs τ , $\lambda(\tau)$ vs τ, $\sigma^2(\tau)$ vs τ, τ_m vs τ. The matrix of the passing probability is also established. All the charts considered in this window show the evolution of the mixture state towards the stationary state.
- *the third window* (SMM3) is used to show the effect of the stirring velocity and of the feed flow on the average residence time. It works with the values of the parameters selected in the first window.

```
1   Initial data /$H=1, h=0.2, n_i=0.1, 0.3, 0.5, 0.7, 0.9, 1.1, 1.3, 1.5, D=1, d=0.4, f(\rho,\eta)=1$; $b=0.1$, etc
2   Initial state/ vector $E(0)=[1,0,0,0,0,0,0]$ // $Q_{ex}=0.0048$//$n_i=n_1$//Vectors volumes..
3 ┌──▶ Preliminary computations/$V_m$ rel. (4.3) ,$V_a$ rel (4.2) , $V_i$ rel (4.1) // Q rel (4.4) //System for $Q_1$ and $Q_2$ by: $Q_1+Q_2=Q$ and $Q_1/Q_2=(H-h)/h$ // The cells volumes : $V_5=V_m$ ,$V_1=V_2=V_3=V_4=V_a/4$ $V_6=V_i$//Values for : $\alpha k=(Q_1+Q_{ex})/V_k$ with k=1,..4 ; $\alpha k=(Q+Q_{ex})/V_k$ with k=5; $\alpha k=(Q_2+Q_{ex})/V_k$ with k=6 ;$\beta=Q_1/(Q+Q_{ex})$ ; $\gamma=Q_2/(Q+Q_{ex})$ ; $\delta=Q_2/(Q_2+Q_{ex})$ ;$\varepsilon=Q_{ex}/(Q_2+Q_{ex})$
4 │   Matrix of transitions// Matrix volume P: 7x7 / matrix elements with (4.17)
5 │   Choose of $\Delta\tau$// $\tau_{apr}=(0.786D*D*H)/Q_{ex}$ ;$\Delta\tau=\tau_{apr}/15$
  │   n=1
6 │ ┌──▶ $E(n)=P*E(n-1)$/ $\tau_m(n)$ rel (4.14) sum until n and with N=7 ,$\sigma^2(n)$ rel. (4.15) sum until n and with N=7 , F(n) rel. (4.13) sum until n and with N=7 , $\lambda(n)$ rel. (4.16) with N=7 / $\tau=n*\Delta\tau$/ Extraction E(n)
  │ │   If $\tau_m(n)>\tau_m(n-1)$+error then
  │ └──── n=n+1 , Return to 6
  │     If $\tau_m(n)<=\tau_m(n)$+error then shows the figures F(n) and $\lambda(n)$ and gives the values of $\sigma^2(n)$ and $\tau_m(n)$
  └──── For $n_i<=8$ then $n_i=n_{i+1}$, Return at the step 3
7   End
```

Figure 4.3 Scheme of the computation algorithm.

```
unit d1;
interface
uses
  Windows, Messages, SysUtils, Classes, Graphics, Controls, Forms, Dialogs,
  StdCtrls;
type
  TForm1 = class(TForm)  Button1: TButton;
    procedure Button1Click(Sender: TObject);
  private  { Private declarations } public { Public declarations }
  end;
  const nc=8;error=1;
var e:array[0..10000,1..7] of real;
taum,lambda:array[0..10000] of real;
repeta:boolean;
V,alfa:array[1..6] of real;P:array[1..7,1..7] of real;
D,dm,b,h,hm,Q,Qex,Q1,Q2,Vm,Va,Vi,f,gamma,delta,epsilon:real;
tauapr,deltatau,tex,tau,suma,suma1,sigmap:real;
i,j,k,n,n1:integer;ni,dt:real;
var
  Form1: TForm1;
implementation
{$R *.DFM}
procedure TForm1.Button1Click(Sender: TObject);
begin         taum[0]:=0;taum[1]:=21;
for i:=1 to 7 do for j:=1 to 7 do P[i,j]:=0;P[7,7]:=1;
 n:=1; D:=1; dm:=0.4; b:=0.1; e[0,1]:=1;
for i:=2 to 7 do e[0,i]:=0;
h:=0.2;
HM:=1; Qex:=0.0048;
ni:=0.1;n:=1;
{3} repeat
n:=1;
Vm:=pi*b/60*(sqr(D)+D*dm/5+dm*dm/5);  {rel 4.3} Va:=pi*D*h/4-Vm/2; {rel 4.3}
Vi:=pi*D*h/4*(HM-h); {rel. 4.1} f:=1;
Q:=10.5*dm*dm*b*ni*f; {f=1 } Q1:=Q/(1+1/((HM-h)*h)); Q2:=Q-Q1;  Q1:=Q*4/5; Q2:=Q-Q1;
for i:=1 to 4 do V[i]:=Va/4; V[5]:=Vm; V[6]:=Vi;
for k:=1 to 4 do alfa[k]:=(Q1+qex)/V[k];
alfa[5]:=(Q+Qex)/V[5]; alfa[6]:=(Q2+Qex)/V[6]; gamma:=Q2/(Q+Qex); delta:=Q2/(Q+Qex);
epsilon:=Qex/(Q2+Qex); tauapr:=(0.768*D*D*HM)/Qex; deltatau:=tauapr/15;
for k:=1 to 4 do P[k,k]:=exp(-(Q1+Qex)/V[k]*deltatau);  P[5,5]:=exp(-(Q+Qex)/V[5]*deltatau);
P[6,6]:=exp(-(Q2+Qex)/V[6]*deltatau); {P[7,7]:=1;  }
for k:=1 to 4 do P[k,k+1]:=1-exp(-(Q1+Qex)/V[k]*deltatau); tex:=1-exp(-(Q+Qex)/V[5]*deltatau);
P[5,1]:=Q1/(Q+Qex)*tex; P[5,6]:=(Q2+Qex)/(Q+Qex)*tex; tex:=1-exp(-(Q2+Qex)/V[6]*deltatau);
P[6,5]:=Q2/(Q2+Qex)*tex; P[6,7]:=Qex/(Q2+Qex)*tex; {n:=1;} tau:=n*deltatau; repeta:=true;
{6} while repeta do begin repeta:=false; for i:=1 to 7 do begin suma:=0;
for j:=1 to 7 do suma:=suma+P[i,j]*E[n-1,j]; E[n,i]:=suma; end;
suma:=0;suma1:=0; for i:=0 to n do begin suma:=suma+(1-e[i,7])*n*deltatau;
suma1:=suma1+(1-e[i,7])*deltatau; end;
sigmap:=2*suma-suma1*suma1; taum[n]:=suma/n; dt:=taum[n]-taum[n-1]; lambda[n]:=E[n,6]/(1-
E[n,7]);
suma:=0; {for i:=1 to n do suma:=suma+E[n,6]*deltatau; taum[n]:=suma;suma:=0;}
if taum[n]>taum[n-1]+error then begin repeta:=true;inc(n);end ;if n=1000 then repeta:=false;
end;   beep; if taum[n]<=taum[n-1]+error then {grafice}; if ni<=1.5 then ni:=ni+0.2
until ni>1.5;
end; end.
```

Figure 4.4 Calculation program written in Matlab® language.



Please enter your data or accept the following inputs:

Qex= 0.002 / 0.00480 / 0.02400 mc/s

d= 0.3 / 0.4 / 0.5 m

h= 0.2 / 0.3 / 0.4 m

ni= 0.1 / 0.3 / 0.5 / 0.7 / 0.9 / 1.1 / 1.3 / 1.5 / 1.7 rot/s

Note: The red values are used in the following windows as base values.

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P=

0.00099	0	0	0	0.775	0	0
0.999	0.00099	0	0	0	0	0
0	0.999	0.00099	0	0	0	0
0	0	0.999	0.00099	0	0	0
0	0	0	0.999	5.62E-38	0.426	0
0	0	0	0	0.225	0.507	0
0	0	0	0	0	0.0676	1

Qex= 0.00480 d= 0.4 h= 0.3 ni= 0.9

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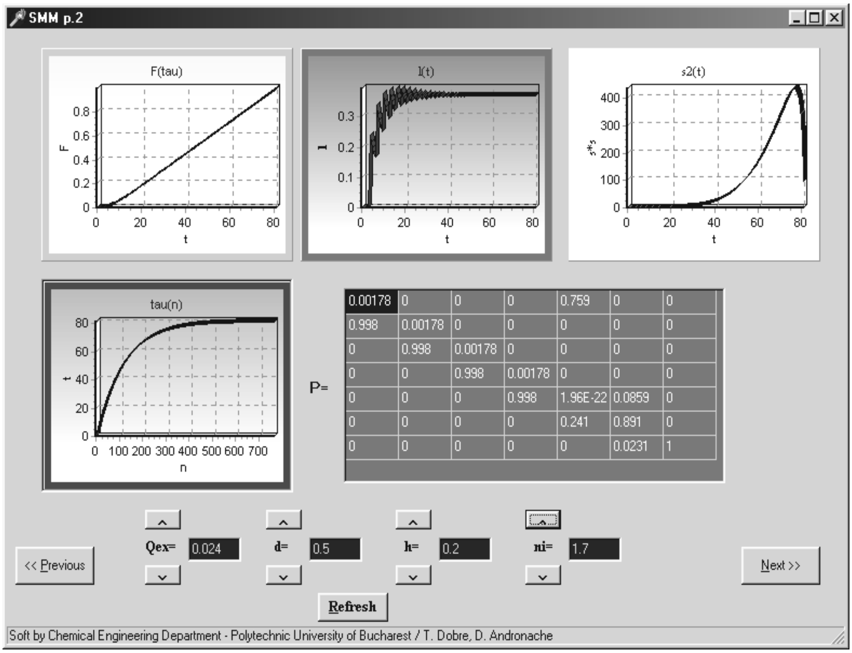
Figure 4.5 Graphic interface for application 4.1.2. (a) First window, (b) second window.

Figures 4.6 and 4.7 show other examples of simulations. For the case considered in the simulation given in Fig. 4.5(b), if, for example at time $\tau = 0$, we start the introduction of a constant signal into the system, the signal obtained at the exit after 500 s becomes stationary according to this value. It should be noticed



P=

0.00178	0	0	0	0.759	0	0
0.998	0.00178	0	0	0	0	0
0	0.998	0.00178	0	0	0	0
0	0	0.998	0.00178	0	0	0
0	0	0	0.998	1.96E-22	0.0859	0
0	0	0	0	0.241	0.891	0
0	0	0	0	0	0.0231	1

Qex= 0.024
d= 0.5
h= 0.2
ni= 1.7

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Figure 4.6 Mixing state when the external parameters take high values.

that the displacement towards the stationary state of mixing is dependent on all the external parameters that characterize this process of liquid mixing with a mechanical stirrer.

It is necessary to notice the very interesting aspect of the evolution of the function that characterizes the mixing intensity. As is observable when the stationary state of mixing is reached, the dispersion of the average residence time quickly moves towards a very small value, this behaviour is characteristic of the combination of the external parameters with the chosen topology.

In all situations, the estimated average residence time according to the ratio of the apparatus volume of liquid and of the flow passing through the apparatus gives smaller values compared to those calculated with the stochastic procedure.

The data presented in Figs. 4.5–4.7 show many interesting aspects with respect to the effect of the external parameters on the state of the mixing process with this type of mechanical stirrer. The most significant conclusions of this example are summarized below:

- The solution to the problem of the mechanical stirring of a liquid medium begins with the identification of the process components. This step is carried out using an identification particle which is placed in the elementary volumes V_1, V_2.........V_6 . The connection process is characterized by the probability showing that the identification particle moves from one volume of the topological space to another.

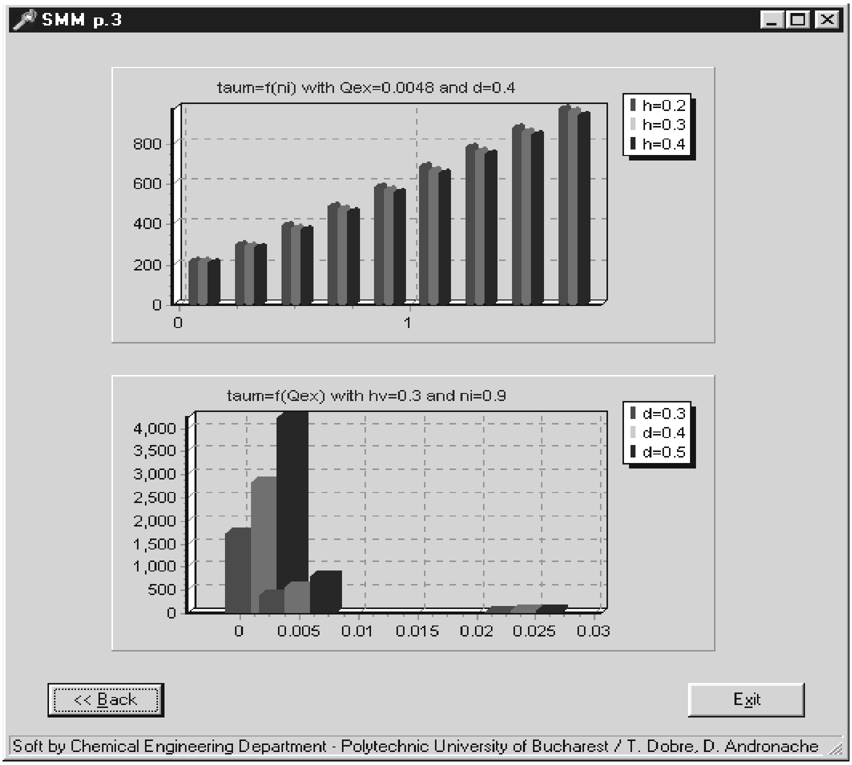

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Figure 4.7 Calculated residence time in function of the external parameters.

- A calculation procedure has been used for the individual states of volumes and the flows circulating in the selected topology, in order to develop a simulation and calculation program of the mechanical stirring in a liquid medium.
- A graphic interface is suggested in order to make rapid simulations about a particular state of the system with the external parameters considered as significant by the researcher.
- The developed simulator allows the calculation of the displacement of the state of the mixing towards the stationary state as well as the characterization of this stationary state.

To end this section we can make some general observations about stochastic modelling:

- The jump from the description of the phenomenological process to its stochastic variant, which shows the process's elementary states and its connection procedure, is strongly dependent on the process cognition in terms of chemical engineering as well as on the researcher's ability and experience.

- The mathematical description of the modelled process uses a combination of one or more stochastic cores and phenomenological parts related to non-stochastic process components.
- The building of the mathematical model of a process with stochastic core and its transpositions as simulator, follows the steps considered in Fig. 3.4.
- The range of the values of the process factors considered by the simulator and the process exits considered by the graphic interface of the simulator requires very careful selection.

At this point in this chapter, it is easy to understand that, using the methodology above, the modelling of a chemical transformation presents no important difficulty if the chemical reaction is fitted in the general framework of the concepts of probability theory. Indeed, the discrete molecular population characterizing a chemical system can be described in terms of the joint probability of the random variables representing the groups of entities in the total population.

Until now, the use of stochastic mathematics to describe flow systems and, in particular, the residence time distribution, has been well developed. However, the models of processes based upon these principles have generally been less popular than those based upon the fundamental equations of motion and continuity (see Section 3.3). A random selection of 20 papers concerning the residence time distribution models shows that 12 of them are based on the stochastic motion of particles. Early stochastic modelling efforts in chemical engineering seem to be concentrated on a variety of generic systems with continuous flow, on processes with simultaneous chemical reaction and dispersion, on processes with internal reflux as well as on processes operating at unsteady state. So, in this domain, many papers and books aim at demonstrating the applicability of stochastic mathematics to the solution of fundamental chemical engineering problems, and in particular to the calculation of residence time and of the state of systems inside this residence time.

Stochastic models present a number of advantages over CFD models as far as the modelling of the residence time distribution of a complex flow system is concerned. These advantages are:

1. stochastic models are simple to develop,
2. they are computationally light,
3. they are simple to adapt to new systems, and
4. they are much simpler to solve than the full mathematical description.

The term “Markov chain” frequently appears in this chapter. This term is named after the Russian mathematician Andre Markov (1856–1922). The Markov theory is widely applied in many fields, including the analysis of stock-markets, traffic flows, queuing theories (e.g. modelling a telephone customer service hotline), reliability theories (e.g. modelling the time for a component to wear out) and many other systems involving random processes.

4.2
Stochastic Models by Probability Balance

The prediction of the results obtained with an industrial process is one of the fundamental objectives of modelling. This process prediction is necessary to obtain good information about the process management as well as a better knowledge of the process itself. If the process is rather complicated or if its laws of evolution are unknown, the application of a deterministic model is very difficult. However, if the elementary process components of the process are identified, then the application of a stochastic model can be realized, often with spectacular success. In this case, modelling begins with a complete descriptive model of the process where the identification of the participant elementary processes, their connections and the space topology where the process develops will be attentively examined. Thanks to this description, we can identify the factors that, all together, determine the process state.

The establishment of stochastic equations frequently results from the evolution of the analyzed process. In this case, it is necessary to make a local balance (space and time) for the probability of existence of a process state. This balance is similar to the balance of one property. It means that the probability that one event occurs can be considered as a kind of property. Some specific rules come from the fact that the field of existence, the domains of values and the calculation rules for the probability of the individual states of processes are placed together in one or more systems with complete connections or in Markov chains.

In the development of stochastic models, there are six successive steps:

1. The objective of the description of a process evolution, considering mainly the specific internal phenomena, is to precede the elementary processes (elementary states) components.
2. The identification of the elementary steps according to which the evolution of the investigated process (phenomena) is held.
3. The determination or the division of the transition probabilities from one state to another and the identification with respect to the connections if the stochastic process accepts a continuous or a discrete way.
4. The establishment of the balance equations of the probabilities. They show the probability of the process to exist in a given state, at a considered time in a formal geometry (system of selected coordinates).
5. The coupling of the univocity conditions to the problem established at the end of the probability balance.
6. The model resolution and its evaluation in order to give the models the requested exits in their relations with the entries.

In the following example, we show a more explicit explanation of the stochastic model genesis, particularization and evaluation.

4.2.1
Solid Motion in a Liquid Fluidized Bed

It is well known that fluidization with liquids is characterized by a very good homogeneity. However, when a liquid–solid suspension is mixed by fluidization and the size or density of the solid are not homogeneous, segregation is observed. To carry out the analysis of this problem, we can consider a two-dimensional fluidization system composed of pure water and 1 mm diameter glass balls. This system operates in the vicinity of a minimum fluidization state. One of these glass balls is coloured and thrown to the centre of the base of the bed [4.24]. The ball displacement will give qualitative and quantitative appreciation of the solid mixing during the fluidization process [4.5, 4.24]. The coloured ball displacement is recorded with a high-speed camera, which makes it possible to identify the trajectory and the displacement mechanism, allowing the identification of forward and backward displacements. The result of such an experiment is shown in Fig. 4.8. We can note that the global particle displacement results in a unique direction, in spite of the forward-and- backward displacements. If we decompose the particle displacement (different steps in Fig. 4.8), we can note that one "evolution of the state" is given by a forward or backward displacement.

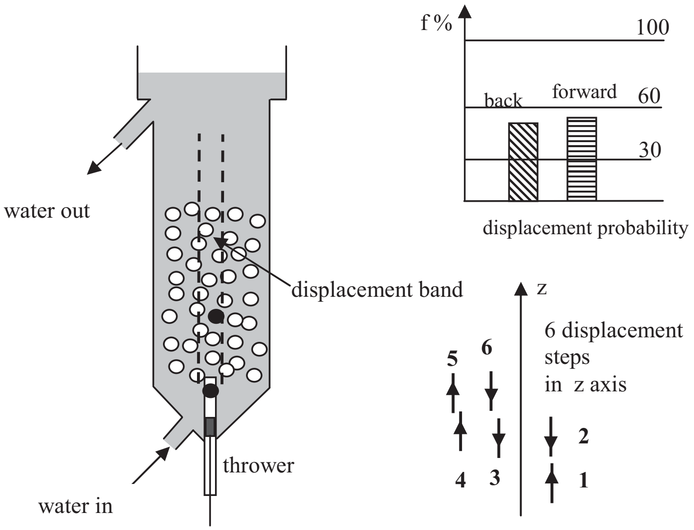


Figure 4.8 Particle displacement in a fluidized bed.

From the analysis of the decomposition of the images, we can observe that the movement ahead is dominant and controls the whole displacement. In the example given in Fig. 4.8, we can observe that the movement ahead (elementary state or process component) presents approximately the same frequency as the backward displacement. A radial movement is also possible but can be neglected if we consider only a very thin band in the centre of the bed. The same has been considered for stagnation. The description given above, shows that the first steps of the stochastic modelling are similar to those of the establishment of the model of transfer phenomena (stage of the descriptive model). The stochastic model here can be described as the mathematical solution given for a problem of forward-and- backward displacement [4.3, 4.4, 4.17] where the elementary processes considered are:

- elementary process of type I – displacement in the direction of the z-axis with velocity v_z.
- elementary process of type II – displacement in the opposite direction to axis z with a mean velocity $-v_z$.

In this case, the elements of the passage matrix of the particularized problem present very clear physical meanings:

- p_{11} is the probability for the coloured particle, which is displaced by a standard process I, to keep on being displaced by the same process (a positive displacement with speed v_z is followed by the same displacement).
- p_{22} is the probability for the coloured particle, which is displaced by a standard process II, to keep on being displaced by the same process (the same consideration as above but with speed $-v_z$).
- p_{12} is the probability for the coloured particle which is displaced by a standard process I, to skip to a standard process II (i.e. a negative displacement with respect to axis z occurs after a positive displacement with a speed v_z).
- p_{21} is the probability for the coloured particle which moves due to a standard process II, to skip to standard process I (i.e. a positive displacement with respect to axis z occurs after a negative displacement with speed $-v_z$).

If P_1 represents the probability for the process that evolved in state I to remains in this state after the interval of time $\Delta\tau$, then, because all the states are characterized by independent probabilities, we can write:

$$P_1 = 1 - \sum_{j=2}^{N} p_{1j} a \Delta\tau \tag{4.18}$$

Here N is the number of the independent states of the process (N = 2 in the analyzed case) and “a” is the frequency of exchange of an individual state. We can notice that the dimension for “a” is time^{-1} (T^{-1}). The same consideration as above can be used for the probability of the process evolving in state II. Then P_2 is written:

$$P_2 = 1 - \sum_{j=1, j\neq 2}^{N} p_{2j} a \Delta\tau \tag{4.19}$$

If we consider that the element is the coloured ball, the following relation writes the equations of the probability balance according to the model:

The probability that the element is in the z position at τ + Δτ and in state I	=	The probability that the element from z–Δz position at τ with state I evolves, in the next Δτ, with the same state	+	The probability that the element from z position at τ with state II evolves, in the following Δτ, towards state I	(4.20)

With relations (4.19) and (4.20), we can establish that $P_1(z, \tau + \Delta\tau)$ is given by Eq.(4.21). Equation (4.22), which gives $P_2(z, \tau + \Delta\tau)$, is written by the same procedure:

$$P_1(z, \tau + \Delta\tau) = P_1(z - v_z\Delta\tau)(1 - p_{12}a\Delta\tau) + P_2(z, \tau)p_{21}a\Delta\tau \tag{4.21}$$

$$P_2(z, \tau + \Delta\tau) = P_2(z + v_z\Delta\tau)(1 - p_{21}a\Delta\tau) + P_1(z, \tau)p_{12}a\Delta\tau \tag{4.22}$$

If we consider that $\Delta\tau \to 0$ in relations (4.21) and (4.22), we can write a two equation system with partial derivates in $P_1(z,\tau)$ and $P_2(z,\tau)$, as follows:

$$\lim_{\Delta\tau \to 0} \frac{P_1(z, \tau + \Delta\tau) - P_1(z - v_z\Delta\tau, \tau)}{\Delta\tau} = -p_{12}aP_1(z - v_z\Delta\tau, \tau) + p_{21}aP_2(z, \tau) \tag{4.23}$$

$$\lim_{\Delta\tau \to 0} \frac{P_2(z, \tau + \Delta\tau) - P_2(z + v_z\Delta\tau, \tau)}{\Delta\tau} = -p_{21}aP_2(z + v_z\Delta\tau, \tau) + p_{12}aP_1(z, \tau) \tag{4.24}$$

$$\begin{cases} \dfrac{\partial P_1(z,\tau)}{\partial \tau} + v_z\dfrac{\partial P_1(z,\tau)}{\partial z} = -ap_{12}P_1(z,\tau) + ap_{21}P_2(z,\tau) & (4.25) \\ \dfrac{\partial P_2(z,\tau)}{\partial \tau} - v_z\dfrac{\partial P_2(z,\tau)}{\partial z} = -ap_{21}P_2(z,\tau) + ap_{12}P_1(z,\tau) & (4.26) \end{cases}$$

In this system, we can take into account that $P_1(z,\tau)$ and $P_2(z,\tau)$ are the probabilities or probability densities, or can be considered as the concentrations which describe the type I or type II elementary action intensity.

To solve the model obtained, it is necessary to link it with the univocity conditions. They are obtained from the physical meanings of the problem:

1. The only way for the coloured ball to get into the layer is by a type I elementary action.
2. After the input, it is impossible for the coloured ball to exit the layer.
3. The only way for the coloured ball to exit the layer is by a type I elementary action (assuming that the marked particle has reached the end of the layer and cannot flow back)

These conditions can also be applied for cases where an impulse or signal is introduced in a continuous flow (for instance see Section 3.3):

$$z = 0 \quad \tau = 0 \quad P_1(0,0) = 1 \quad P_2(0.0) = 0 \tag{4.27}$$

$$z = H \quad \tau = 0 \quad P_1(H,0) = 0 \quad P_2(H.0) = 0 \tag{4.28}$$

$$z = 0 \quad \tau \succ 0 \quad P_1(0,\tau) = 0 \quad P_2(0.\tau) \neq 0 \tag{4.29}$$

$$z = H \quad \tau \succ 0 \quad P_1(H,\tau) \neq 0 \quad P_2(H.\tau) = 0 \tag{4.30}$$

In this example, two main situations can be considered:

Under the condition that $p_{12} = p_{21} = 1/2$, the system formed by Eqs. (4.25) and (4.26) takes the form:

$$\frac{\partial P_1(z,\tau)}{\partial \tau} + v_z \frac{\partial P_1(z,\tau)}{\partial z} = -\alpha P_1(z,\tau) + \alpha P_2(z,\tau) \tag{4.31}$$

$$\frac{\partial P_2(z,\tau)}{\partial \tau} - v_z \frac{\partial P_2(z,\tau)}{\partial z} = -\alpha P_2(z,\tau) + \alpha P_1(z,\tau) \tag{4.32}$$

where α corresponds to $ap_{12} = ap_{21} = a/2$.

From a practical point of view, the main interest may be given to the sum $P(z,\tau) = P_1(z,\tau) + P_2(z,\tau)$. It describes the density of probability when the particle reaches position z, at time τ, no matter what elementary action (type I or II), it has been subjected to. The derivation of Eqs.(4.31) and (4.32) with respect to τ and z, coupled to an algebraic calculation for $P_1(z,\tau)$ and with the elimination of $P_2(z,\tau)$ gives the following relation:

$$\frac{\partial P(z,\tau)}{\partial \tau} + \frac{1}{2\alpha}\frac{\partial^2 P(z,\tau)}{\partial \tau^2} = \frac{v_z^2}{2\alpha}\frac{\partial^2 P(z,\tau)}{\partial z^2} \tag{4.33}$$

In the resulting equation, we have the derivatives of the known transport equation as well as the second order derivative of the variable of the process with respect to the time. The type of model considered here is known as the hyperbolic *model.* Scheidegger [4.25] obtained a similar result and called it: *correlated random displacement.*

The hyperbolic model is easily reduced to a parabolic model if the value of the parameter α is large enough to reduce the expression $\frac{1}{2\alpha}\frac{\partial^2 P(z,\tau)}{\partial \tau^2}$ as much as possible. We have already noticed that "a" and then α correspond to the measurement of the passage frequency.

We can easily imagine the case of a group of very small particles (molecules for example), which quickly change positions; this produces the image describing the diffusion movement. Equation (4.34) describes the diffusion model or the model with a *parabolic* equation:

$$\frac{\partial P(z,\tau)}{\partial \tau} = \frac{v_z^2}{2\alpha}\frac{\partial^2 P(z,\tau)}{\partial z^2} \tag{4.34}$$

If we consider now that the condition (4.29) changes in order to obtain $P_2(0, \tau) = 0$ then according to the sum of Eqs.(4.27) and (4.29) we obtain the initial condition of a Dirac's pulse:

$$P(z,0) = \delta(z) = \left| \begin{array}{ll} 1 & z = 0 \\ \hline 0 & z \neq 0 \end{array} \right. \tag{4.35}$$

The coloured particle is displaced in the fluidized bed according to the model and the laws of diffusion. Indeed, the solution to the diffusion model described by Eq. (4.34) and by the initial condition (4.35) is the following [4.26, 4.27]:

$$P(z,\tau) = \sqrt{\frac{\alpha}{2v_z^2\tau}} \exp\left(-\frac{\alpha z^2}{2v_z\tau}\right) \tag{4.36}$$

The elliptic model given by Eq. (4.33) and the initial condition (4.35) gives the solution obtained with the relation (4.37) [4.5]:

$$P(z,\tau) = \frac{\alpha\exp(-\alpha\tau)}{2v_z}\left[I_0\left(\alpha\tau\sqrt{1-\frac{z^2}{2v_z^2\tau^2}}\right) + \frac{1}{\sqrt{1-\frac{z^2}{v_z^2\tau^2}}} I_1\left(\alpha\tau\sqrt{1-\frac{z^2}{2v_z^2\tau^2}}\right)\right],$$

$$|z| \prec v_z\tau$$

$$P(z,\tau) = 0. \qquad |z| \succ v_z\tau \tag{4.37}$$

$I_0(x)$ and $I_1(x)$, in Eq. (4.37), are the Bessel functions with imaginary arguments and they can be written as follows:

$$I_0(x) = \sum_{k=0}^{\infty} \frac{\left(\frac{x}{2}\right)^{2k}}{(k!)^2} \quad , \quad I_1(x) = \sum_{k=0}^{\infty} \frac{\left(\frac{x}{2}\right)^{2k+1}}{(k!)(k+1)!}. \tag{4.38}$$

The graphical representations of solutions (4.36) and (4.38) are given in Fig. 4.9. The dimensionless variables $z_a = z/H$ and $t_a = \frac{v^2}{H^2}\left(\frac{\tau}{2a}\right)$ have been used here. The curves considered in this figure were drawn taking into account the values of $v_z = 0.1$ m/s, $\alpha = 10$ s^{-1} and H = 0.2 m. In Fig. 4.9, we can observe that:

1. Both models represent the same phenomenon because the curves $P(z,\tau)$ versus z_a and t_a (for the same conditions) are almost identical. The only difference is observed in the fields of very small times which are not of interest in this analysis.
2. The low values of $P(z, \tau)$, which are presented for $z_a > 0.15$, show that the marked particle has a strong conservative tendency because it keeps its position near the injection point where z_a is small.
3. In this particular case, the values considered for α and v_z are chosen without any deep experimental appreciation. How-

ever, in other situations, intensive experimental work would be necessary.

4. The mixing process is axial and the particle displacement is well represented by both models. However, the elliptic model seems to be a little more illustrative because it considers small values of z_a and t_a.

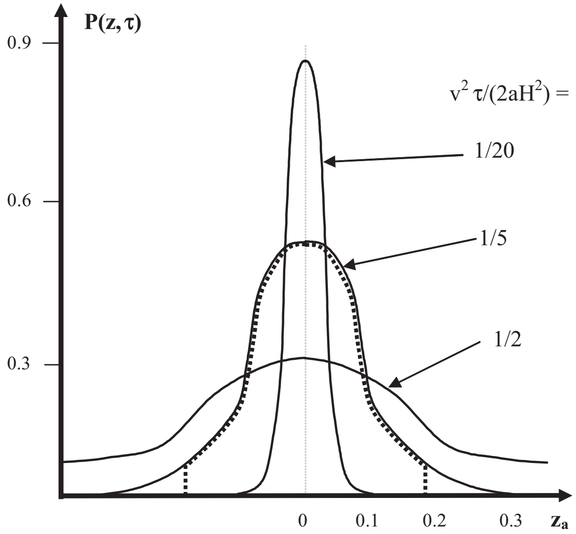


Figure 4.9 The space–time evolution of P (z, τ) by the elliptic model (dashed line) and hyperbolic model (continuous line).

In this problem of axial mixing, it should be specified that the calculated value of $\frac{v_z^2}{2\alpha}$ was approximately 10^{-3} m^2/s; this is comparable with the typical experimental values of the axial dispersion coefficient in fluidized beds with liquids.

Another stochastic model (4.27)–(4.32) treatment can be made when the aim is to calculate the average time of residence and the axial dispersion coefficient. In this problem, we use the properties of the characteristic function, which is associated with the distribution function of the average time of residence [4.28, 4.29]. For this analysis we start with the Laplace transformation of the stochastic model when the system (4.31)–(4.32) is considered:

$$\begin{cases} sP_1(z,s) - P_1(z,0) + v_z\dfrac{dP_1(z,s)}{dz} = -p_{12}aP_1(z,s) + p_{21}aP_2(z,s) & (4.39) \\ sP_2(z,s) - P_2(z,0) - v_z\dfrac{dP_2(z,s)}{dz} = -p_{21}aP_2(z,s) + p_{12}aP_1(z,s) & (4.40) \end{cases}$$

Taking into account the univocity conditions (for instance, look at relations (4.27)–(4.30)), $P_1(z, 0) = P_2(z,0) = 0$), the equations above can be written:

$$\begin{cases} v_z \dfrac{dP_1(z,s)}{dz} = -(s + p_{12}a)P_1(z,s) + p_{21}aP_2(z,s) & (4.41) \\ v_z \dfrac{dP_2(z,s)}{dz} = (s + p_{21}a)P_2(z,s) - p_{12}aP_1(z,s) & (4.42) \end{cases}$$

Now, if Eq.(4.41) is derived according to s and in the obtained result, we make two replacements ($dP_2(z,s)/dz$ by its value given in Eq. (4.42) and $P_2(z,s)$ by its value from Eq. (4.41)), then both equations combine to give:

$$v_z \frac{d^2P_1(z,s)}{dz^2} + a(p_{12} - p_{21})\frac{dP_1(z,s)}{dz} - \left[\frac{(ap_{12})^2 - (s + ap_{12})^2}{v_z}\right]P_1(z,s) = 0 \quad (4.43)$$

After the group of relations (4.27) to (4.30) we can consider that the conditions that have to be coupled with Eq. (4.43) are:

$$P_1(0,0) = 1 \quad , \quad P_1(0,s) = 0 \quad , \quad P_1(H,0) = 0 \quad (4.44)$$

These conditions introduce a complication with respect to the solution to the problem: $dP_1(0,0)/dz$ is absent and the top condition is opposed to the integration ($z = H$). This problem can be circumvented if we consider that the pulse at the input of the fluidized layer can be coupled or not with a particular condition on the output. To simplify the problem, we can choose in Eq.(4.43) $v_z = 1$ as the conventional unit/second. This selection implies that the z dimension (and thus H) would be measured in a conventional unit. When $p_{12} = p_{21} = p_{11} = p_{12} = 0.5$, Eq. (4.43) is simplified to Eq. (4.45), which has the general solution (4.46). Here, λ is given by relation (4.47):

$$\frac{d^2P_1(z,s)}{dz^2} - \left[\left(\frac{2s + a}{2}\right)^2 - \left(\frac{a}{2}\right)^2\right]P_1(z,s) = 0 \quad (4.45)$$

$$P_1(z,s) = C_1 e^{-\lambda z} + C_2 e^{+\lambda x} \quad (4.46)$$

$$\lambda^2 = \left[\left(\frac{2s + a}{2}\right)^2 - \left(\frac{a}{2}\right)^2\right] \quad (4.47)$$

The solution of the system has to check the value of constants C_1 and C_2 (4.46). The relations (4.48) are thus obtained and lead to the solution (4.49):

$$C_1 = \frac{(1 + \lambda)^2}{(1 + \lambda)^2 - (1 - \lambda)^2 e^{-2\lambda H}} \qquad C_2 = \frac{(1 - \lambda)^2 e^{-2\lambda H}}{(1 + \lambda)^2 - (1 - \lambda)^2 e^{-2\lambda H}} \quad (4.48)$$

$$P_1(z,s) = \frac{(1 + \lambda)^2 e^{-\lambda z} - (1 - \lambda)^2 e^{-2\lambda(H - z)}}{(1 + \lambda)^2 - (1 - \lambda)^2 e^{-2\lambda H}} \quad (4.49)$$

Once Eq. (4.41) is adapted to the modifications carried out above, it can be used to give an expression for P_2 (z,s), then we can write:

$$P_2(z,s) = \frac{(1-\lambda)^2 e^{-\lambda z} - (1-\lambda)^2 e^{-2\lambda(H-z)}}{(1+\lambda)^2 - (1-\lambda)^2 e^{-2\lambda H}} \tag{4.50}$$

The function of the distribution of the residence time from 0 up to H can be obtained by the sum of the probabilities of the exit from the way. This is possible at z = H with an elementary action of type I and at z = 0 with a standard elementary action II. Thus, for the function of residence time distribution, the following equation can be written:

$$f(\tau) = P_1(H,\tau) + P_2(0,\tau) \tag{4.51}$$

The characteristic function for a distribution law of a random variable is the Laplace transform of the expression of the distribution law. For the analysis of the properties of the distribution of a random variable, the characteristic function is good for the rapid calculation of the centred or not, momentum of various orders. Here below, we have the definition of the characteristic function $\varphi_\tau(s)$ and its particularization with the case under discussion:

$$\varphi_\tau(s) = \int_0^\infty f(\tau)e^{-s\tau}d\tau = \int_0^\infty (P_1(H,\tau) + P_2(H,\tau))e^{-s\tau}d\tau = P_1(H,s) + P_2(0,s) \tag{4.52}$$

Relations (4.49) and (4.50) rapidly show what P_1 (H, s) and P_2 (0,s) are known and thus, in this case, Eq. (4.52) is written as follows:

$$\varphi_\tau(s) = \frac{Ch(\lambda Hs) + \frac{1-\lambda^2}{2\lambda}Sh(\lambda H) - \frac{1+\lambda^2}{2\lambda}Sh(\lambda Hs)}{\frac{1+\lambda^2}{2\lambda}Sh(\lambda H) + Ch(\lambda H)}$$

Here, the sine and cosine hyperbolic functions (Sh and Ch) are well-known expressions. The average value of the residence time in the way 0–H can be described with the assistance of the characteristic function:

$$\tau_m = \int_0^\infty \tau f(\tau)d\tau = -\varphi_\tau{}'(0) \tag{4.53}$$

The calculation of an analytical derivative for $\varphi_\tau(s)$ by using relation (4.52) is very difficult and tedious. Here below, we make the numerical calculation for the derivative at s = 0. To do so, we use the relation that defines the derivative of a function in a point. We then obtain:

$$
\begin{aligned}
\varphi_\tau'(0) &= \lim_{s\to 0}\frac{\varphi_\tau(s)-\varphi_\tau(0)}{s-0} = \lim_{s\to 0}\frac{\varphi_\tau(s)-1}{s} \\
&= \lim_{s\to 0}\frac{\mathrm{Ch}(\lambda Hs)-\lambda \mathrm{Sh}(\lambda H)-\mathrm{Ch}(\lambda H)-\frac{1+\lambda^2}{2\lambda}\mathrm{Sh}(\lambda Hs)}{\frac{1+\lambda^2}{2\lambda}s\mathrm{Sh}(\lambda H)+s\mathrm{Ch}(\lambda H)} \\
&= \frac{\lim_{s\to 0}[(\lambda' Hs+\lambda H)\mathrm{Sh}(\lambda Hs)-\lambda' H\mathrm{Sh}(\lambda H)]-\lim_{s\to 0}\frac{\lambda^2 H}{s}\frac{\mathrm{Sh}(\lambda H)}{\lambda H}-\lim_{s\to 0}\frac{(1+\lambda^2)H}{2}\frac{\mathrm{Sh}(\lambda Hs)}{\lambda Hs}\ldots}{1\lim_{s\to 0}[\frac{1+\lambda^2}{2\lambda}\mathrm{Sh}(\lambda H)+\mathrm{Ch}(\lambda H)} \\
&= -\left[aH^2+aH+\frac{H}{2}\right]/\left[\frac{H}{2}+1\right] = -\frac{2aH^2+2aH+H)}{H+2}
\end{aligned}
\tag{4.54}
$$

Consequently, the expressions of the mean residence time in the way 0–H and those of the linear distance traversed during motion can be written as follows:

$$
\tau_m = \frac{2aH^2+2aH+H)}{H+2} \quad , \quad l_m = v_Z\tau_m = \frac{(2aH^2+2aH+H)*1}{H+2}
\tag{4.55}
$$

It is necessary to pay careful attention to these last two expressions where H is considered in conventional length units, which corresponds to a $v_z = 1$. For example if $v_z = 1$ cm/s, then the conventional unit (cu) is cm, therefore, in the relations, H would be expressed in cm. Another example shows that $v_z = 0.02$ m/s; so a value of the conventional length unit of 1 cu = 0.02 m is requested to make $v_z = 1$ cu/s. If, in this case, the trajectory is 0.2 m, for example, then, for H, H = 0.2/0.02 = 10 is used which corresponds to a dimensionless value. For very large H values, relation (4.55) can be simplified as follows: $\tau_m = 2a(H+1) \approx 2aH$. This simplification can guide us towards various speculative conclusions with respect to the covered linear distance. Categorically, the result obtained can be explained by the perfect similarity of the final relationships with the well-known formulas used in mechanics.

The problem of theoretical calculation of an axial dispersion coefficient for this example of displacement of the coloured ball is solved in an way identical to the stochastic problem with three equal probable elementary actions (for instance look at the example of axial mixing in a mobile bed column).

If we consider that $p_{12} \neq p_{21}$. From a phenomenological point of view, it is easier to accept a difference between p_{12} and p_{21}. This is typical for a case where a directional internal force acts on a marked particle. As an example, we can consider a particle displacement given by a difference between the weight and the Archimedes force. In this case, the model to be analyzed is described by relations (4.43) and (4.44). For $v_z = 1$ u.c/s, Eq. (4.43) is written as below:

$$
\frac{d^2P_1(z,s)}{dz^2} + a(p_{12}-p_{21})\frac{dP_1(z,s)}{dz} - \left[(ap_{12})^2-(s+ap_{12})^2\right]P_1(z,s) = 0
\tag{4.56}
$$

If $\alpha = ap_{12}, \beta = ap_{21}$ and $\lambda^2 = s(s + 2\alpha)$, then Eq. (4.56) becomes:

$$\frac{d^2P_1(z,s)}{dz^2} + (\alpha - \beta)\frac{dP_1(z,s)}{dz} - -\lambda^2 P_1(z,s) = 0 \tag{4.57}$$

The discriminant associated with the characteristic equation connected to Eq. (4.57) is always positive ($\Delta = (\alpha - \beta)^2 + 4\lambda^2$) and the solution of the differential equation (4.57) is written like a sum of the exponential terms. In addition, the solution for $\alpha = \beta$ must find the former case presented. According to the example already discussed, we have new expressions for $P_1(z, s)$ and $P_2(z, s)$:

$$P_1(z,s) = \frac{(1+\lambda)^2 e^{-\frac{[(\alpha-\beta)+\sqrt{(\alpha-\beta)^2+4\lambda^2}}{2}z} - (1-\lambda)^2 e^{-2\left[(\alpha-\beta)-\sqrt{(\alpha-\beta)^2+4\lambda^2}\right](H-z)}}{(1+\lambda)^2 - (1-\lambda)^2 e^{-2\lambda H}}$$

$$P_2(z,s) = \frac{(1-\lambda)^2 e^{-\frac{[(\alpha-\beta)+\sqrt{(\alpha-\beta)^2+4\lambda^2}}{2}z} - (1-\lambda)^2 e^{-2\left[(\alpha-\beta)-\sqrt{(\alpha-\beta)^2+4\lambda^2}\right](H-z)}}{(1+\lambda)^2 - (1-\lambda)^2 e^{-2\lambda H}}$$

Now there is no obstacle to continuing with the estimation of the characteristic function, average residence time etc.

The last two applications, where the genesis, particularization and evaluation of a stochastic model were improved, undoubtedly show the capacity and the force of stochastic modelling.

4.3
Mathematical Models of Continuous and Discrete Polystochastic Processes

Polystochastic models are used to characterize processes with numerous elementary states. The examples mentioned in the previous section have already shown that, in the establishment of a stochastic model, the strategy starts with identifying the random chains (Markov chains) or the systems with complete connections which provide the necessary basis for the process to evolve. The mathematical description can be made in different forms such as: (i) a probability balance, (ii) by modelling the random evolution, (iii) by using models based on the stochastic differential equations, (iv) by deterministic models of the process where the parameters also come from a stochastic base because the random chains are present in the process evolution.

As was described in the section concerning modelling based on transfer phenomena, a general model can generate many particular cases. The same situation occurs in stochastic modelling processes. The particularization of some stochastic models results in a new image of chemical engineering processes. It is called the stochastic or polystochastic image. It is actually well accepted that almost all chemical engineering processes have a stochastic description [4.5–4.7, 4.30, 4.31].

Some ideas and rather simple concepts, which are fundamental for the alphabet of stochastic modelling, will be described here for some particular cases. It is obvious that knowledge of the alphabet of stochastic methods is only one area of knowledge necessary to become an expert in stochastic modelling. To this aim, a major study of the literature and especially a great personal experience in solving problems, together with a clear knowledge of the corresponding theory are necessary. Some of the aspects presented below will show how to apply polystochastic modelling in chemical engineering.

4.3.1
Polystochastic Chains and Their Models

In the problem of polystochastic chains, different situations can be considered. A first case is expressed by one or several stochastic chains, which keep their individual character. A second case can be defined when one or several random chains are complementary and form a completely connected system. In the first case, it is necessary to have a method for connecting the elementary states which define a chain.

4.3.1.1 Random Chains and Systems with Complete Connections

If we consider the example described at the beginning of this chapter, the element of study in stochastic modelling is the particle which moves in a trajectory where the local state of displacement is randomly chosen. The description for this discrete displacement and its associated general model, takes into consideration the fact that the particle can take one of the positions $i = 0,\pm1,\pm2,\pm3$ ..... where i is a number contained in Z. The particle displacement is carried out step by step and randomly according to the type of component process (elementary state). The type of motion (of the process component) followed by the particle is denoted k. Here, $k \in K$, K is a field of the finite values and p_{ek} is the probability of passage from e to k. In addition, ε is a random variable, which gives the length of displacement for each process component; thus ε_k represents the length of displacement for the k-type motion. The distribution function of this random variable (ε) is written: $p_k(a)$, $a \in Z$. It represents the probability to have a step with length ‘a’ for a k-type displacement.

The process described above is thus repeated with constant time intervals. So, we have a discrete time $\tau = n\Delta\tau$ where n is the number of displacement steps. By the rules of probability balance and by the prescriptions of the Markov chain theory, the probability that shows a particle in position ‘i’ after n motion steps and having a k-type motion is written as follows:

$$P_k(n,i) = \sum_{e \in K} \sum_{a \in Z} P_k(n-1, i-a) p_{ek} p_k(a) \tag{4.58}$$

In order to begin the calculations, we need to know some parameters such as the process components ($k = 2$ or $k = 3$, etc.), the trajectory matrix (p_{ek} in the model), and the equation that describes the distribution function of the path length for displacement k and for the initial state of the process

$P_k(0, i-a)$, $\forall i \in Z$ and $k \in K$. In our example, when the particle displacement is realized by unitary steps and in a positive direction (type I) or in a negative direction (type II) and where the path length distribution is uniform with a unitary value for both component processes, we have:

$$k = 1, 2 \quad , \; p_1(a) = \begin{cases} 1 & \text{for } a = 1 \\ 0 & \text{for } a \neq 1 \end{cases} \; , \; p_2(a) = \begin{cases} 1 & \text{for } a = -1 \\ 0 & \text{for } a \neq -1 \end{cases}$$

For this case, the particularization of the relation (4.58) gives the following system:

$$\begin{cases} P_1(n,i) = P_1(n-1, i-1)p_{11} + P_2(n-1, i-1)p_{21} \\ P_{21}(n,i) = P_1(n-1, i+1)p_{12} + P_2(n-1, i+1)p_{22} \end{cases} \tag{4.59}$$

If, in addition to the standard process components (type I and II), we introduce a third one (position or displacement $k = 3$), which considers that the particle can keep a rest position, then the general model produces the following particularization:

$$\begin{cases} P_1(n,i) = P_1(n-1, i-1)p_{11} + P_2(n-1, i-1)p_{21} + P_3(n-1, i-1)p_{31} \\ P_2(n,i) = P_1(n-1, i+1)p_{12} + P_2(n-1, i+1)p_{22} + P_3(n-1, i+1)p_{32} \\ P_3(n,i) = P_1(n-1, i)p_{13} + P_2(n-1, i)p_{23} + P_3(n-1, i)p_{33} \end{cases} \tag{4.60}$$

$$p_k(a) = \begin{cases} \underline{1 \quad \text{for} \quad (k = 1,\ a = 1); (k = 2,\ a = -1); (k = 3,\ a = 0)} \\ \qquad\qquad 0 \quad \text{for other cases} \end{cases} \tag{4.61}$$

Schmaltzer and Hoelscher [4.32] had suggested this model for the description of the axial mixing and the mass transfer in a packed column. Another particularization can be made in the case when the types of trajectory are chains corresponding to the completely random displacement (for example in the steps $k = 1$, which represent a displacement ahead, it is possible to have a small step towards the right or the left. In a k-type chain, the probability to realize a step towards the right is noted p_k whereas q_k represents the probability for the particle to realize a step towards the left (then, the probability $p_k(a)$ is expressed according to relation (4.63)).

The model which is obtained can be described by relations (4.62) and (4.63).

$$P_k(n,i) = \sum_{e \in K} \left[p_k P_e(n-1, i-a_k) + q_k P_e(n-1, i+a_K) \right] p_{ek} \tag{4.62}$$

$$p_k(a) = \begin{cases} p_k \text{ for } a = a_k \\ q_k \text{ for } a = -a_k \\ 0 \text{ for } a \neq a_k \text{and } a \neq -a_k \end{cases} \tag{4.63}$$

For the mathematical characterization of polystochastic chains, we often use the theory of systems with complete connections. According to the definition given in

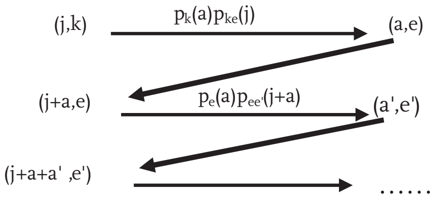
Section 4.1, the group $[(A,\underline{\mathbf{A}}),(B,\underline{\mathbf{B}}),u,P]$ defines a random system with complete connections. For each one of these systems two chains of the random variables are associated: S_n with values in A and E_n with values in B; the causal dependence between both chains is given by the function u as is shown here below:

$$\begin{tikzcd}
S_0 \arrow[r, "P(S_0,\alpha)"] & E_1 \arrow[dl] \\
S_1=u(S_0,E_1) \arrow[r, "P(S_1,\alpha)"] & E_2 \arrow[dl] \\
S_2=u(S_1,E_2) \arrow[r, "P(S_2,\alpha)"] & E_3\ldots\ldots
\end{tikzcd} \tag{4.64}$$

In system (4.64), $P(S_0,\alpha)$, $P(S_1,\alpha)$, etc., represent the conditioned probabilities of temporary transition from $(A,\underline{\mathbf{A}})$ to $(B,\underline{\mathbf{B}})$. The probability $P(S_n,\alpha)$ is given according to the following statement: *"$P(S_n,\alpha)$ is the probability that the phenomenon produced at time $n+1$ (E_{n+1}) belongs to α (with $\alpha\subset A$) with the condition that, at time n, the S_n state has already occurred"*. The chain S_n with values in A, gives a Markov chain E_n (with values in B) which is in fact a complete connections chain. Before particularizing the model given in relation (4.58) into a case with two random variables, we need to explain the case of a particle displacement in a random system with complete connections [4.33]. As shown here, the jumps of a particle are randomly dimensioned by $a\in Z$; if we have a conditioned probability $p_k(a)$ in state $k\in K$, then the component elements characterized by $k\in K$ are different according to their nature (trajectory velocity, medium conditions, etc.). If the particle is positioned at $j\in Z$ and k is its temporary state, the passage probability to a new process $e\in K$ is $p_{ke}(j)$.

At the beginning of the process with $j\in Z$, where the state is a k-type process, the particle jumps distance a and, at the same time, evolves towards process e with the probability $p_e(a)p_{ke}(j)$. Consequently, it reaches $j + a$ in state e. Now, the new beginning is in $j + a$ and in the e state and it jumps a' distance and realizes a state commutation towards e' ($e'\in K$) with $p_{e'}(a)p_{ee'}(j + a)$ probability.

The system keeps evolving considering that it is a random system with complete connections $[(A,\mathbf{A}),(B,\mathbf{B}),u,P]$ and with the following particularizations: $A = B = ZxK$, $u(S_n,E_{n+1}) = u((j,k),(a,e)) = (j+a,e)$ and $P(S_n,\ldots E_1S_1,S_0) = P((j,k);(a,e)) = p_e(a)p_{ke}(j)$ (please look at the definition of a random system with complete connections). The statement above is supported by the fact that $P(S_n,\ldots E_1,S_1,S_0) = P((j,k);(a,e))$ with values in K is a real probability (we can observe that $\sum\limits_{k\in K} p_e(a)p_{ke}(j) = 1$ because $\sum\limits_{a\in Z} p_e(a) = 1$ and $\sum\limits_{e\in Z} p_{ke}(j) = 1$). The particle displacement, described above, is represented by relation (4.64), which is particularized as follows:



(4.65)

A complete particularization can be made in order to show more precisely that the case considered is a random system with complete connections. In this case, S_n is the first random vector:

$$S_n = \left|\frac{S_n{}'}{S_n{}''}\right| = \left|\frac{\text{particle position at time } n}{\text{process component at time } n}\right|$$

whereas E_{n+1} is the second random vector:

$$E_{n+1} = \left|\frac{E_{n+1}{}'}{E_{n+1}{}''}\right| = \left|\frac{\text{jump distance at time } n}{\text{process component at time } n}\right|$$

The function u is given by $S_{n+1} = u(S_n,E_{n+1})$ and the probability $P(S_n,\ldots.E_1,S_1,S_0)$ can be expressed as:

$$P\left(E_1 = \left|\frac{a}{e}\right|/S_0 = \left|\frac{j}{k}\right|\right) = P((j,k);(a,e))$$

$$P\left(E_{n+1} = \left|\frac{a}{e}\right|/S_n, E_n, \ldots S_1, E_1; S_0\right) = P(S_n;(a,e)) \tag{4.66}$$

Obviously, S_n is a homogeneous Markov chain with a passage probability given by $P(S_{n+1} = (j,e)/S_n = (i,k)) = p_e(j-i)p_{ke}(i)$, whereas, E_n is a complete connection chain. In this case, the stochastic model (4.58) is known as the Chapman–Kolmogoraov model; it can be generalized by the Eq. (4.67):

$$P_k(n,i) = \sum_{e\in K}\sum_{a\in Z} P_k(n-1,i-a)p_{ek}(i-a)p_k(a) \tag{4.67}$$

In the case when the transition probabilities do not depend on the position, noted here by i, they are constant and therefore the chain E_n is a Markov chain.

4.3.2
Continuous Polystochastic Process

The stochastic models can present discrete or continuous forms. The former discussion was centred on discrete models. The continuous models are developed according to the same base as the discrete ones. Example 4.3.1 has already shown this method, which leads to a continuous stochastic model. This case can be generalized as follows: a particle in the z position moves in a medium with velocity v_k $k = 1,2,3,......n$, where n is a finite number; in the interval of time $\Delta\tau$, the probability to pass from speed v_k to v_j is $p_{kj} = \alpha_{kj}\ \Delta\tau$. This corresponds to a connection process of the Markov type. If $P_k(z,\tau + \Delta\tau)$ is the probability that the particle reaches z at $\tau + \Delta\tau$ with velocity v_k, then we can write:

$$P_k(z,\tau+\Delta\tau) = \sum_{j=1}^{n} P_j(x - v_k\Delta\tau,\tau)p_{jk}\ ;\ 1 <= j,\ k <= n \tag{4.68}$$

We can notice that relation (4.68) describes the evolution of the particles having reached position z in time $\tau + \Delta\tau$ which were originally positioned among the particles at the distance $v_k\Delta\tau$ with respect to z. In the interval of time $\Delta\tau$, their velocity changes to v_k. In the majority of the displacement processes with v_k velocity, a complete system of events appears and, consequently, the matrix of passage from one velocity to another is of the stochastic type. This means that the addition of the probabilities according to the unit value limit is: $\sum_{j=1}^{n} p_{kj} = 1\ ,\ \forall k = 1, n$. If, in relation (4.68), we replace $p_{kk} = 1 - \sum_{j=1, j\neq k}^{n} p_{kj}$ then, we can write:

$$\begin{aligned} P_k(z,\tau+\Delta\tau) = {} & P_k(z - v_k\Delta\tau,\tau) - \left(\sum_{j=1,j\neq k}^{n} p_{kj}\right) P_k(z - v_k\Delta\tau,\tau) \\ & + \sum_{j=1}^{n} p_{jk}P_j(z - v_j\Delta\tau,\tau) \end{aligned} \tag{4.69}$$

In the equation system (4.69), the subscripts j, k are limited by the number of elementary states. Thus, we always have $0 <= j,\ k <= n$. Now, if we use a development around the point (x, τ) for the first term of Eq. (4.69) we have:

$$P_k(z - v_k\Delta\tau,\tau) = P_k(z,\tau) - v_k\frac{\Delta P_k(z,\tau)}{\Delta z} + ... \tag{4.70}$$

The development described above transforms system (4.69) into the following system of n equations ($k = 1, n$) with partial derivatives:

$$\frac{\partial P_k(z,\tau)}{\partial\tau} + v_k\frac{\partial P_k(z,\tau)}{\partial z} = -\left(\sum_{j=,j\neq k}^{n} \alpha_{kj}\right) P_k(z,\tau) + \sum_{j=1,j\neq k}^{n} \alpha_{jk}P_j(z,\tau) \tag{4.71}$$

If the parameters α_{kj} have constant values, then the model described by system (4.71) corresponds to a Markov connection linking the process components. In this case, as in general, the process components represent the individual displacements which can be characterized globally through the convective mixing of their spectra of speeds (v_k, $k = 1,N$).

The model developed in Section 4.3.1 is a particular case of the model (4.71) where $k = 2, v_1 = v_z$, $v_2 = -v_z$ (for instance see relations (4.25), (4.26)):

$$\frac{\partial P_1(z,\tau)}{\partial \tau} + v_z \frac{\partial P_1(z,\tau)}{\partial z} = -\alpha_{12}P_1(z,\tau) + \alpha_{21}P_2(z,\tau) \tag{4.72}$$

$$\frac{\partial P_2(z,\tau)}{\partial \tau} - v_z \frac{\partial P_{21}(z,\tau)}{\partial z} = -\alpha_{21}P_2(z,\tau) + \alpha_{12}P_2(z,\tau) \tag{4.73}$$

For k = 3 , $v_1 = v_z$,$v_2 = -v_z$ $v_3 = 0$ (at $v_3 = 0$ the particle keeps a stationary position) we have the model (4.74)–(4.76) which has been successfully used in the analysis of axial mixing for a fluid that flows in a packed bed column [4.28]:

$$\frac{\partial P_1(z,\tau)}{\partial \tau} + v_z \frac{\partial P_1(z,\tau)}{\partial z} = -(\alpha_{12} + \alpha_{13})P_1(z,\tau) + \alpha_{21}P_2(z,\tau) + \alpha_{31}P_3(z,\tau) \tag{4.74}$$

$$\frac{\partial P_2(z,\tau)}{\partial \tau} - v_z \frac{\partial P_{21}(z,\tau)}{\partial z} = -(\alpha_{21} + \alpha_{23})P_2(z,\tau) + \alpha_{12}P_1(z,\tau) + \alpha_{32}P_3(z,\tau) \tag{4.75}$$

$$\frac{\partial P_1(z,\tau)}{\partial \tau} = -(\alpha_{31} + \alpha_{32})P_3(z,\tau) + \alpha_{13}P_1(z,\tau) + \alpha_{23}P_2(z,\tau) \tag{4.76}$$

A second continuous polystochastic model can be obtained from the transformation of the discrete model. As an example, we consider the case of the model described by Eqs. (4.62) and (4.63). If $P_k(z,\tau)$ is the probability (or, more correctly, the probability density which shows that the particle is in the z position at time τ with a k-type process) then, p_{kj} is the probability that measures the possibility for the process to swap, in the interval of time $\Delta\tau$, the elementary process k with a new elementary process (component) j. During the evolution with the k-type process state, the particle moves to the left with probability β_k and to the right with probability γ_k (it is evident that we take into account the fact that $\beta_k + \gamma_k = 1$). For this evolution, the balance of probabilities gives relation (4.77), which is written in a more general form in Eq. (4.78):

$$P_k(z,\tau+\Delta\tau) = \sum_{j=1}^{n} p_{jk}[\beta_k P_j(z-\Delta z,\tau) + \gamma_k P_j(z+\Delta z,\tau)] \; ; 1 <= j, k <= n \tag{4.77}$$

$$P_k(z,\tau+\Delta\tau) = \sum_{m}\sum_{j=1}^{n} P_k(z-\Delta z_m,\tau)p_{jk}(z-\Delta z_m)p_i(\Delta z_m) \tag{4.78}$$

Equation (4.78) is developed with the assistance of relation (4.77). To do so, it is necessary to consider the values of $p_{jk}(z - \Delta z_m) = p_{jk}$ as constant and the following relation for $p_i(\Delta z_m)$:

$$p_i(\Delta z_m) = \begin{cases} \beta_k & \text{for } \Delta z_m = \Delta z_k \\ \gamma_k & \text{for } \Delta z_m = -\Delta z_k \\ 0 & \text{for other cases} \end{cases}$$

Now, we have to take into account the following considerations for relation (4.77):

- the passage matrix is stochastic, it results in:

$$\sum_{j=1}^{n} p_{kj} = 1; .p_{kk} = 1 - \sum_{j=1,j\neq k}^{n} p_{kj}.$$

- the connection process is of Markov type and then: $p_{kj} = \alpha_{kj}\Delta\tau$.
- the probabilities $P_k(z - \Delta z,\tau)$ and $P_k(z + \Delta z,\tau)$ are continuous functions and can be developed around (z,τ):

$$P_k(z \mp \Delta z, \tau) = P_k(z, \tau) \mp \Delta z_i \frac{\Delta P_k(z, \tau)}{\Delta z_i} + \frac{\Delta z_i^2}{2} \frac{\Delta^2 P_k}{(\Delta z_i)^2} \mp .....$$

- the displacements to the left and to the right by means of an elementary k-process have the same probability and then $\beta_k = \gamma_k = 1/2$.

These considerations result in the following equation:

$$\frac{\partial P_k(z, \tau)}{\partial \tau} = D_k \frac{\partial^2 P_k(z, \tau)}{\partial z^2} - \left(\sum_{j=1, j\neq k}^{n} \alpha_{kj} \right) P_k(z, \tau) + \sum_{j=1, j\neq k}^{n} \alpha_{jk} P_j(z, \tau) \; ;$$
$$1 < = j, \, k < = n \tag{4.79}$$

In Eq. (4.79), D_k represents the limit $D_k = \lim\limits_{\Delta\tau \to 0} \frac{\Delta z_k^2}{\Delta \tau}$, which has a finite value, and the dimension of a diffusion coefficient. It is called: *diffusion coefficient of the elementary k-process.*

If the displacement velocity of the particle is described by $+v_x$ and $-v_x$ in the x axis, $+v_y$ and $-v_y$ in the y axis and finally $+v_z$ and $-v_z$ in the z axis, we can consider the following diffusion coefficients:

$$D_{xx} = \lim_{\Delta\tau \to 0} \frac{\Delta x^2}{\Delta \tau}, \; D_{yy} = \lim_{\Delta\tau \to 0} \frac{\Delta y^2}{\Delta \tau}, D_{zz} = \lim_{\Delta\tau \to 0} \frac{\Delta z^2}{\Delta \tau}, \; D_{xy} = \lim_{\Delta\tau \to 0} \frac{\Delta x \Delta y}{\Delta \tau}, \text{ etc.}$$

This definition of diffusion coefficients considers the non-isotropic diffusion behaviour in some materials. So, this stochastic modelling can easily be applied for the analysis of the oriented diffusion phenomena occurring in materials with designed properties for directional transport.

Model (4.79) describes an evolutionary process, which results from the coupling of a Markov chain assistance with some individual diffusion processes. This model is well known in the study of the coupling of a chemical reaction with diffusion phenomena [4.5, 4.6, 4.34, 4.35]. The models described by relations (4.63) and (4.79) can still be particularized or generalized. As an example, we can notice that other types of models can be suggested if we consider that the values of α_{kj} are functions of z or τ or $P_k(z,\tau)$ in Eq.(4.79). However, it is important to observe that the properties of the Markov type connections cannot be considered when $\alpha_{kj} = f(P_K(z, \tau))$.

Using *stochastic differential equations* can also represent the stochastic models. A stochastic differential equation keeps the deterministic mathematical model but accepts a random behaviour for the model coefficients. In these cases, the problems of integration are the main difficulties encountered. The integration of stochastic differential equations is known to be carried out through working methods that are completely different from those used for the normal differential equations

[4.36, 4.37]. We can overcome this difficulty if, instead of using the stochastic differential equations of the process, we use the analysis of the equations with partial derivatives that become characteristic for the passage probabilities (Kolmogorov-type equations).

The following practical example will illustrate this problem: a mobile device passes through an arbitrary space with a variable velocity. By means of the classic dynamics analysis, we can write that $\frac{dX(\tau)}{d\tau} = kv(\tau)$. In the stochastic language, this equation can be written as follows:

$$\frac{dX(\tau)}{d\tau} = F(X(\tau), v(\tau)),\ X(0) = X_0 \tag{4.80}$$

where F(X,v) is an operator (F(X,v) = kv for example), defined for $R^n x R^m$ with values in R^n. It is able to be derivate in X, keeping the continuity in v.

- v(τ) is a Markov diffusion process (for instance, look at the model described by Eq. (4.79)). The following relations give the variances and the average (mean) values of this diffusion process:
- the variances:

$$\sigma_{ij} = \lim_{\Delta\tau \to 0} E\left\{[v_i(\tau + \Delta\tau) - v_i(\tau)][v_j(\tau + \Delta\tau) - v_j(\tau)]/v(\tau) - v\right\} \tag{4.81}$$

- the mean values

$$m_j(v) = \lim_{\Delta\tau \to 0} E\left\{[(v_j(\tau) - v(\tau)]/v(\tau)\right\} = v \tag{4.82}$$

Here, i, j = 1, 2,...m are subscripts which indicate the individual states of the device speed. The coupled process (X(τ),v(τ)) is a Markov process with values in R^{n+m} and with mean value and variances (X,v), (X,X) given by the following relations:

$$\lim_{\Delta\tau \to 0} \frac{1}{\Delta\tau} E\left\{(X_i(\tau + \Delta\tau) - X(\tau))/(X(\tau), v(\tau))\right\} = F_i(X(\tau), v(\tau)) \tag{4.83}$$

$$\lim_{\Delta\tau \to 0} \frac{1}{\Delta\tau} E\left\{[X_i(\tau + \Delta\tau) - X(\tau)][v_j(\tau + \Delta\tau) - v_j(\tau)]/(X(\tau), v(\tau))\right\} = 0 \tag{4.84}$$

$$\lim_{\Delta\tau \to 0} \frac{1}{\Delta\tau} E\left\{[X_i(\tau + \Delta\tau) - X(\tau)][X_j(\tau + \Delta\tau) - X_j(\tau)]/(X(\tau), v(\tau))\right\} = 0 \tag{4.85}$$

If F(X,v) = v or if v is the device speed, then the stochastic differential equation (4.80) shows that the state of the device is a function which depends on position and speed. The device passes from one speed to another with the rules defined by a diffusion process and with an average value $m_j(v)$ and a variance $\sigma_{i\,j}$, $1 <= i, j <= n$. It is important to note that the passage probability densities of the coupled Markov process (X(τ),v(τ)) – written: $p = p(\tau, X, v, X_0, v_0)$ – should verify the following equation:

$$\frac{\partial p}{\partial \tau} = \frac{1}{2}\sum_{i,j=1}^{m}\frac{\partial^2[\sigma_{ii}(v)p]}{\partial v_i \partial v_j} - \sum_{j=1}^{m}\frac{\partial[m_j(v)]}{\partial v_j} - \sum_{i=1}^{n}\frac{\partial[F_j p]}{\partial x_j} \tag{4.86}$$

The initial condition used with Eq. (4.86) shows that, at time $\tau = 0$, the stochastic evolution begins according to a signal impulse:

$$p(0, X, v, X_0, v_0) = \delta(X - X_0)\delta(v - v_0) \tag{4.87}$$

In Eq. (4.86), F_j is the average value for the coupled Markov process (see Eq. (4.83)). In Eq. (4.87) $p = p(\tau,X,v,X_0,v_0)$ corresponds to the probability density of the coupled process $(X(\tau),v(\tau))$. To calculate this density of probability at a predefined time $(p(\tau,X,v))$, we use the initial condition:

$$p(0, X, v) = \rho_v(0, v)\delta(X - X_0) \tag{4.88}$$

where $\rho_v(0, v)$ is the probability density of the process $v(\tau)$ at the start.

With solution $p(\tau,X,v)$, we can calculate the distribution process $X(\tau)$ after the integration for all the possible speeds:

$$p(\tau, X) = \int_{-\infty}^{\infty} p(\tau, X, v)dv \tag{4.89}$$

This method to solve stochastic differential equations has also been suggested to calculate the solutions of the stochastic models originated from the theory of random evolution [4.38, 4.39].

In the following paragraph, we will explain how this method is particularized for two examples. A random evolution is described with the assistance of a model, which is based on a dynamic system with operation equations called state equations, which have to undergo random variations. The first example is given by the evolution of a bacterial population that develops in a medium with a randomly changing chemical composition. A second example can be represented by the atmospheric distribution for polluting fumes produced by a power station when atmospheric turbulences change randomly. Many other examples illustrate these typical situations where a system in evolution changes its mode of evolution according to the random changes of the medium or according to the changing conditions of the process development. In these systems the process can evolve (move) into a stochastic or deterministic way at time "t" and, suddenly, at time "τ", the process undergoes another random descriptive evolution.

From a mathematical point of view, a random evolution is an operator $O(\tau,t)$ that is improved at both t and τ times. The linear differential equation is Eq. (4.90):

$$\frac{dO(\tau, t)}{d\tau} = -V(X(\tau))O(\tau, t) \quad \text{or} \quad \frac{dO(\tau, t)}{dt} = O(\tau, t)V(X(t)) \tag{4.90}$$

$V(X(\tau)$ (or $V(X(t))$ is the expression of an operator which depends on parameter X (or $X(t)$), which is the stochastic parameter characterizing the process. It is important to note that the correct expression of X(t) is X(t, e), where $e \in \Omega$. Here, Ω is the region where the elementary steps characterizing the process occur.

If we consider that V(X(t)) is a first order linear differential operator like $V(X) = v(X)\frac{d}{dz}$ with v(X) in R, then for each X value (1 ,2 ,...n,) v(X) will be a constant that multiplies the operator $\frac{d}{dz}$ out. With this type of random evolution operator, we can describe the behaviour of a particle that at present moves in the z-axis with a random speed. This velocity is included in the speed spectrum of the integral process.

The concept of infinitesimal operator is frequently used when the random evolutions are the generators of stochastic models from a mathematical point of view. This operator can be defined with the help of a homogeneous Markov process X(t) where the random change occurs with the following transition probabilities:

$$p(t-\tau, X, A) = P(X(t) \in A / X(\tau) = X) \tag{4.91}$$

We have to notice that, for different X(t) values, we associate different values for the elements of the matrix of transition probabilities. When the movement randomly changes the value of X into a value around A, Eq. (4.91) is formulated with expressions giving the probability of process X(t) at different states. The infinitesimal operator [Qf] ([Qf] = Q by function f) is defined as the temporary derivative of the mean value of the stochastic process for the case when the process evolves randomly:

$$[Qf] = -\frac{d}{d\tau}\bigg|_{\tau=t} \left(\int f(y) p(t-\tau, X) dy\right) = -\frac{d}{d\tau}\bigg|_{\tau=t} E_{x/\tau}(f(X(t))) \tag{4.92}$$

If the Markov process, considered in Eq. (4.91), is characterized by n states, then the infinitesimal operator Q corresponds to a matrix (n, n) where the q_{ij} elements are:

$$q_{ij} = \lim_{t \to \tau} \frac{1}{t-\tau} [p_{ij}(t-\tau) - \delta_{ij}]$$

In the case where X(t) or X(t, e) corresponds to a diffusion process (the stochastic process is continuous), it can be demonstrated that Q is a second order elliptic operator [4.39– 4.42]. The solution of the equation, which defines the random evolution, is given by a formula that yields O(τ,t). In this case, if we can consider that $e_m(t, X)$ is the mean value of X(t)(which depends on the initial value of X_0), then, we can write the following equation:

$$e_m(t, X) = E_{X0}\{O(0, t) f(X(t))\} \tag{4.93}$$

Here, $e_m(t, X)$ gives the solution for Eq. (4.94) where the operators V(X) and Q work together:

$$\frac{de_m(t, X)}{dt} = V(X)e(t, X) + Qe_m(t, X) \quad \text{where} \quad e_m(0, X) = f(X) \tag{4.94}$$

The condition $e_m(0,X) = f(X)$ in the previous equation is a result of O(t,t) = I where I is the identity operator.

Two examples, which show the methodology to be used in order to establish the random evolution operator, are developed below:

1. When X(t) or, more correctly, X(t, e) is a Brownian motion process (a displacement with multiple direction changes) and V(X) is a function of real values, Eq. (4.90) gives the following solution:

$$O(\tau, t) = \exp \int_{\tau}^{t} V(X(\alpha)d\alpha) \tag{4.95}$$

   Here, $e_m(t,X)$ is given to the computation with the relation (4.93). We obtain formula (4.96) where we can observe that $E_X = E_{X0}$ is a Wiener integral.

$$e_m(t,X) = E_{X0}\left\{\exp\left(\int_0^t V(X(\alpha)d\alpha)f(X(t))\right)\right\} \tag{4.96}$$

   As far as the infinitesimal operator is elliptic $\left(Q = \frac{1}{2}\frac{d}{dX^2}\right)$, Eq. (4.94) gives, for $e_m(t,X)$, the following equation of partial derivatives:

$$\frac{\partial e_m}{\partial t} = V(X)e_m + \frac{1}{2}\frac{\partial^2 e_m}{\partial X^2} \quad \text{where} \quad e_m(0,X) = f(X) \tag{4.97}$$

2. When X(t, e) is a "n states" process with the infinitesimal generator Q and when V(X) with X = 1,2,3,...n are first order differential generators, the particularization of relation (4.94) is given by a system of hyperbolic equations with constant coefficients. So when $V(X) = v(X)\frac{d}{dz}$ and v(X) is in R, this system is described by Eq. (4.98). Here q_{xy} are the elements of the infinitesimal generator:

$$\frac{\partial e_m(t,X,z)}{\partial t} = v(X)\frac{\partial e_m(t,X,z)}{\partial z} + \sum_{y=1}^{n} q_{xy} e_m(t,X,z) \; 1<X<n \tag{4.98}$$

   For relation (4.98), the initial condition $e_m(0,X,z) = f(X,z)$ can be established according to the form considered for v(X). This condition shows that, at the beginning of the random evolution and at each z position, we have different X states for the process. The examples described above show the difficulty of an analysis when the required process passes randomly from one stochastic evolution to another.

As was stated previously, the method of analysis for the stochastic differential equations, which gives the probability density p(τ,X,v) as a model solution, can be applied to build and analyze the models developed from the random evolution theory. At the same time, from the mathematical point of view, we have shown that a model solution for a process with random exchanges from one stochastic evolution to another can be carried out as $e_m(\tau, X, v)$ mean values. With reference to this model solution form, Gikham and Shorod [4.43] show that, in a stochastic process (X,v), the mean values for the process trajectories ($e_m(\tau, X, v)$) are given by:

$$e_m = e_m(\tau, X, v) = E_{Xv}\{f(X(\tau), v(\tau))\} \tag{4.99}$$

otherwise these mean values satisfy the indirect equations of Kolmogorov:

$$\frac{\partial e_m}{\partial \tau} = \frac{1}{2}\sum_{i,j=1}^{m} \sigma_{ij}(v)\frac{\partial^2 e_m}{\partial v_j \partial v_i} + \sum_{j=1}^{m} m_j(v)\frac{\partial e_m}{\partial v_j} + \sum_{j=1}^{n} F_j(X, v)\frac{\partial e_m}{\partial X_j} \quad ;$$

$$e_m(0, X, v) = f(X, v) \tag{4.100}$$

The practical example given below illustrates this type of process evolution and its solution. Here, we consider a displacement process such as diffusion with $v(\tau)$. The process presents a variance $\sigma(v)$ and a mean value $m(v)$ whereas $X(\tau)$ is an associated process which takes scalar values given by:

$$\frac{dX(\tau)}{d\tau} = h(v(\tau))X(\tau)\ , \quad X(0) = X \tag{4.101}$$

It is evident that we must have real values for $h(v(\tau))$ so, $h(v)$: $R \to R$ where R is the domain of real numbers. The solution to Eq. (4.101) is:

$X(\tau) = X\exp[\int_0^\tau h(v(\alpha)d\alpha]$ and its average value, calculated by the Kolmogorov relation ((4.100)), corresponds to one of the possible solutions of Eq. (4.102). In this example relation (4.102) represents the particularization of Eq. (4.100).

$$\frac{\partial e_m}{\partial \tau} = \frac{1}{2}\sigma(v)\frac{\partial^2 e_m}{\partial v^2} + m(v)\frac{\partial e_m}{\partial v} + h(v)X\frac{\partial e_m}{\partial X}\quad ,\ e_m(0, X, v) = f(X, v) \tag{4.102}$$

If the function f(X,v), which gives the mean value, is particularized as f(X,v) = Xg(v), where the derivative of g(v) can be calculated, then the expression for e_m becomes: $e_m = e_m(t, X, v) = E_{Xv}\{f(X(\tau), v(\tau))\}$ = XH(v,τ). It is observable that it is easy to write that $H(v, \tau) = E_v[\exp[\int_0^\tau h(v(\alpha)d\alpha)]g(v(t))]$. At the same time, H(v,τ) verifies the partial derivative equation (4.103) which is developed from the replacement of the average value e_m and the function f(X,v) inside Eq. (4.102):

$$\frac{\partial H}{\partial \tau} = \frac{1}{2}\sigma(v)\frac{\partial^2 H}{\partial v^2} + m(v)\frac{\partial H}{\partial v} + h(v)V\ , \qquad H(0, v) = g(v) \tag{4.103}$$

These equations and the example shown in Section 4.3.1 can be related if we consider that, when v(τ) is a Markov process with discrete valuesi = 1,.......n and with the infinitesimal generator Q, then, the e_{mi} mean values ($e_{mi} = e_{mi}(t, X) = E_{Xi}\{f_i(X(\tau))\}$) are the solutions to the following differential equation:

$$\frac{\partial e_{mi}}{\partial \tau} = \sum_{j=1}^{m} q_{ij} e_{mi} + \sum_{k=1}^{n} F_k(X, v_i) \frac{\partial e_{mi}}{\partial X_k} \ , \quad e_{mi}(0, X) = f_i(X) \qquad (4.104)$$

A discussion concerning the equations assembly (4.104) can be carried out dividing it into its different component terms. If we consider the first term alone, we can observe that it represents a connection for the elementary processes with the passage matrix $e^{Q\tau}$ The second term corresponds to the transport or convection process at different speeds. Indeed, v(τ) is a two-states process with the infinitesimal generator Q and the function F(X,v) given by the following formula:

$$Q = \left| \frac{-\alpha \quad \alpha}{\alpha \quad -\alpha} \right| , \ F(X, \pm v) = \pm v \qquad (4.105)$$

The particularization of the equations assembly (4.104) results in system (4.106):

$$\begin{cases} \dfrac{\partial e_{m1}}{\partial \tau} - v\dfrac{\partial e_{m1}}{\partial X} = -\alpha e_{m1} + \alpha e_{m2} \\ \dfrac{\partial e_{m2}}{\partial \tau} + v\dfrac{\partial e_{m2}}{\partial X} = -\alpha e_{m2} + \alpha e_{m1} \end{cases}$$

$$e_{m1}(0, X) = f_1(X) \ , \quad e_{m2}(0, X) = f_2(X) \qquad (4.106)$$

If the process takes place along the z-axis, then we can write that X = z. Considering now that e_{m1} and e_{m2} are the average or mean probabilities for the process evolution with +v or –v states at the z position, we can observe a similitude between system (4.106) and Eqs. (4.31) and (4.32) that describe the model explained in the preceding paragraphs. The solution of the system (4.106) [4.5] is given in Eq. (4.107). It shows that the process evolution after a random movement depends not only on the system state when the change occurs but also on the movement dynamics:

$$e_{m1,2}(X, t) = E\left[f_{1,2}(X)(X + \int_0^t v(s) ds) \right] \qquad (4.107)$$

4.3.3

The Similarity between the Fokker–Plank–Kolmogorov Equation and the Property Transport Equation

In Chapter 3, it was established that the local concentration Γ_A characterizes the state of one property (momentum, heat, mass of species, etc.) in a given system. In terms of the Γ_A concentration field, the differential form for the conservation of the property can be written as follows:

$$\frac{\partial \Gamma_A}{\partial \tau} + \mathrm{div}(\vec{w}\Gamma_A) = \mathrm{div}(D_{\Gamma A}\overrightarrow{\mathrm{grad}}\Gamma_A) + \mathrm{div}(\vec{J}_{SA}) + J_{V\Gamma}$$

This equation shows that the conservation of a property depends on the fortuitous or natural displacement of the property produced by vector $\vec{w}$, when that is generated through a volume ($J_{V\Gamma}$) or/and by a surface process (vector J_{SA}). The mentioned displacement is supplemented by a diffusion movement ($D_{\Gamma A}$ in the right part of the conservation equation). This movement is characterized by steps of small dimension occurring with a significant frequency in all directions. When the diffusion movement takes place against the vector $\vec{w}$ it is often called counter-diffusion. In the case of a medium, which does not generate the property, the relation can be written as follows:

$$\frac{\partial \Gamma_A(\tau,\bar{x})}{\partial \tau} + \frac{\partial}{\partial \bar{x}}(w(\tau,\bar{x})\Gamma_A(\tau,\bar{x})) = \frac{\partial}{\partial \bar{x}}\left(D_{\Gamma A}\frac{\partial}{\partial \bar{x}}(\Gamma_A(\tau,\bar{x}))\right) \tag{4.108}$$

where τ represents the time, $\bar{x}$ is a vector with n dimensions which represents the coordinates, $w(\tau,\bar{x})$ is also an n dimension vector and gives the speed which is bound to the position,$D_{\Gamma A}$ is an $n \times n$ matrix that contains the diffusion coefficients of the property with the local concentration Γ_A. If we assume that the component values of the diffusion matrix depend on the concentration values of the local property then Eq. (4.108), can be written as:

$$\begin{aligned}\frac{\partial \Gamma_A(\tau,\bar{x})}{\partial \tau} = & -\frac{\partial}{\partial \bar{x}}\left(\left(w(\tau,\bar{x}) + \frac{\partial D_{\Gamma A}(\tau,\bar{x})}{\partial \Gamma_A}\frac{\partial \Gamma_A}{\partial \bar{x}}\right)\Gamma_A(\tau,\bar{x})\right) + \\ & \frac{\partial}{\partial \bar{x}}\frac{\partial}{\partial \bar{x}}(D_{\Gamma A}(\tau,\bar{x})\Gamma_A(\tau,\bar{x}))\end{aligned} \tag{4.109}$$

The vectors and the matrix described by relations (4.108) and (4.109) are given in Table 4.1. It should be specified that only the axial anisotropy in the case of an anisotropic medium was considered. However, if we want to take into account the anisotropy through the plane or the surface, we have to consider the terms of type $D_{\Gamma Axy}$ in the $D_{\Gamma A}(\tau,\bar{x})$ matrix.

Table 4.1 Vectors of Eqs. (4.108) and (4.109).

Case	**Mono-dimensional**	**Tri-dimensional**	**n × n dimensions**
vector			
$\bar{x}$	$\bar{x} = x$	$\bar{x} = \begin{pmatrix} x \\ y \\ z \end{pmatrix}$	$\bar{x} = \begin{pmatrix} x_1 \\ x_2 \\ x_3 \\ - \\ x_n \end{pmatrix}$
$w(\tau,\bar{x})$	$w(x,\tau)$	$\begin{pmatrix} w_x(x,y,z,\tau) \\ w_y(x,y,z,\tau) \\ w_z(x,y,z,\tau) \end{pmatrix}$	$\begin{pmatrix} w_{x1}(x_1,x_2,\ x_n,\tau) \\ w_{x2}(x_1,x_2,\ x_n,\tau) \\ w_{x3}(x_1,x_2,\ x_n,\tau) \\ - \\ w_{xn}(x_1,x_2,\ x_n,\tau) \end{pmatrix}$

Case	Mono-dimensional	Tri-dimensional	n × n dimensions
$D_{\Gamma A}(\tau,\bar{x})$	$D_{\Gamma A}$	$\begin{pmatrix} D_{\Gamma A} & 0 & 0 \\ 0 & D_{\Gamma A} & 0 \\ 0 & 0 & D_{\Gamma A} \end{pmatrix}$ isotropic medium	$\begin{pmatrix} D_{\Gamma A} & 0 & - & 0 \\ 0 & D_{\Gamma A} & - & 0 \\ - & - & - & 0 \\ 0 & 0 & - & D_{\Gamma A} \end{pmatrix}$ isotropic medium
		$\begin{pmatrix} D_{\Gamma x} & 0 & 0 \\ 0 & D_{\Gamma y} & 0 \\ 0 & 0 & D_{\Gamma z} \end{pmatrix}$ anisotropic medium	$\begin{pmatrix} D_{\Gamma x1} & 0 & - & 0 \\ 0 & D_{\Gamma x2} & - & 0 \\ - & - & - & 0 \\ 0 & 0 & - & D_{\Gamma xn} \end{pmatrix}$ anisotropic medium
$\frac{\partial D_{\Gamma A}}{\partial \Gamma_A}\frac{\partial \Gamma_A}{\partial \bar{x}}$	$\frac{\partial D_{\Gamma A}}{\partial \Gamma_A}\frac{\partial \Gamma_A}{\partial x}$	$\begin{pmatrix} \frac{\partial D_{\Gamma A}}{\partial \Gamma_A}\frac{\partial \Gamma_A}{\partial x} \\ \frac{\partial D_{\Gamma A}}{\partial \Gamma_A}\frac{\partial \Gamma_A}{\partial y} \\ \frac{\partial D_{\Gamma A}}{\partial \Gamma_A}\frac{\partial \Gamma_A}{\partial z} \end{pmatrix}$	$\begin{pmatrix} \frac{\partial D_{\Gamma A}}{\partial \Gamma_A}\frac{\partial \Gamma_A}{\partial x1} \\ \frac{\partial D_{\Gamma A}}{\partial \Gamma_A}\frac{\partial \Gamma_A}{\partial x2} \\ \frac{\partial D_{\Gamma A}}{\partial \Gamma_A}\frac{\partial \Gamma_A}{\partial xn} \end{pmatrix}$

If, in Eq. (4.109), we use the following notation:

$A(\tau,\bar{x}) = \left(w(\tau,\bar{x}) + \frac{\partial D_{\Gamma A}}{\partial \Gamma_A}\frac{\partial \Gamma_A}{\partial \bar{x}}\right)$ then, we can write:

$$\frac{\partial \Gamma_A(\tau,\bar{x})}{\partial \tau} = -\frac{\partial}{\partial \bar{x}}(A(\tau,\bar{x})\Gamma_A(\tau,\bar{x})) + \frac{\partial}{\partial \bar{x}}\frac{\partial}{\partial \bar{x}}(D_{\Gamma A}(\tau,\bar{x})\Gamma_A(\tau,\bar{x})) \tag{4.110}$$

A careful observation of Eqs. (4.79), (4.80), (4.100) and their respective theoretical basis [4.44, 4.45], allows one to conclude that the probability density distribution that describes the fact that the particle is in position $\bar{x}$ at τ time, when the medium is moving according to one stochastic diffusion process (see relation (4.62) for the analogous discontinuous process), is given by Eq. (4.111). This relation is known as the Fokker–Planck–Kolmogorov equation.

$$\frac{\partial P(\tau,\bar{x})}{\partial \tau} = -\frac{\partial}{\partial \bar{x}}(A(\tau,\bar{x})P(\tau,\bar{x})) + \frac{\partial}{\partial \bar{x}}\frac{\partial}{\partial \bar{x}}(D(\tau,\bar{x})P(\tau,\bar{x})) \tag{4.111}$$

There is an important analogy between the Fokker–Planck–Kolmogorov equation and the property transport equation. Indeed, the term which contains $A(\tau,\bar{x})$ describes the particle displacement by individual processes and the term which contains $D(\tau,\bar{x})$ describes the left and right movement in each individual displacement or diffusion. We can notice the very good similarity between the transport and the Kolmogorov equation. In addition, many scientific works show that both equations give the same result for a particular problem. However, large and important differences persist between both equations. The greatest difference is given by the presence of the speed vector in the $A(\tau, \bar{x})$ expression in Eq. (4.110).

Undeniably, the speed vector, by its size and directional character, masks the effect of small displacements of the particle. Another difference comes from the different definition of the diffusion coefficient, which, in the case of the property transport, is attached to a concentration gradient of the property; it means that there is a difference in speed between the mobile species of the medium. A second difference comes from the dimensional point of view because the property concentration is dimensional. When both equations are used in the investigation of a process, it is absolutely necessary to transform them into dimensionless forms [4.6, 4.7, 4.37, 4.44].

Both equations give good results for the description of mass and heat transport without forced flow. Here, it is important to notice that the Fokker–Plank–Kolmogorov equation corresponds to a Markov process for a stochastic connection. Consequently, it can be observed as a solution to the stochastic equations written below:

$$dX_\tau = A(\tau, X_\tau)d\tau + B(\tau, X_\tau)dW_\tau \tag{4.112}$$

Here, X_τ is the stochastic state vector, $B(\tau,X_\tau)$ is a vector describing the contribution of the diffusion to the stochastic process and W_τ is a vector with the same dimensions as X_τ and $B(\tau,X_\tau)$. After Eqs. (4.94) and (4.95), the W_τ vector is a Wiener process (we recall that this process is stochastic with a mean value equal to zero and a gaussian probability distribution) with the same dimensions as $D(\tau, X_\tau)$:

$$D(\tau, \bar{x}) = B(\tau, \bar{x})B^T(\tau, \bar{x}) \quad ; \quad D(\tau, X_\tau) = B(\tau, X_\tau)B^T(\tau, X_\tau) \tag{4.113}$$

By comparision with the property transport equation the advantage of a stochastic system of equations (SDE) is the capacity for a better adaptation for the numerical integration.

4.3.3.1 Stochastic Differential Equation Systems for Heat and Mass Molecular Transport

A good agreement is generally obtained between the models based on transport equations and the SDE for mass and heat molecular transport. However, as explained above, the SDE can only be applied when convective flow does not take place. This restrictive condition limits the application of SDE to the transport in a porous solid medium where there is no convective flow by a concentration gradient. The starting point for the transformation of a molecular transport equation into a SDE system is Eq. (4.108). Indeed, we can consider the absence of convective flow in a non-steady state one-directional transport, together with a diffusion coefficient depending on the concentration of the transported property:

$$\frac{\partial\Gamma_A}{\partial\tau}=\frac{\partial}{\partial\bar{x}}\left(D_{\Gamma A}(\Gamma_A)\frac{\partial\Gamma_A}{\partial\bar{x}}\right) \tag{4.114}$$

By introducing the stochastic Markov type connection process through the following equation:

$$\frac{\partial^2}{\partial x^2}(D_{\Gamma A}(\Gamma_A)\Gamma_A)=\frac{\partial}{\partial x}\left[D_{\Gamma A}\frac{\partial\Gamma_A}{\partial x}+\frac{dD_{\Gamma A}}{d\Gamma_A}\frac{\partial\Gamma_A}{\partial x}\Gamma_A\right] \tag{4.115}$$

the right term of Eq. (4.114) can be written as:

$$\frac{\partial}{\partial x}\left(D_{\Gamma A}(\Gamma_A)\frac{\partial\Gamma_A}{\partial x}\right)=-\frac{\partial}{\partial x}\left[\frac{dD_{\Gamma A}}{d\Gamma_A}\frac{\partial\Gamma_A}{\partial x}\Gamma_A\right]+\frac{\partial^2}{\partial x^2}(D_{\Gamma A}(\Gamma_A)\Gamma_A) \tag{4.116}$$

If we replace Eq. (4.116) by Eq. (4.114) we have:

$$\frac{\partial\Gamma_A}{\partial\tau}=-\frac{\partial}{\partial x}\left[\frac{dD_{\Gamma A}}{d\Gamma_A}\frac{\partial\Gamma_A}{\partial x}\Gamma_A\right]+\frac{\partial^2}{\partial x^2}(D_{\Gamma A}(\Gamma_A)\Gamma_A) \tag{4.117}$$

A simultaneous comparison between Eqs. (4.114), (4.117) and (4.113) results in the following identifications:

$$A(\tau,x)=\frac{dD_{\Gamma A}}{d\Gamma_A}\frac{\partial\Gamma_A}{\partial x},\quad D(\tau,x)=D_{\Gamma A}(\Gamma_A),\quad B(\tau,x)=(D_{\Gamma A}(\Gamma_A))^{1/2}$$

Then, the SDE system can be written in the form:

$$dX(\tau)=\frac{dD_{\Gamma A}}{d\Gamma_A}\frac{\partial\Gamma_A}{\partial x}d\tau+(D_{\Gamma A}(\Gamma_A))^{1/2}dW(\tau) \tag{4.118}$$

The SDE and transport equation can be used with the same univocity conditions. For simple univocity conditions and functions such as $D_{\Gamma A}(\Gamma_A)$, the transport equations have analytical solutions. Comparison with the numerical solutions of stochastic models allows one to verify whether the stochastic model works properly. The numerical solution of SDE is carried out by space and time discretization into space subdivisions called bins. In the bins j of the space division i, the dimensionless concentration of the property ($\Gamma=\Gamma_A/\Gamma_{A0}$) takes the Γ_j value. Taking into consideration these previous statements allows one to write the numerical version of relation (4.118):

$$X_i(\tau+\Delta\tau)=X_i(\tau)+\left(\frac{\Gamma_{j+1}-\Gamma_{j-1}}{2\Delta x}\right)\left(\frac{dD_{\Gamma A}}{d\Gamma_j}\right)_{\Gamma_j}\Delta\tau+(2D_{\Gamma Aj}(\Gamma_j)\Delta\tau)^{1/2}\varphi_i \tag{4.119}$$

Here, φ_i is a random number for the calculation step "i". It is given by a standard procedure for the normal distribution values with a mean value of zero where $D_{\Gamma Aj}$ and Γ_j are the corresponding $D_{\Gamma A}$ and Γ values for the j bin and the particle position "i". The only limitation of the numerical method is concentrated in the fact that $\Delta\tau$ must have very small values in order to eliminate all the problems of non-convergence caused by the second term on the right half of the equation (4.119).

The approximated master equation, such as Eq. (4.111) with its associate (4.112), has computational advantages besides its obvious similarity to the convective-diffusion form. Even when this equation cannot be solved exactly, the numerical techniques for computing such equations are well established. More importantly, the derivation of this equation gives a clue to the identification of the terms of the vectors $A(\tau, X_\tau)$ and $B(\tau, X_\tau)$, which can be found independently without knowing the details of the transition probabilities required in the master equation (see assemblies (4.25)–(4.26) or (4.74)–(4.79)) and this is a great advantage. The set up of the Fokker–Planck–Kolmogorov equation into the form of Eq. (4.112) needs to take a time interval so small that X_τ does not change significantly but the Markovian assumption is still valid.

The Fokker–Planck–Kolmogorov approximation of the master equation is based on the assumption that all the terms greater than second order, which are extracted from the Taylor expansion of $P_k(z \pm \Delta z, \tau)$, vanish. This is rarely true in practice, however, and a more rational way of approximating the master equation is to systematically expand it in powers of a small parameter, which can be chosen approximately. This parameter is usually chosen in order to have the same size as the system.

4.4
Methods for Solving Stochastic Models

Once the stochastic model has been established, it is fed with data which characterize the inputs and consequently, if the model works correctly it produces data which represent the process output. The model solution is obtained:

- By an analytical solution given by a relation or by an assembly of relations and their exploitation algorithm showing how the output solutions are developed when the inputs are selected.
- By a numerical solution and the corresponding software.
- By another model, obtained by the transformation of the original model towards one of its boundaries and which can also be solved by an analytical or numerical solution. These models are called "limit stochastic models" or "asymptotic stochastic models".

The numerical as well as the asymptotic model solutions are estimated solutions, which often produce characteristic outputs of the model in different forms when compared to the natural state of the exits. Both stochastic and transfer phenomenon models present the same type of resolution process. The analysis developed in the paragraphs below can be applied equally to both types of models.

4.4.1
The Resolution of Stochastic Models by Means of Asymptotic Models

It is well-known that, from a practical view point, it is always interesting to be aware of the behaviour of a process near the boundaries of validity. The same statement can be applied to the stochastic model of a process for small stochastic disturbances which occur at large intervals of time. In this situation, we can expect the real process and its model not to be appreciably modified for a fixed time called "system answer time" or "constant time of the system". This statement can also be taken into account in the case of random disturbances with measurements realized at small intervals of time.

At the same time, it is known that, during exploitation of stochastic models, cases that show great difficulty concerning the selection and the choice of some parameters of the models frequently appear. As a consequence, the original models become unattractive for research by simulation. In these cases, the models can be transformed to equivalent models which are distorted but exploitable. The use of stochastic distorted models is also recommended for the models based on stochastic chains or polystocastic processes where an asymptotic behaviour is identified with respect to a process transition matrix of probabilities, process chains evolution, process states connection, etc. The distorted models are also of interest when the stochastic process is not time dependent, as, for example, in the stochastic movement of a marked particle occurring with a constant velocity vector, like in diffusion processes.

The diffusion model can usually be used for the description of many stochastic distorted models. The equivalent transformation of a stochastic model to its associated diffusion model is fashioned by means of some limit theorems. The first class of limit theorems show the asymptotic transformation of stochastic models based on polystochastic chains; the second class is oriented for the transformation of stochastic models based on a polystochastic process and the third class is carried out for models based on differential stochastic equations.

4.4.1.1 Stochastic Models Based on Asymptotic Polystochastic Chains

We begin the discussion by referring to the stochastic model given by relation (4.58), which is rewritten here as shown in relation (4.120). Here for a finite Markov connection process we must consider the constant time values for all the elements of the matrix $P = [p_{ik}]_{i,k \in K}$.

$$P_k(n,i) = \sum_{e \in K} \sum_{a \in Z} P_k(n-1, i-a) p_{ek} p_k(a) \tag{4.120}$$

The interest is to produce a model for the computation of the probability to have the particle at the i position after n passages. This probability, which is denoted as $P(n,i)$, can be calculated by summing up all $P_k(n,i)$. So, $P(n,i) = \sum_k P_k(n,i)$. Now, if we consider that the connection in our stochastic model is given by a Markov chain, which presents the quality to be a regular chain, then we can show that there exists a n_0 value, where the matrix P contains values which are constant and positive. Indeed we can write: $P^{n_0} \succ 0$. In this case, for the matrix connections, we reach the situation of $\lim\limits_{n \to \infty} P^n = \Pi$, where Π is a stable stochastic matrix having identical lines. It is not difficult to observe that the elements of the stable matrix Π result from the product of the unity matrix I and the vector V_Π', which is a transposition of the vector that contains the unchangeable transition probabilities from one state to another (V_Π). At the same time, vector V_Π has the quality to be the proper vector of the matrix of probabilities P and, consequently, its elements are the solution of the linear algebraic equation system: $\sum\limits_{e \in K} \pi_e p_{ek} = \pi_k, k \in K$. The π_k substitution by p_{ek} in Eq. (4.120) gives the asymptotic model (4.121). Relation (4.122), where $P^{as}(n, i)$ is the result of the addition of probabilities $P_k^{(as)}(n, i)$, allows the calculation of the probability to have the particle in state i after n time sequences.

$$P_k^{as}(n, i) = \sum_{e \in K} \sum_{a \in Z} P_k^{as}(n-1, i-a) \pi_k p_k(a) \tag{4.121}$$

$$P^{as}(n, i) = \sum_{k \in K} \pi_k \sum_{a \in Z} P^{as}(n-1, i-a) p_{ek} p_k(a) \tag{4.122}$$

The model described by Eq. (4.122) is known as *the generalized random displacement or generalized random walk.*

Relation (4.123) is obtained when the model relation (4.122) is written for the case of a stochastic process with two states and constant length of the particle displacement (this model was previously introduced with relation (4.59)).

$$P^{as}(n, i) = \pi_1 P^{as}(n-1, i-1) + \pi_2 P^{as}(n-1, i+1) \tag{4.123}$$

With $\pi_1 = \pi_2 = 1/2$ we observe that relation (4.123) has the same form as the relation used for the numerical solving of the unsteady state diffusion of one species or the famous Schmidt relation. The model described by Eq. (4.123) is known as the *random walk with unitary time evolution.*

In order to identify the conditions that allow an asymptotic transformation, we show a short analysis particularized to the case of the model given by the assembly of relations (4.59). To this aim, we focus the observations on one property of a generator function which is defined as a function which gives the following equation for the probabilities of the distribution with the general discrete values $P_k(n, i)$:

$$G_k(n, z) = \sum_{i \in Z} P_k(n, i) z^i \quad , \ k = 1, 2, \ldots \ , \ z = e^i \tag{4.123}$$

If we particularize this last relation for the stochastic model given by the assembly of equations (4.59), we obtain the following relation for the vector $G(n.z)$:

$$G(n,z) = [G_1(n,z), G_2(n,z)] = G(0,z)\left[P\begin{pmatrix} z & 0 \\ 0 & 1/z \end{pmatrix}\right]^n \qquad (4.123)$$

Here $P = [p_{ek}]_{e,k\in K=(1,2)}$ represents the matrix of the transition probabilities between both states of the process.

If we accept that the $\lim\limits_{n\to\infty} P^n = \Pi$, then, using relation (4.123) we derive the equation of the asymptotic generator function:

$$G^{as}(n,z) = G(0,z)\left(\pi_1 z + \frac{\pi_2}{z}\right)^n \qquad (4.124)$$

By computing the values of the generator function for $\theta \to 0$ (relations (4.123) and (4.124)), we can observe similarities (identities) between both relations. Indeed, we corroborate that these functions come from a process with identical behaviour and we have a correct asymptotic transformation of the original model. We can conclude that in the case when the transition matrix of probabilities has a regular state, the generator function of the polystochastic chain process when $n \to \infty$ goes from one generator function to a Markov chain related with the model that is, for the present discussion, characterized by relation (4.123)

All other discrete stochastic models, obtained from polystochastic chains, attached to an investigated process, present the capacity to be transformed into an asymptotic model. When the original and its asymptotic model are calculated numerically, we can rapidly observe if they converge by direct simulation. In this case, the comparison between the behaviour of the original model and the generator function of the asymptotic stochastic model is not necessary.

4.4.1.2 **Stochastic Models Based on Asymptotic Polystochastic Processes**

For the derivation of one asymptotic variant of a given polystochastic model of a process, we can use the perturbation method. For this transformation, a new time variable is introduced into the stochastic model and then we analyze its behaviour. The new time variable is $\tau' = \varepsilon^r t$, which includes the time evolution t and an arbitrary parameter ε, which allows the observation of the model behaviour when its values become very small ($\varepsilon \to 0$). Here, we study the changes in the operator $O(\tau, t)$ when $\varepsilon \to 0$ whilst paying attention to having stable values for t/ε or t/ε^2.

Two different types of asymptotic transformation methods can be used depending on the ratio of t/ε used: in the first type we operate with fixed values of t/ε whereas in the second type we consider t/ε^2.

As an example, we show the equation that characterizes a random evolution (see relation (4.90)) written without the arguments for the operator $O(\tau, t)$, but developed with the operator $V(X(\tau))$. We also consider that, when the random process changes, the operator $O(\tau, t)$ will be represented by an identity operator ($I = I(\tau, t)$):

$$\frac{dO}{d\tau} = VO = (\varepsilon V_1(\tau) + \varepsilon^2 V_2(\tau) + \varepsilon^3 V_3(X,\tau)O \quad ; \quad O(\tau,\tau) = I \qquad (4.125)$$

Each operator considered in the total operator $V(X(\tau),\tau)$ keeps its own mean action when it is applied to one parameter (for example the mean action of operator V_1 on the parameter (function) f will be written as follows: $\overline{V}_1 f = \lim\limits_{u\to\infty} \frac{1}{u} \int\limits_t^{t+u} E\{V_1(f(t))dt\}$.

The introduction of terms of higer order in Eq. (4.125) is not necessary as far as, in the characterization of chemical engineering processes, the differential equations are limited to equations of order two.

Some restrictions are imposed when we start the application of limit theorems to the transformation of a stochastic model into its asymptotic form. The most important restriction is given by the rule where the past and future of the stochastic processes are mixed. In this rule it is considered that the probability that a fact or event C occurs will depend on the difference between the current process ($P(C) = P(X(\tau) \in A/V(X(\tau)))$) and the preceding process ($P_\tau(C/e)$). Indeed, if, for the values of the group (τ, e), we compute $\pi_\tau = \max[P_\tau(C/e) - P(C)]$, then we have a measure of the influence of the process history on the future of the process evolution. Here, τ defines the beginning of a new random process evolution and π_τ gives the combination between the past and the future of the investigated process. If a Markov connection process is homogenous with respect to time, we have $\pi_\tau = 1$ or $\pi_\tau \to 0$ after an exponential evolution. If $\pi_\tau \to 0$ when τ increases, the influence of the history on the process evolution decreases rapidly and then we can apply the first type limit theorems to transform the model into an asymptotic model. On the contrary, if $I = \int\limits_0^\infty \pi_\tau^{1/2} d\tau$, the asymptotic transformation of an original stochastic model can be carried out by a second-type limit theorem.

For the example considered above (Eq. (4.125)), the mean value of the random evolution at time t is $e_m = e_m(t, X) = E_X[O(0, X)]$ and this process parameter verifies Eq. (4.126). Here, Q is the infinitesimal generator that characterizes the connection processes of the stochastic model of the process. This property of $e_m = e_m(t, X) = E_X[O(0, X)]$ is a consequence of relation (4.94). So we can write:

$$\frac{de_m}{d\tau} = (\varepsilon V_1(t) + \varepsilon^2 V_2(t) + \varepsilon^3 V_3(t, X)e_m + Qe_m \tag{4.126}$$

In Eq. (4.126) we can change variable $\tau = t/\varepsilon$ in order to obtain a limit transformation after the first type theorem. The result is:

$$\frac{de_m}{d\tau} = (V_1(\tau/\varepsilon) + \varepsilon V_2(\tau/\varepsilon) + \varepsilon^2 V_3(\tau/\varepsilon, X)e_m + \frac{1}{\varepsilon} Qe_m \tag{4.127}$$

If the stochastic evolution $X(\tau,e)$ complies with the mixing condition ($\lim\limits_{\tau\to\infty} \pi_\tau = 0$) then, if $\varepsilon \to 0$; $O(0, \tau/\varepsilon)$ becomes $\tau\overline{V}_1$ through a probabilistic way. This shows that e_m, which is the solution of the differential equation (4.126), becomes e_m^{as} when $\varepsilon \to 0$ for a fixed τ/ε:

$$\frac{de_m^{as}}{d\tau} = \overline{V}_1 e_m^{as} \ ; \qquad e_m^{as}(0, X) = I \tag{4.128}$$

Considering this last mathematical derivation, we observe that the stochastic process has been distorted by another one with a similar behaviour. In order to explain the meaning of $\overline{V}_1$ we consider the case of a connection between the two states of a stochastic process with the following infinitesimal generator:

$$Q = \begin{bmatrix} -q_1 & q_1 \\ q_2 & -q_2 \end{bmatrix}$$

The invariable measure for the infinitesimal generator is a stable matrix that complies with Eq. (4.17) and the following conditions: $PQ_s = Q_sP = O_s$,$OQ_s = Q_sO = 0$, $Q_s{}^2 = Q_s$. Here, P is the matrix of transition probabilities. For our considered case (stochastic process with two states) we obtain $Q_s = \begin{bmatrix} \dfrac{q_2}{q_1+q_2} & \dfrac{q_1}{q_1+q_2} \end{bmatrix}$; consequently, $\overline{V}_1$ can be written as: $\overline{V}_1 = \dfrac{q_2V_1(1)+q_1V_1(2)}{q_1+q_2}$.

If we continue with the particularization of the two-state stochastic process, by considering that the first state is the diffusion type and the second state concerns convection (for instance see relations (4.72), (4.73), (4.79), (4.98) and (4.100)), then the equation system (4.127) can be written as follows:

$$\frac{de_{m1}}{d\tau} = \frac{d^2e_{m1}}{dz^2} - \frac{q_1e_{m1}}{\varepsilon} + \frac{q_1e_{m2}}{\varepsilon}$$

$$\frac{de_{m1}}{d\tau} = \frac{de_{m1}}{dz} - \frac{q_2e_{m1}}{\varepsilon} - \frac{q_2e_{m2}}{\varepsilon}$$

$$e_{m1}(0,z) = e_{m2}(0,z) = f(z) \tag{4.129}$$

Looking at this assembly of equations and relation (4.127) simultaneously, we can easily identify that $V_1(1) = d^2/dz^2$ (i.e. is an elliptic operator), $V_1(2) = d/dz$, $V_2 = 0$, $V_3 = 0$. With these identifications and in accordance with the transformation theorem of the first type (Eq. (4.128)) when $\varepsilon \to 0$, e_{m1} and e_{m2} will be solution of following equation:

$$\frac{dv}{d\tau} = \frac{q_2}{q_1+q_2}\frac{d^2v}{dz^2} + \frac{q_1}{q_1+q_2}\frac{dv}{dz} \quad ; \quad v(0,z) = f(z) \tag{4.130}$$

The condition $v(0,z) = f(z)$(see relation (4.130)) corresponds to the situation when we have $e_{m1}(0,z) = e_{m2}(0,z) = f(z)$; otherwise, we use $v(0,z)$ as:

$$v(0,z) = \frac{q_2f_1(z)+q_1f_2(z)}{q_1+q_2}.$$

This shows that the invariable measure determining the mixing procedures of stochastic process states is extended over the initial conditions of the process.

If we obtain $\overline{V}_1 = \dfrac{q_2V_1(1)+q_1V_1(2)}{q_1+q_2} = 0$ for an experiment, we can conclude that the use of the theorems for the first type transformation is not satisfactory.

Then we have to apply the asymptotic model transformation by using the second type theorems. To do so, we choose the new time variable $\tau = \varepsilon^2 t$ and the relation (4.127) becomes:

$$\frac{de_m}{d\tau} = (\frac{1}{\varepsilon}V_1(\tau/\varepsilon^2) + V_2(\tau/\varepsilon^2) + \varepsilon V_3(\tau/\varepsilon^2, X)e_m + \frac{1}{\varepsilon^2}Qe_m \tag{4.131}$$

The theorems for the two-type transformation are based on the observation that, for $\varepsilon \to 0$ and fixed τ/ε^2, we have the operator $O\left(0, \frac{\tau}{\varepsilon^2}\right) \to \exp(\tau\overline{V})$, where $\overline{V} = \overline{V}_2 + \overline{V}_{11}$. Indeed, the mean value of the stochastic process from relation (4.131), noted as ε_m, becomes v, which is the solution of the differential equation $\frac{dv}{d\tau} = \overline{V}v \;\; ; \;\; v(0) = I$. For a stochastic process with connections between two states the infinitesimal generator of connection is $Q_s = \left[\frac{q_2}{q_1 + q_2} \quad \frac{q_1}{q_1 + q_2}\right]$, here $\overline{V}_2$ and $\overline{V}_1$ (and then $\overline{V}$) are given by the following equations: $\overline{V}_2 = \frac{q_2V_2(1) + q_1V_2(2)}{q_1 + q_2}, \overline{V}_1 = \frac{-2V(1)V_2(2)_1}{q_1 + q_2}$.

Now, we have to identify $\overline{V}_2$ and $\overline{V}_{11}$. To do so, we consider the case of two connected stochastic processes where each process is a diffusion type with two states. The example concerns one marked particle that is subjected to a two-state diffusion displacement. The particle can be considered as a molecular species (so the particle movement describes a mass transport process) and we can also take into account the total enthalpy of the process (heat transport process). This particular case of stochastic model, can be described with the assembly of relations (4.79). In the model, the mean probability of the existence of local species (e_{m1}) and the mean probability of the existence of local enthalpy (e_{m2}) are given by the assembly of relations (4.132):

$$\frac{\partial e_{m1}}{\partial \tau} = \frac{g(z)}{\varepsilon}\frac{\partial e_{m1}}{\partial z} + \alpha 1(z)\frac{\partial^2 e_{m1}}{\partial z^2} - \frac{q}{2}e_{m1} + \frac{q}{2}e_{m2}$$

$$\frac{\partial e_{m2}}{\partial \tau} = \frac{g(z)}{\varepsilon}\frac{\partial e_{m2}}{\partial z} + \alpha 2(z)\frac{\partial^2 e_{m2}}{\partial z^2} - \frac{q}{2}e_{m2} + \frac{q}{2}e_{m1}$$

$$e_{m1}(0, z) = f_1(z) \;\; ; \quad e_{m2}(0, z) = f_2(z) \tag{4.132}$$

If, in the assembly of equations, we consider $q_1 = q_2 = q$ in the equation of the infinitesimal generator then, we can identify $V_1(1) = -V_1(2) = g(z)\frac{\partial}{\partial z}$, $V_2(1) = \alpha 1(z)\frac{\partial^2}{\partial z^2}$, $V_2(2) = \alpha 2(z)\frac{\partial^2}{\partial z^2}$, $V_3 = 0$. After the theorem of the two-type transformation, the solutions for e_{m1} and e_{m2} will tend towards the solution of the following particularization of the asymptotic model $\frac{dv}{d\tau} = \overline{V}v \;\; ; \;\; v(0) = I$:

$$\frac{\partial v}{\partial \tau} = \frac{1}{2}\frac{\partial}{\partial z}\left(g(z)\frac{\partial v}{\partial z}\right) + \frac{\alpha 1(z) + \alpha 2(z)}{2}\frac{\partial^2 v}{\partial z^2} = \overline{V}_{11}v + \overline{V}_2 v \qquad (4.133)$$

$$v(0,z) = \frac{f_1(z)}{2} + \frac{f_2(z)}{2} \qquad (4.134)$$

To complete this short analysis, we can conclude that, for the asymptotic transformation of a stochastic model, we must identify: (i) the infinitesimal generator; (ii) what type of theorem will be used for the transformation procedure.

4.4.1.3 **Asymptotic Models Derived from Stochastic Models with Differential Equations**

Studies of the transformation of a stochastic model characterized by an assembly of differential equations to its corresponding asymptotic form, show that the use of a perturbation method, where we replace the variable t by: $t = \varepsilon^r \tau$, can be recommended without any restrictions [4.47, 4.48].

If we consider a process where the elementary states $v_1, v_2, ...v_N$ work with a Markov connection, this connection presents an associated generator of probability $(p_1, p_2, ...p_N)$ that verifies the invariable measure $\sum\limits_{i=1}^{N} p_i v_i = 0$. Now, if the elementary states are represented by displacements with constant speed, then $X(\tau)$ can take scalar values and, consequently, $F(X, v_i) = v_i$. For this case, we consider that the mean values of $X(\tau)$, determined by their X_0 initial values and noted as $e_{mi}, i = 1, N$, verify relations (4.135) (see for instance Eq. (4.98)). The equations (4.135) consider that the displacement associated with space X occurs after the z direction; consequently we have:

$$\frac{\partial e_{mi}}{\partial \tau} = \sum_{j=1}^{N} q_{ij} e_{mj} + v_i \frac{\partial e_{mi}}{\partial z} \quad ; \quad e_{mi}(0,X) = f_i(z) \quad ; \quad i = 1...N \qquad (4.135)$$

Here, we use the classical perturbation procedure ($\varepsilon \to 0$ when $\tau \to \infty$) for the analysis of the asymptotic behaviour of mean values $e_{mi}(\tau, X) = e_{mi}(\tau, z)$. The following expression can be written for $e_{mi}(\tau, X)$, when we use the perturbation $t = \tau\varepsilon^2$:

$$e^*_{mi} = e^*_{mi}(\tau, X) = E_i\left\{ (f_v(\tau/\varepsilon^2)(X + \varepsilon \int\limits_{0}^{\tau/\varepsilon^2} v(\alpha)d\alpha) \right\} \qquad (4.136)$$

For the expected mean values $e^*_{mi}(\tau, X)$, as a result of the application of the time perturbation to the system (4.135), we derive the following differential equations system:

$$\frac{\partial e^*_{mi}}{\partial \tau} = \frac{1}{\varepsilon^2}\sum_{j=1}^{N} q_{ij} e^*_{mi} + \frac{1}{\varepsilon^2} v_i \frac{\partial e^*_{mi}}{\partial z} \; ; \; e^*_{mi}(0,X) = e^*_{mi}(0,z) = f_i(z) \; ; \; i = 1...N \quad (4.137)$$

Now, we can write Eq. (4.136) as:

$$e^*_{mi} = e^*_{mi}(\tau, X) = E_i\left\{(f_v(\tau/\varepsilon^2)(X + \sqrt{\tau}\frac{1}{\sqrt{\tau}}\int_0^\tau v(\alpha)d\alpha)\right\} \tag{4.138}$$

For our considered process, where the states $v_1, v_2, ...v_N$ are Markov connected, the variable term for this last relation $\left(\frac{1}{\sqrt{\tau}}\int_0^\tau v(\alpha)d\alpha\right)$ tends [4.5] towards a normal random variable with a zero mean value and variance $\sigma = \frac{1}{\tau}\int_0^\tau\int_0^\tau E\{v(\alpha)v'(\alpha')\}d\alpha d\alpha'$. Coupling this observation with relation (4.138) results in:

$$\lim_{\tau\to\infty} e^*_{mi}(\tau, X) = \int_{-\infty}^{\infty}\left\{\sum_{i=1}^{N} p_i f_i(z + \sqrt{\tau})\right\}\frac{e^{-\xi^2/2\tau^2}}{\sqrt{2\pi\sigma}}d\xi \tag{4.139}$$

Indeed, for $\varepsilon \to 0$ and $0 < \tau < \tau_0$, the solution of the system (4.137) with respect to $e^*_{mi}(\tau, X)$ will be uniformly displaced with respect to X (or z when the movement occurs along this direction) and the solution can be written as:

$$\frac{\partial v^o}{\partial \tau} = \frac{1}{2}\sigma^2\frac{\partial^2 v^0}{\partial z^2} \quad ; \quad v^O(0, X) = v^O(0, z) = \sum_{i=1}^{N} p_i f_i(z) \tag{4.140}$$

This last equation has a form similar to the famous equation of the single direction diffusion of a property in an unsteady state, the property here being the local concentration v^0. The diffusion coefficient is represented by the variance of the elementary speeds which are given by their individual states $v_1, v_2, ..., v_N$. It is important to notice the consistency of the definition of the diffusion coefficient.

Very difficult problems occur with the asymptotic transformation of original stochastic models based on stochastic differential equations where the elementary states are not Markov connected. This fact will be discussed later in this chapter (for instance see the discussion of Eq. (4.180)).

4.4.2
Numerical Methods for Solving Stochastic Models

In Section 4.2 we have shown that stochastic models present a good adaptability to numerical solving. In the opening line we asserted that it is not difficult to observe the simplicity of the numerical transposition of the models based on polystochastic chains (see Section 4.1.1). As far as recursion equations describe the model, the numerical transposition of these equations can be written directly, without any special preparatives.

When a stochastic model is described by a continuous polystochastic process, the numerical transposition can be derived by the classical procedure that change the derivates to their discrete numerical expressions related with a space discretisation of the variables. An indirect method can be used with the recursion equations, which give the links between the elementary states of the process.

The following examples detail the numerical transposition of some stochastic models. The numerical state of a stochastic model allows the process simulation.

Indeed, we can easily produce the evolution of the outputs of the process when the univocity conditions and parameters of the process are correctly chosen.

The first example concerns a stochastic model which is known as the Chapmann–Kolmogorov model and is mathematically characterized by Eq. (4.67). This model accepts a numerical solution that is developed using implicit methods and then computation begins with the corresponding initial and boundary conditions. If we particularize the Chapmann–Kolmogorov model to the situation where we have two elementary states of the process with constant displacement steps and without an i position dependence of the transition probabilities ($a = 1$, $p_k(a) = 1$ and $p_{ek}(i-a) = p_{ek}$) then, we obtain the model (4.59). Figure 4.10 presents its numerical structure. Many researchers have been using programs of this type to characterize the transport of species through various zeolites [4.49–4.52].

```
1   **Definition** :matrix $P_1(N,M)$ ,matrix $P_2(N,M)$/ N-passages ,M-positions/
2   **Data**: $p_{11}=$ , $p_{21}=$ $p_{12}=$ $p_{22}=$ N= M=
3   **Univocity**: $P_1(1,1)=1$ ;$P_1(I+1,1)=0$ for I=1,N-1;$P_2(I,1)=0$ for I=1,N-1
4   **Start**
5   I=2
6   J=2
7   $P_1(I,J)=p_{11}P_1(I-1,J-1)+p_{21}P_2(I-1,J-1)$
8   $P_2(I,J)=p_{12}P_1(I-1,J-1)+p_{22}P_2(I-1,J-1)$
9   for J<M
10  **Write**:$P_1(I,J)$ ,$P_2(I,J)$
11  J=J+1
12  **Back to** 7
13  for J>M and I<N
14  **Write**:$P_1(I,J)$ ,$P_2(I,J)$
15  I=I+1
16  **Back to** 6
17  **Data treatment**: $P_1(I,J)$ ,$P_2(I,J)$/ Graphiques;other calculations..:
18  **Stop**
```

Figure 4.10 Numerical text of the stochastic model given in Eq. (4.59).

The second example discusses the numerical transposition of the asymptotic models based on polystochastic chains (see Section 4.4.1.1) where to compute the limit transition probabilities, we must solve the system $\sum_{e\in K} \pi_e p_{ek} = \pi_k$ $k = 0, 1, ..N$. If the number of process components, here noted as k, is greater than two, then we can use a successive approximation method for the estimation of the column vector Π. More precisely, we use the iteration chain $P\Pi^{(m+1)} = \Pi^{(m)}$ with the stop condition $\left\|\Pi^{(m)} - \Pi^{(m+1)}\right\| \le M\lambda_2$. The determinant value λ_2 from the stop condition represents the second decreasing proper value of the transition probabilities matrix (P). In the stop condition, M is considered as an arbitrary constant value.

The third example presents the problem of numerical transposition of continuous stochastic models, which is introduced by the following general equation:

$$\frac{\partial P}{\partial \tau} + A\frac{\partial P}{\partial z} = BP + F \tag{4.141}$$

where P is the vector that contains the probabilities $P_i(z,\tau)$ $i = 1, 2, ...N$;

A is the quadratic N×N matrix where the elements are constant numerical values; B the quadratic N×N matrix that contain functions of z and τ arguments; F the vector with elements defined by functions of z and τ arguments.

Before carrying out the discretization of the equations, we have to make a careful mathematical analysis of the problem in order to establish what its most convenient rewriting in order to facilitate the numerical solution. First we observe that between the matrix A, the proper values λ_j and the (left) proper vectors z_j, we have the equality $z_j A = \lambda_j z_j$. Consequently, as a result, the multiplication of Eq. (4.141) by z_j gives:

$$z_j \frac{\partial P}{\partial \tau} + z_j A \frac{\partial P}{\partial z} = z_j BP + z_j F \tag{4.142}$$

$$z_j \left(\frac{\partial P}{\partial \tau} + \lambda_j \frac{\partial P}{\partial z} - BP - F \right) = 0 \tag{4.143}$$

If the value of z_j is not zero, then relation (4.144) becomes:

$$\frac{\partial P}{\partial \tau} + \lambda_j \frac{\partial P}{\partial z} = BP + F \tag{4.144}$$

The left term of this last equation represents the differential state of vector P with respect to time for the family of curves $dz/d\tau = \lambda_j^{-1}, j = 1, 2, ...N$. So we can write relation (4.144) as:

$$\left(\frac{dP}{d\tau} \right)_{\lambda_j} = BP + F \tag{4.145}$$

where, for $\left(\frac{dP}{d\tau} \right)_{\lambda_j}$, we define the differential state of P after the normal curves $dz/d\tau = \lambda_j^{-1}$. The transformation given above, is still valid when all values $\lambda_j, j = 1, ...N$ are real and strictly different. However, if the A matrix gives complex values for some λ_j, then we can assert that our original model (described by Eq. (4.141)) is not a hyperbolic model. At the same time, the proper values of the matrix $A(\lambda_j, j = 1, ...N)$ give important information for fixing univocity conditions and solving the model. The following situations are frequently presented:

- when all λ_j verify that $\lambda_j \succ 0$, $j = 1, ...N$, we can specify the initial values $P(z)$, $z \succ 0$ and the boundary values at each time: $P(z_f, \tau)$, $\tau \succ 0$. The values $P(0, \tau)$ and $P(z_e, \tau)$ will be specified when the boundaries of the process are $z = 0$ and $z = z_e$;
- when all λ_j verify that $\lambda_j \prec 0$, $j = 1, ...N$ and when values $P(z_f, \tau)$ at the boundary line $z_f = 0$ are needed, we must specify the initial values of the probabilities for $z \le 0$;
- for positive and negative values λ_j , $j = 1, ...N$, we separate two domains with their respective univocity problems; when we have the following specifications $0 \prec z \prec z_e$, $\lambda_j \succ 0$, $j = 1, ...l$ with $l \prec N$ and $P(z, 0) = f(z)$ simultaneously, we must complete the

univocity problem with functions or data for P(z,0), P(0,τ) and P(z_e,τ), respectively.

After the establishment of the univocity conditions, we can begin the numerical treatment of the model. For this purpose, we can use the simplified model form (see relations (4.145)) or its original form (4.141)).

The change of a continuous polystochastic model into its numerical form is carried out using the model described by Eq. (4.71) rewritten in Eq. (4.146). The solution of this model must cover the variable domain $0 \prec z \prec z_e$, $0 \prec \tau \prec T$. In accordance with the previous discussion, the following univocity conditions must be attached to this stochastic model. Here, $f_k(z), g_k(\tau)$ and $h(\tau)$ are functions that must be specified.

$$\frac{\partial P_k(z,\tau)}{\partial \tau} + v_k \frac{\partial P_k(z,\tau)}{\partial z} + \left(\sum_{j=1, j \neq k} \alpha_{kj} \right) P_k(z,\tau) - \sum_{j=1, j \neq k} \alpha_{jk} P_j(z,k) \quad ; \ k = 1, N \tag{4.146}$$

$$\tau = 0 \quad , \quad 0 < z < z_e, \quad P_k(z,0) = f_k(z)$$

$$\tau > 0 \quad , \quad z = 0 \quad , \quad \begin{cases} P_k(0,\tau) = g_k(\tau) \text{ for } v_k(0,\tau) > 0 \\ \dfrac{dP_k(0,\tau)}{dz} = 0 \ \text{ for } v_k(0,\tau) < 0 \end{cases}$$

$$\tau > 0 \quad , \quad z = z_e \quad , \quad \begin{cases} P_k(z_e,\tau) = h_k(\tau) \ \text{ for } \ v_k(0,\tau) < 0 \\ \dfrac{dP_k(z_e,\tau)}{dz} = 0 \ \text{ for } \ v_k(0,\tau) > 0 \end{cases} \tag{4.147}$$

Concerning the boundary conditions of this problem, we can have various situations: (i) in the first situation, the probabilities are null but not the probability gradients at $z = 0$ zero. For example, for a negative speed $v_k(0,\tau)$, the particle is not in the stochastic space of displacement. However, at z = 0, we have a maximum probability for the output of the particle from the stochastic displacement space. Indeed, the flux of the characteristic probability must be a maximum and, consequently, $dP_k(0,\tau)/dz = 0$; (ii) we have a similar situation at $z = z_e$; (iii) in other situations we can have uniformly distributed probabilities at the input in the stochastic displacement space; then we can write the following expression:

$$g_k(\tau) = P_k(0,\tau) = p_k \text{ for } k = 1, N-1 \ , \ g_N(\tau) = P_N(0,\tau) = 1 - \sum_{k=1}^{N-1} p_k \, .$$

It is important to notice that the univocity conditions must adequately correspond to the process reality. Concerning the numerical discretisation of each variable space, model (4.146) gives the following assembly of numerical relations:

$$z = i * \Delta z \quad , \quad \tau = g * \Delta\tau \ , \ i = 0, \ r \ ; \ g = 0, s \tag{4.148}$$

- For $v_k(z,\tau) > 0$

$$\frac{P_k(z,\tau+\Delta\tau)-P_k(z,\tau)}{\Delta\tau}+v_k(z,\tau)\frac{P_k(z+\Delta z,\tau)-P_k(z,\tau)}{\Delta z}+$$
$$\left(\sum_{j=1,j\neq k}\alpha_{kj}\right)P_k(z,\tau)-\sum_{j=1,j\neq n}\alpha_{jk}P_j(z,\tau)=0$$

- For $v_k(z,\tau) < 0$

$$\frac{P_k(z,\tau+\Delta\tau)-P_k(z,\tau)}{\Delta\tau}+v_k(z,\tau)\frac{P_k(z,\tau)-P_k(z-\Delta z,\tau)}{\Delta z}+$$
$$\left(\sum_{j=1,j\neq k}\alpha_{kj}\right)P_k(z,\tau)-\sum_{j=1,j\neq n}\alpha_{jk}P_j(z,\tau)=0$$

The balance between the unknown variables and the relations available for their estimation is given here: (i) for $T/\ \tau = s$ and $z_e/z = r$ we obtain $r*s*N$ unknowns (for each solving network point we must determine the values of $P_1(z,\tau)$, $P_2(z,\tau)$....$P_N(z,\tau)$); (ii) the system of equations to compute unknowns is made considering the particularization of:

- the relation (4.148) for all network points that are not in the boundaries; it gives a total of $(r-2)*s*N$ equations.
- the second condition from the univocity problem of the model (4.146)–(4.147); this particularization gives $P_k(0,1),....P_k(0,s)$ so $s*N$ equations;
- the third condition from the univocity problem of the model (4.146)–(4.147); this particularization gives s*N equations.

The algorithm to compute a stochastic model with two Markov connected elementary states is shown in Fig. 4.11. Here, the process state evolves with constant v_1 and v_2 speeds. This model is a particularization of the model commented above (see the assembly of relations (4.146)–(4.147)) and has the following mathematical expression:

$$\frac{\partial P_1(z,\tau)}{\partial\tau}+v_1\frac{\partial P_1(z,\tau)}{\partial z}+\alpha P_1(z,\tau)-\beta P_2(z,\tau)=0$$

$$\frac{\partial P_2(z,\tau)}{\partial\tau}-v_2\frac{\partial P_1(z,\tau)}{\partial z}+\beta P_2(z,\tau)-\alpha P_1(z,\tau)=0$$

$$P_1(z,0)=0\quad;\quad P_2(z,0)=0$$

$$P_1(0,0)=1\quad;\quad P_1(0,\tau)=0\quad;\quad P_2(0,\tau)=P_2(\Delta z,\tau)$$

$$P_2(z_e,\tau)=0\quad;\quad P_1(z_e,\tau)=P_1(z_e-\Delta z,\tau)\tag{4.149}$$

It can easily be observed that the considered case (4.149) corresponds to the situation for $\tau = 0$: only one marked particle evolves through a stochastic trajectory (a type 1 displacement with v_1 speed). This example corresponds to a Dirac type input and the model output response or the sum $P_1(z_e, \tau) + P_2(0, \tau)$, represents the distribution function of the residence time during the trajectory (see also application 4.3.1).

```
1  Definition : Matrix $P_1(r,s)$ ; Matrix $P_2(r,s)$
2  Data: r= , s= , $v_1$= , $v_2$= , $\alpha$= , $\beta$= , $\Delta\tau$= , $\Delta z$=
3  Initial conditions : $P_1(j,0)=0$ , $P_2(j,0)=0$ for j=1,r
4  Boundary conditions z=0 : $P_1(0,0)=1$, $P_1(0,g)=0$  for g=1,s
5  Boundary conditions $z=z_e$: $P_2(r,h)=0$ for h=0,s
6  i=1
7  System solution:
           J=1,r
           $P_2(0,i)-P_2(1,i)=0$
           $(P_1(j,i)-P_1(j,i-1))/\Delta\tau+v_1(P_1(j,i)-P_1(j-1,i))/\Delta z+\alpha P_1(j,i)-\beta P_2(j,i)=0$
           $(P_2(j,i)-P_2(j,i-1))/\Delta\tau-v_2(P_2(j,i)-P_2(j-1,i))/\Delta z-\alpha P_1(j,i)+\beta P_2(j,i)=0$
           $P_1(r,i)-P_1(r-1,i)=0$
8  Write and transfer through data processing: $P_1(j,i)$,$P_2(j,i)$
9  For i<s
10 i=i+1
11 Back to 7
12 For i>s
13 Stop
```

Figure 4.11 Numerical text of the stochastic model given by Eq. (4.149).

4.4.3
The Solution of Stochastic Models with Analytical Methods

Examples 4.2 and 4.3 and the models from Section 4.4 show that the stochastic models can frequently be described mathematically by an assembly of differential partial equations.

The core of a continuous stochastic model can be written as Eq. (4.150). Here, $P(z,\tau)$ and $a(z)$, $b(z)$, $c(z)$ are quadratic matrices and L is one linear operator with action on the matrix $P(z,\tau)$. In the mentioned equation, $f(z)$ is a vector with a length equal to the matrix $P(z,\tau)$. In this model, z can be extended to a two- or a three-dimensional displacement:

$$\frac{\partial P(z,\tau)}{\partial \tau} + a(z)\frac{\partial P(z,\tau)}{\partial z} + b(z)\frac{\partial^2 P(z,\tau)}{\partial z^2} + c(z)L(P(z,\tau)) = f(z) \tag{4.150}$$

This mathematical model has to be completed with realistic univocity conditions. In the literature, a large group of stochastic models derived from the model described above (4.150), have already been solved analytically. So, when we have a new model, we must first compare it to a known model with an analytical solution so as to identify it. If we cannot produce a correct identification, then we must analyze it so as to determine whether we can obtain an analytical solution. In both situations, we have to carry out different permissive but accepted manipulations of the original model:

- all algebraic transformations are accepted, especially the combination of model variables;
- model transformation with dimensionless variables and parameters;
- all integral transformations that produce a model and univocity conditions similar to those given in a problem with an analytical solution.

The analysis of the univocity conditions attached to the model shows that, here, we have an unsteady model where nonsymmetrical conditions are dominant.

The analytical solution of the model imposes the use of integral transformation methods [4.53]. With the kernel K(z,μ), the finite integral transformation of the function P(z,τ) is the function $P^1(\mu,\tau)$, which is defined with the following relation:

$$P^1(\mu,\tau) = \int_0^{z_e} K(\mu,z)P(z,\tau)dz \tag{4.151}$$

The Laplace integral transformation, used in Section 4.3.1, allows the indentification of its kernel as $K(z,\mu) = K(z,s) = e^{-s\tau}$. It corresponds to the case when we produce a transformation with time. So, for this case, we particularize the relation (4.151) as:

$$P^1(z,s) = \int_0^{\infty} P(z,\tau)e^{-s\tau}d\tau \tag{4.152}$$

So as to show how we use the integral transformation in an actual case, we simplify the general model relation (4.150) and its attached univocity conditions to the following particular expressions:

$$\frac{\partial P(z,\tau)}{\partial \tau} = a\left(\frac{\partial^2 P(z,\tau)}{\partial z^2}\right) + F(z,\tau) \tag{4.153}$$

$$z = 0\ ,\ \tau > 0\ ,\ c_1 a\frac{dP}{dz} + \alpha_1 P = 0$$

$$z = z_e\ ,\ \tau > 0\ ,\ c_2 a\frac{dP}{dz} + \alpha_2 P = 0$$

$$z > 0\ ,\ \tau = 0\ ,\ P = f_0(z) \tag{4.154}$$

In Eqs. (4.153) and (4.154), we recognize the general case of an unsteady state diffusion displacement in a solid body.

The particularization of relation (4.151) to Eqs. (4.153) and (4.154) results in one image of the original model:

$$\frac{\partial P^1(\mu,\tau)}{\partial \tau} = a\left(\frac{\partial P^1(\mu,\tau)}{\partial \mu}\right) + F^1(\mu,\tau) \tag{4.155}$$

$$z = 0\ ,\ \tau > 0\ ,\ (c_1 a + \alpha_1)P^1(\mu,\tau) = f_1(\tau)\int_0^{z_e} K(\mu,z)dz$$

$$z = z_e\ ,\ \tau > 0\ ,\ (c_2 a + \alpha_2)P^1(\mu,\tau) = f_2(\tau)\int_0^{z_e} K(\mu,z)dz$$

$$z > 0\ ,\ \tau = 0\ ,\ P^1(\mu,\tau) = \int_0^{z_e} f_0(z)K(\mu,z)dz = f_0^1(\mu) \tag{4.156}$$

It is easy to observe that the conditions from Eq. (4.154) have been completed with the evolution with time of the stochastic trajectory at the start ($z = 0$) and at the end ($z = z_e$) (for instance, note the presence of $f_1(\tau)$ and $f_2(\tau)$ inside the assembly of conditions (4.156)). The image of the model has the analytical solution given by Eq. (4.157) [4.53]. The notations used here are specified thanks to relations (4.158) and (4.159):

$$P^1(\mu_n,\tau) = e^{-(a\mu_n^2/z_e^2)\tau}\left\{f_0^1(\mu_n) + \int_0^{\tau} e^{(a\mu_n^2/z_e^2)\tau}A(\mu_n,\tau)d\tau\right\} \tag{4.157}$$

$$A(\mu_n,\tau) = \frac{1}{c_1}F^1(\mu_n,\tau) + \left[\frac{K(\mu_n,z)}{c_1}f_1(\tau)\right]_{z=0} + \left[\frac{K(\mu_n,z)}{ac_2}\right]_{z=z_e} f_2(\tau) \tag{4.158}$$

$$F^1(\mu_n,\tau) = \int_0^{z_e} F(z,\tau)K(\mu_n,z/z_e)dz \tag{4.159}$$

The analytical solution for the original $P(z,\tau)$ is obtained with the inversion formula [4.53]. This solution is an infinite sum where the proper values μ_n, $n = 1,2,..\infty$ represent the summing parameters:

$$P(z,\tau) = \sum_{n=1}^{\infty} K(\mu_n,z/z_e)e^{-(a\mu_n^2/z_e^2)\tau}\left\{f_0^1(\mu_n) + \int_0^{\tau} e^{(a\mu_n^2/z_e^2)\tau}A(\mu_n,\tau)d\tau\right\} \tag{4.160}$$

Table 4.2 gives the kernels and characteristic equations for cases with various boundary conditions. Here h_1 and h_2 are defined by Fig. 4.12: $h_1 = \alpha_1/c_1 a$, $h_2 = \alpha_2/c_2 a$.

Table 4.2 The kernels and characteristic equations for the stochastic model given by relations (4.153)–(4.154).

Univocity conditions		**Kernel expression: $K(\mu_n, z/z_e)$**	**Equation for μ_n**
z = 0	**z = z_e**		
$h_1 = \infty$	$h_2 = \infty$	$(\sqrt{2/z_e}) \sin \mu_n z/z_e$	$\sin(\mu) = 0$
$h_1 = \infty$	$h_2 = 0$	$(\sqrt{2/z_e}) \sin \mu_n z/z_e$	$\cos(\mu) = 0$
$h_1 = 0$	$h_2 = \infty$	$(\sqrt{2/z_e}) \cos \mu_n z/z_e$	$\sin(\mu) = 0$
$h_1 = 0$	$h_2 = 0$	$(\sqrt{2/z_e}) \cos \mu_n z/z_e$	$\sin(\mu) = 0$
$h_1 = 0$	$h_2 = ct$	$(\sqrt{2/z_e}) \left[\frac{\mu_n^2 + h_2^2 z_e^2}{\mu_n^2 + h_2^2 z_e^2 + h_2 z_e}\right]^{1/2} \cos(\mu_n z/z_e)$	$\mu\tan(\mu) = h_2 z_e$
$h_1 = ct$	$h_2 = \infty$	$(\sqrt{2/z_e}) \left[\frac{\mu_n^2 + h_1^2 z_e^2}{\mu_n^2 + h_1^2 z_e^2 + h_1 z_e}\right]^{1/2} \sin(\mu_n(1 - z/z_e))$	$\mu\cot(\mu) = -h_1 z_e$
$h_1 = ct$	$h_2 = 0$	$(\sqrt{2/z_e}) \left[\frac{\mu_n^2 + h_1^2 z_e^2}{\mu_n^2 + h_1^2 z_e^2 + h_1 z_e}\right]^{1/2} \cos(\mu_n(1 - z/z_e))$	$\mu\tan(\mu) = h_1 z_e$
$h_1 = ct$	$h_2 = ct$	$(\sqrt{2/z_e})*$ $\left[\frac{\mu_n \cos \mu_n z/z_e + h_1 z_e \sin \mu_n z/z_e}{[\mu_n^2 + h_1^2 z_e^2 (1 + h_2 z_e/(\mu_n^2 + h_2^2 z_e^2) + h_1 z_e]^{1/2}}\right]$	$\tan(\mu) = \frac{\mu(h_1 + h_2) z_e}{\mu^2 - h_1 h_1 z_e^2}$

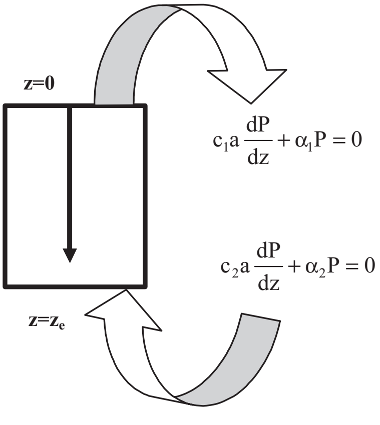


Figure 4.12 Univocity conditions of the model of diffusive and unidirectional displacement (4.153).

We can illustrate this actual case by reaching an analytical solution if the following considerations are taken into account:

- $f_0(z) = 1$: this fact shows that we have uniformly distributed marked particles onto the displacement trajectory at the initial instant;

- $f_1(\tau) = f_2(\tau) = 0$ for $\tau \geq 0$ and $F(z,\tau) = 0$ for $0 \leq z \leq z_e$ and $\tau \geq 0$: we do not have any external intervention on boundaries, and it is not possible to have a generation of marked particles along the moving trajectory;
- $h_1 = 0$ and $h_2 = \infty$: the marked particle can leave the trajectory only at position $z = 0$.

In Table 4.2 our actual case can be identified to accept the kernel $K(\mu_n\, z/z_e) = (\sqrt{2/z_e}) \cos \mu_n z/z_e$ and $\sin(\mu) = 0$ as the characteristic equation for the proper values $\mu_n, n = 1, \ldots \infty$. At the same time, it is identified that $A(\mu_n,\tau) = 0$ and, consequently, after a little modification, solution (4.160) becomes:

$$P(z,\tau) = \sum_{n=1}^{\infty} e^{-(a\mu_n^2/z_e^2)\tau} \cos(\mu_n z/z_e) \tag{4.161}$$

Figure 4.13 shows this dependence as a trend; here parameter Fo is recognized as the Fourier number ($Fo = a\tau/z_e^2$).

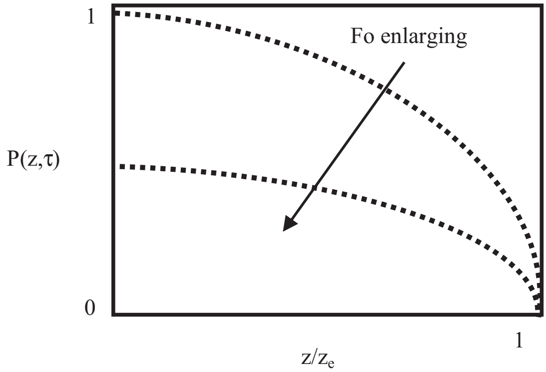


Figure 4.13 Time and space evolution of $P(z,\tau)$ (case of model (4.153)–(4.154)).

The model (4.140), which has been transformed, can easily accept this analytical solution. The desorption of one species from a saturated membrane, when the membrane surface respects the nonpermeable condition, can be described by this solution. Other cases seem to be more interesting, as for example, when the value of h_2 is constant and not null. In this last example, the conversion $P(z,\tau) = c(z,\tau)/c_0$ allows the calculation of the concentration field of mobile species through the membrane thickness.

The following section contains the particularization of the integral Laplace transformation for the case of the stochastic model given by the assembly of relations (4.146)–(4.147). This particularization illustrates how the Laplace transformation is used to solve partial differential equations. We start by applying the integral Laplace operator to all the terms of relation (4.146); the result is in:

$$\int_0^\infty e^{-s\tau}\left(\frac{\partial P_k(z,\tau)}{\partial \tau}+v_k\frac{\partial P_k(z,\tau)}{\partial \tau}+\left(\sum_{j=1,J\neq k}^{N}\alpha_{kj}\right)P_k(z,\tau)-\sum_{j=1,j\neq k}^{N}\alpha_{jk}P_j(z,\tau)\right)d\tau=0 \tag{4.162}$$

The computing of the above integrals gives:

$$sP_k(z,s)-P_k(z,0)+v_k\frac{dP_k(z,s)}{dz}+\left(\sum_{j=1,j\neq k}^{N}\alpha_{kj}\right)P_k(z,s)-\sum_{j=1,j\neq k}^{N}\alpha_{jk}P_j(z,s)=0 \tag{4.163}$$

This last result can be written as Eq. (4.164) and completed with the univocity conditions (4.165) resulting from the Laplace transformation of the original conditions written with relation (4.147):

$$v_k\frac{dP_k(z,s)}{dz}=-\left(s+\sum_{j=1,j\neq k}^{N}\alpha_{kj}\right)P_k(z,s)+\sum_{j=1,j\neq k}^{N}\alpha_{jk}P_j(z,s)+P_k(0) \tag{4.164}$$

$$s\succ 0 \quad ; \quad z=0 \quad ; \quad \begin{cases} P_k(0,s)=\int_0^\infty e^{-s\tau}g_k(\tau)d\tau \text{ for } v_k\succ 0 \\ dP(0,s)/dz=0 \quad \text{for} \quad v_k\prec 0 \end{cases}$$

$$s\succ 0 \quad ; \quad z=z_e \quad ; \quad \begin{cases} P_k(z_e,s)=\int_0^\infty e^{-s\tau}h_k(\tau)d\tau \text{ for } v_k\prec 0 \\ dP(z_e,s)/dz=0 \quad \text{for} \quad v_k\succ 0 \end{cases} \tag{4.165}$$

From a mathematical view-point, this result is made up of a system of ordinary differential equations with its respective integration conditions. In many situations, similar systems for probabilities $P_k(z,s)$, $k = 1,..N$ also have an analytical solution. Using the inverse transformation (Mellin–Fourier transformation) of each $P_k(z,s)$, $k = 1,...N$, we obtain the originals $P_k(z,\tau)$, $k = 1,..N$ as an analytical expression. We complete the problem of inverse transformation of each $P_k(z,s)$, $k = 1,...N$ with two observations: (i) the original is frequently obtained by using a table of the Laplace transformed functions; in this table more associations for the image-original assembly can be tabulated; (ii) all the non-destroying algebraic manipulations of the Laplace image are accepted when we want an analytical expression for its original.

When system (4.164)–(4.165) does not have any analytical solution, we can use numerical integration coupled with interpolation for each function $P_k(z,s)$, $k = 1,...N$; then we can obtain the originals $P_k(z,\tau)$, $k = 1,...N$. However, this procedure gives an approximate result when compared to the direct numerical integration of the original model.

When we have discrete stochastic models, as those introduced through the polystochastic chains, we can obtain their image by using different methods: the Z transformation, the discrete Fourier transformation, the characteristic function of the process or the developing of the function of the process generator. The use of a characteristic or generator function has already been discussed in this book in some particular cases. Now we will focus on the use of the Z transformation to solve discrete stochastic models. For a function $u(\tau)$ and with a time network given as $\tau = n * \Delta\tau$, we can introduce the transformation Z by means of:

$$Z[u(\tau)] = Z[u(n)] = \sum_{n=0}^{\infty} u(n\Delta\tau)z^{-n} = \sum_{n=0}^{\infty} u(n)z^{-n} = F(z) \tag{4.166}$$

It is not difficult to observe the recurrence property (4.167), which can be of interest for the F (z) construction:

$$Z[u(\tau - \Delta\tau)] = \frac{F(z)}{z} \tag{4.167}$$

For the discrete stochastic model given by the group of relations (4.58), written considering a unitary and uniform displacement length for the step k: $\left(p_k(a) = \begin{cases} 1 \text{ for } a = a_k \\ 0 \text{ for } a \neq a_k \end{cases}\right)$, the application of the Z transformation results in the following expression:

$$Z[P_k(n,i)] = \sum_{e \in K} Z[p_{ek}P_k(n-1, i-a_k)] \tag{4.168}$$

Considering the notation $F_k(z,j) = \sum_{n=0}^{\infty} P_k(n,j)z^{-n}$, we can rewrite this expression as shown in relation (4.169). If we particularize the model to address the simplification that considers non-fractionary values for the steps a_k, then we can easily solve the transformed model after $F_k(z,j)$. To do so, we must use a new discrete transformation where n in the $F_k(z,j)$ expression is replaced by j.

$$zF_k(z,j) = \sum_{e \in K} p_{ek}F_k(z, j-a_k) \tag{4.169}$$

The Z transformation for a random and discrete variable results in facilitating the computation of the most important parameters used for a process characterization (mean values, momenta of various order, etc.). In example 4.3.1, we can use the obtained functions $F_k(z,j)$ to compute some parameters of this type because, in this case, we have a solution to the characteristic function of the stochastic model but not a complete and proper solution. The knowledge of the behaviour of the mean values of random variables is frequently enough to provide the stochastic model of the investigated process. For this purpose, the vector which contains the probability distributions of the process random variables $P_k(z,\tau)$, is used together with relation (4.170) in a finite space, to compute the mean values of the random variables of various order (non-centred moment of various order). The integration will carefully be corrected by bordering the space of the integral.

$$E_k^m(\tau) = \int_{-\infty}^{+\infty} z^m P_k(z,\tau)dz \quad , \ k \geq 0 \tag{4.170}$$

The derivate of the probabilities vector on the z axis results in:

$$\int_{-\infty}^{+\infty} \frac{dP_k(z,\tau)}{d\tau} z^m dz = z^m P_k(z,\tau)/_{-\infty}^{+\infty} - m \int_{-\infty}^{+\infty} z^{m-1} P_K(z,\tau) = -mE_k^{m-1} \tag{4.171}$$

Now we can particularize this transformation method (called method of momenta) for the model case given by the group of relations (4.146)–(4.147):

$$\frac{dE_k^m(\tau)}{d\tau} = -\left(\sum_{j=1,j\neq k}^{N} \alpha_{kj}\right) E_k^m(\tau) + mv_k E_k^{m-1}(\tau) + \sum_{j=1,j\neq k}^{N} \alpha_{jk} E_j^m(\tau) \tag{4.172}$$

$$\tau = 0 \quad , \quad E_k^m(0) = \int_{-\infty}^{+\infty} z^m f_k(z) dz \tag{4.173}$$

If the obtained formulation $E_k^m(\tau)$ does not have any analytical solution, we can carry out its Laplace transformation. In this case, the images $E_k^m(s)$ can be written with the following recurrence relations:

$$\left(s + \left(\sum_{j=1,j\neq k}^{N} \alpha_{kj}\right)\right) E_k^m(s) - mv_k E_k^{m-1}(s) - \sum_{j=1,j\neq m}^{N} \alpha_{jk} E_j^m(s) - E_k^m(0) = 0 \; ;$$

$$k = 1, N \tag{4.174}$$

The solution of this equation system gives expressions $E_k^m(s),\ k = 1, N$, which can be solved analytically by using an adequate inversion procedure. Indeed, the stochastic model has now an analytical solution but only with mean values. It is important to notice that when the analytical solution of a stochastic model prodiuces only mean values it is important to make relationships between these results and the experimental work. This observation is significant because more of the experimental measurements allow the determination of the mean values of the variables of the process state, for the model validation or for the indentification of process parameters.

At the end of this short analysis about solving stochastic models using integral transformation, we can conclude that:

- by these methods we transform an original stochastic model into its image that is simpler and consequently more easily explored;
- we transform: (i) a problem with singular coefficients into a non-singular coefficient problem; (ii) a problem with a weak dependence on one parameter into an independent problem with respect to this parameter; (iii) an n order differential equation or a system with n differential equations into a system with n–1 order algebraic equations.
- by looking at the presented examples of transformation, it is not difficult to consider the problem of a model transformation as a general problem: indeed, the transformation presents a general form $v(t) = E(u(\tau(t)))$, where $\tau(t)$ is for each t a time randomly distributed with the law $h(s,t)$ and E is the mean value operator.

4.5
Use of Stochastic Algorithms to Solve Optimization Problems

In recent times, stochastic methods have become frequently used for solving different types of optimization problems [4.54–4.59]. If we consider here, for a steady state process analysis, the optimization problem given schematically in Fig. 4.14, we can wonder where the place of stochastic methods is in such a process. The answer to this question is limited to each particular case where we identify a normal type distribution for a fraction or for all the independent variables of the process ($\mathbf{X} = [X_i]$). When we use a stochastic algorithm to solve an optimization problem, we note that stochastic involvement can be considered in [4.59]:

- the stochastic selection of the starting point of optimization. This shows that each starting point of optimization is selected by a stochastic procedure where all points have the same probability of being chosen; so we have here a multi-start problem for the objective function and the algorithm of optimization.
- the selection procedure for the establishment of a value for each independent variable of the process. Here, we use a random procedure in which a stochastic generator gives a value between the minimal and maximal accepted value for each variable of the process. We retain only the selected values producing a vector X that minimizes or maximizes the objective function of the process.

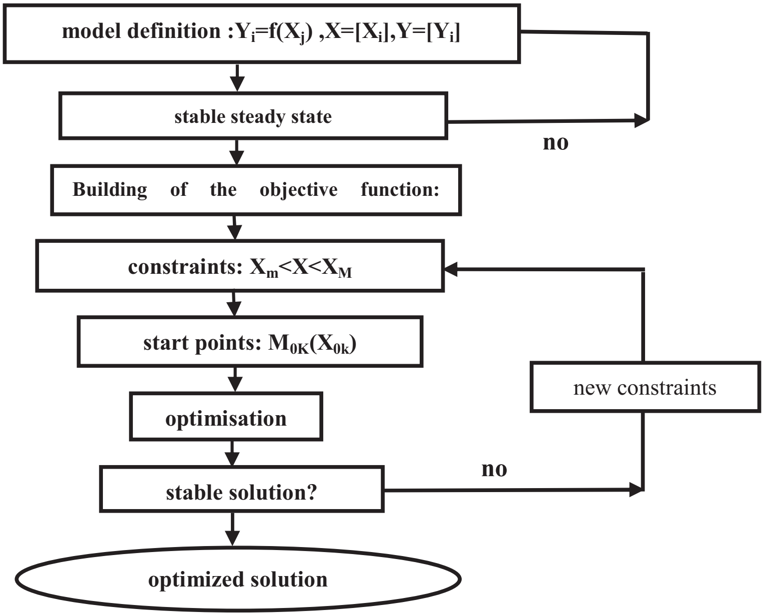


Figure 4.14 Description of the problem of optimization of a steady state process.

Figure 4.15 details this computation procedure, here s_{max} and i_{max} are respectively considered as the number of starting points and the number of acceptable iterations for one start.

```
1   Define the stationary mathematical model $Y=f(X,Y)$
2   Define an objective function $F=F(X,Y)$
3   Define the constraints $C=C(X,Y)$
4   Select a lower and upper bound for X  such as  $X_{mi}<X_i<X_{Mi}$ for all $i=1,N$
5   Input $s_{max}$ and $i_{max}$ and start the selection of the  state vectors $X_0(s)$ , $s=1,s_{max}$
6   Random select $X=X_0=X_0(s)$
7   $i=1$
8   Solve the  system $Y^0=f(X^0,Y^0)$
9   Compute $F^I=F(X^I,Y^I)$
10  Random select $X=X^I$ near$X^{I-1}$
11  Solve the system $Y^1=f(X^1,Y^1)$ and compute $F^I_{new}$
12  Control of the  constraints violations
13  For violations go back at 10
14  For $F^I_{new}<F^I$ go back at  10
15  For $F^I_{new}>F^I$   $F^I=F^I_{new}$ ,$X^I=X^0$; store and write $F^I$ and $X^I$
16  For $i<i_{max}$ go back at 8
17  For $s<s_{max}$ go back at 6
18  End
```

Figure 4.15 The summary description of a stochastic procedure used for the maximization of the objective function.

The success of this computation method depends strongly on the dimension of the computation field which is considered here with the values of s_{max} and i_{max}. Indeed, when the values of i_{max} and s_{max} are greater than $2*10^4$ and 10 respectively, using this method can be problematic because of the size of the computation volume. It is important to notice that this method works without the preparations considered in the gradient optimizing procedures (see Section 3.5.5).

This procedure can easily be transformed to identify the parameters of a process as is shown in Fig. 4.15.

4.6
Stochastic Models for Chemical Engineering Processes

Stochastic modelling has been developing exponentially in all the domains of scientific research since 1950, when the initial efforts for the particularization of the stochastic theory in some practical domains were carried out. In 1960, James R. Newman, who was one of the first scientists in modern statistical theory, wrote the following about the stochastic theory particularization: *Currently in the period of dynamic indetermination in science, there is a serious piece of research that, if treated realistically, does not involve operations on stochastic processes* [4.8].

The stochastic process theory has been a major contribution to the opportune renewal of the basic stochastic theory resulting from some actual requirements and forced by the necessity of characterizing modern scientific processes. The scientific literature for the theory and practice of stochastic processes has been extensively scattered in many books and magazines. Many reviews and specialized books discuss the basic research lines in the theory of stochastic processes or present very interesting applications [4.8].

The practical applications of the stochastic process theory are multiple. This is a consequence of the capacity for this theory for predicting the future of a dynamic system by use of its history and its current state. Among the most famous applications we can note:

- The analysis of all types of movements, from atomic and molecular level [4.61–4.62] to the evolution of macroscopic systems such as atmospheric phenomena [4.63–4.64].
- The analysis of dynamic links for networks with locations where the time of service is stochastically distributed (computer networks, internet networks, etc.).
- The analysis of virtual experiments given with a stochastic model [4.65].
- The analysis of capital and fund movement [4.66, 4.67].
- The analysis and development of all types of games [4.68].
- The optimization and the control of all types of dynamic systems [4.68].

The applications of the stochastic theory in chemical engineering have been very large and significant [4.5–4.7, 4.49–4.59, 4.69–4.78]. Generally speaking, we can assert that each chemical engineering operation can be characterized with stochastic models. If we observe the property transport equation, we can notice that the convection and diffusion terms practically correspond with the movement and diffusion terms of the Fokker–Plank–Kolmogorov equation (see for instance Section 4.5) [4.79].

The following sections describe applications where stochastic models are used for the characterization of some momentum, heat and mass transport examples. For the beginner in stochastic modelling, these applications are relevant, firstly as practical examples, secondly as an explanation of the procedures and methodology for the creation of stochastic models and thirdly as examples of the use of stochastic models to obtain computation formula or algorithms for one or more investigated parameters of chemical engineering processes.

4.6.1
Liquid and Gas Flow in a Column with a Mobile Packed Bed

Columns packed with a moving bed are highly efficient for mass transfer in gas–liquid or vapour–liquid systems. This high transfer efficiency is a consequence of the rapid interface renewal brought about by the rapid movements of the packing particles [4.80–4.82].

In this example, we consider two types of operation carried out in the same type of packed column (shown in Fig. 4.16). The operating conditions depend on the values of the gas and liquid flow rates. In the former mode of operation, the column works in a wetted state whereas in the latter, we have a flooded packed state. The mobile packing bed is composed of spherical spheres with diameter 1–3 cm and density no greater than 500 kg/m^3. For this type of device, recognized as mobile wetted packed bed (MWPB), the liquid and gas flow are usually characterized either by processing the parameters' relationships or through models that show:

- The state of gas and liquid hold-up for specified values of factors and parameters affecting the operation of the mobile packed bed;
- The state of phase mixing at each level of the working factors of the MWPB.

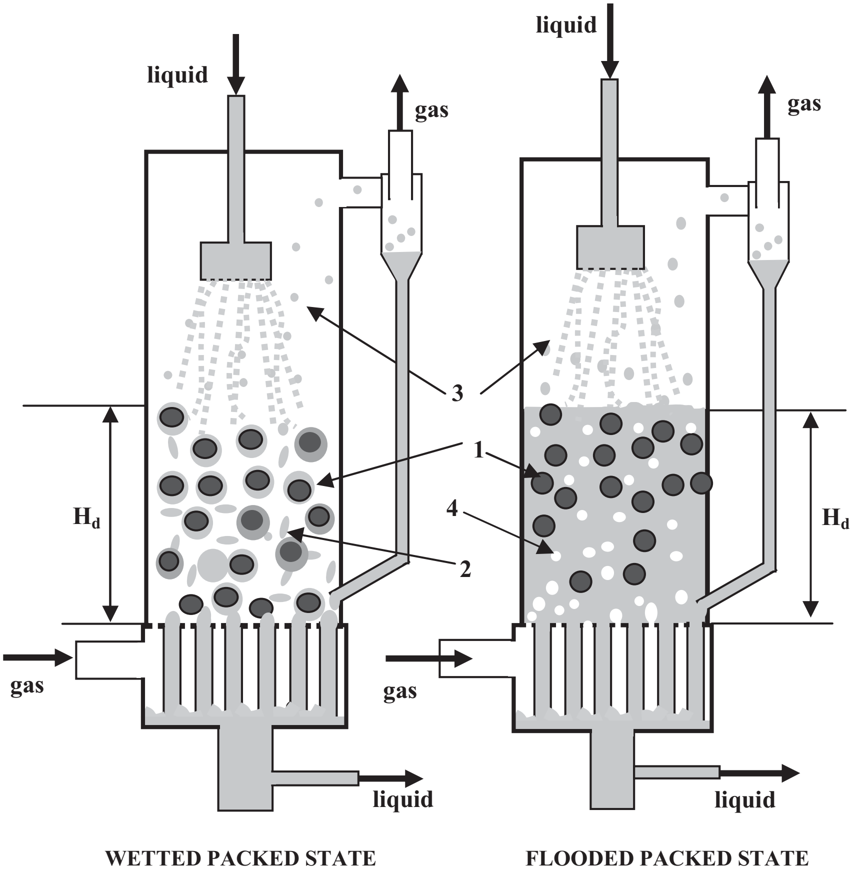


Figure 4.16 Regimes of work of the moving bed column. 1 – solid bed particle, 2 – drops of liquid in the bed, 3 – small drops, 4 – gas bubbles.

To deal with this problem, and more specifically with the working state of the MWPB, we will use stochastic modelling of the liquid and gas flow. When the MWPB operates with small liquid retention (wetted packed state) the liquid and gas hold-up are described by the concept of mean residence time (τ_{ml}, τ_{mg}) and the flow rate density (q_{vl}, q_{vg}) as follows:

$$\varepsilon_l = q_{vl}\tau_{ml}/H_d \tag{4.175}$$

$$\varepsilon_g = q_{vg}\tau_{mg}/H_d \tag{4.176}$$

The residence time for a liquid element flowing in a MWPB can be described by Eq. (4.176). Here τ_{ml0} is the liquid mean residence time for a standard mobile packed bed with a d_{p0}-diameter solid packing and a q_{vl0}-density liquid flow rate:

$$\varepsilon_l = \frac{q_{vl}\left(\dfrac{d_{p0}}{d_p}\right)^{\alpha}\left(\dfrac{q_{vl0}}{q_{vl}}\right)^{\beta}\tau_{ml0}}{H_d} \tag{4.177}$$

A stable hydrodynamic state (where the particles move about, in all directions, without any preferences) occurs in working states with a small liquid hold-up (mobile and wetted packed bed or MWPB). This displacement is the driving force of the liquid flow and we can then characterize the liquid flow by means of one stochastic model with three evolution states (for instance, see Fig. 4.17). Indeed, after this model, we accept that a liquid element is in motion with three independent evolution states:

- The liquid element moves with a flow rate $+v_x$ towards the positive direction of x;
- the liquid element moves with a flow rate $-v_x$ along the negative direction of x;
- the liquid element moves through the normal plane to x, or keeps its position.

After this description, we can appreciate the evolution of the liquid element in a MWPB through a continuous stochastic process. So, when the liquid element evolves through an i state, the probability of skipping to the j type evolution is written as $p_{ij}a\Delta\tau$. Consequently, we express the probability describing the possibility for the liquid element to keep a type I evolution as:

$$P_i = 1 - \sum_{j\neq i} p_{ij}a\Delta\tau \tag{4.178}$$

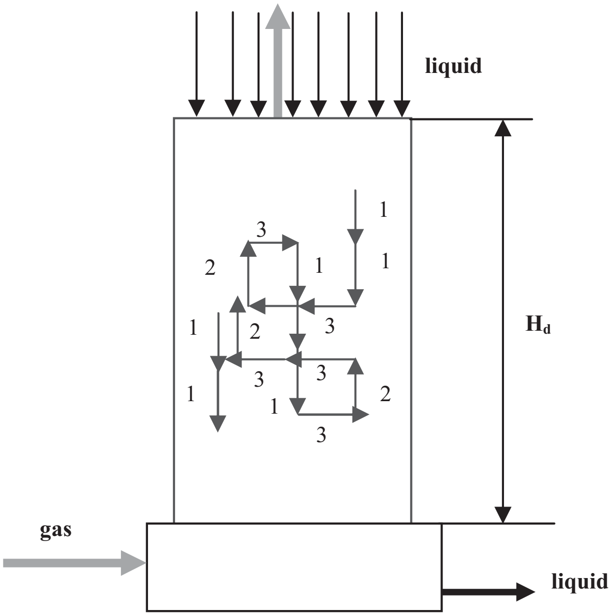


Figure 4.17 Elementary processes for the evolution of a liquid element in a MWPB.

If we consider the evolution of the liquid element together with the state of probabilities of elementary evolutions, we can observe that we have a continuous Markov stochastic process. If we apply the model given in Eq. (4.68), $P_1(z, \tau)$ is the probability of having the liquid element at position x and time τ evolving by means of a type 1 elementary process (displacement with a $+v_x$ flow rate along a positive direction of x). This probability can be described through three independent events:

- The liquid element which evolves at time τ, with the rate of evolution $+v_x$ to the position $x - \Delta x$, keeps the same evolution for the interval of time $\Delta\tau$; the probability of this occurrence is mathematically written as: $(1 - p_{12}a\Delta\tau - p_{13}a\Delta\tau)P_1(x - v_x\Delta\tau, \tau)$;
- the liquid element, which has evolved with rate $-v_x$ to position x in a time τ, changes to evolution rate $+v_x$ at the interval of time $\Delta\tau$; $p_{31}a\Delta\tau P_3(x, \tau)$ describes the probability of this occurrence;
- the last event is represented by the possibility for the liquid element that evolves at a rate 0 to a position x in a time τ, to change its evolution rate to $+v_x$ in the interval of time $\Delta\tau$; $p_{21}a\Delta\tau P_2(x, \tau)$, describes the probability of this occurrence.

Considering the type 1 evolution, we notice that $P_1(z, \tau)$ is obtained by the sum of the probabilities of independent events; so we obtain:

$$\begin{aligned} P_1(x, \tau + \Delta\tau) = &[1 - (p_{12} + p_{13})a\Delta\tau]P_1(x - v_x\Delta\tau, \tau) + \\ &p_{21}a\Delta\tau P_2(x, \tau) + p_{31}a\Delta\tau P_3(x, \tau) \end{aligned} \tag{4.179}$$

By the same procedure, we obtain the probabilities of having the liquid element at x position in a time $\tau + \Delta\tau$ with a type 2 or type 3 evolution. The relations below describe these probabilities:

$$\begin{aligned} P_2(x, \tau + \Delta\tau) = &[1 - (p_{21} + p_{23})a\Delta\tau]P_1(x - v_x\Delta\tau, \tau) + \\ &p_{12}a\Delta\tau P_1(x, \tau) + p_{32}a\Delta\tau P_3(x, \tau) \end{aligned} \tag{4.180}$$

$$\begin{aligned} P_3(x, \tau + \Delta\tau) = &[1 - (p_{31} + p_{32})a\Delta\tau]P_3(x - v_x\Delta\tau, \tau) + \\ &p_{13}a\Delta\tau P_1(x, \tau) + p_{23}a\Delta\tau P_2(x, \tau) \end{aligned} \tag{4.181}$$

The probabilities $P_1(H_d, \tau)$ and $P_3(0, \tau)$ show the possibilities for the liquid element to leave the MWPB; these will consequently be used to compute the residence time of the liquid. When the time increases, $\Delta\tau$ is very small (near zero) and relations (4.180)–(4.181) become a particularization of the model (4.74)–(4.76), (for instance see Section 4.4.2):

$$\frac{\partial P_1(x, \tau)}{\partial \tau} + v_x \frac{\partial P_1(x, \tau)}{\partial x} = -(p_{12} + p_{13})aP_1(x, \tau) + p_{21}aP_2(x, \tau) + p_{31}aP_3(x, \tau) \tag{4.182}$$

$$\frac{\partial P_3(x, \tau)}{\partial \tau} - v_x \frac{\partial P_3(x, \tau)}{\partial x} = -(p_{31} + p_{31})aP_3(x, \tau) + p_{13}aP_1(x, \tau) + p_{23}aP_2(x, \tau) \tag{4.183}$$

$$\frac{\partial P_2(x, \tau)}{\partial \tau} = -(p_{21} + p_{23})aP_2(x, \tau) + p_{12}aP_1(x, \tau) + p_{32}aP_3(x, \tau) \tag{4.184}$$

The univocity conditions, necessary to solve the model, are established by the following considerations;

- when the liquid element gets into WPB at $\tau = 0$, it will not be present on the points where $x > 0$:

$$\tau = 0 \quad , \quad x > 0 \quad , \quad P_1(x, 0) = P_2(x, 0) = P_3(x, 0) = 0 \tag{4.185}$$

- when the liquid element gets into WPB at $x = 0$ with only an elementary type 1 process, we have:

$$\tau = 0 \quad , \quad x = 0 \quad , \quad P_1(0, 0) = 1 \tag{4.186}$$

- for all $\tau > 0$ at $x = 0$ and $x = H_d$, the liquid element cannot evolve with a type 1 or a type 3 process:

$$\tau > 0 \quad , \quad x = 0 \quad , x = H_d \quad , \quad P_1(0,\tau) = 0 \quad , \quad P_3(H_d,\tau) = 0 \tag{4.187}$$

The process model expressed as a Laplace image is given by the following system of differential equations:

$$\begin{aligned} v_x\frac{dP_1(x,s)}{dx} = &\left[-(s + ap_{12} + ap_{13}) + \frac{p_{21}ap_{12}a}{s + p_{21}a + p_{23}a}\right]P_1(x,s) + \\ &\left[p_{31}a + \frac{p_{21}ap_{23}a}{s + p_{21}a + p_{23}a}\right]P_3(x,s) \end{aligned} \tag{4.188}$$

$$\begin{aligned} v_x\frac{dP_3(x,s)}{dx} = &\left[+(s + ap_{12} + ap_{13}) - \frac{p_{23}ap_{32}a}{s + p_{21}a + p_{23}a}\right]P_3(x,s) + \\ &\left[p_{13}a + \frac{p_{12}ap_{23}a}{s + p_{21}a + p_{23}a}\right]P_1(x,s) \end{aligned} \tag{4.189}$$

Here, the image $P_2(x.s)$ has been eliminated from the expressions that resulted from the first form of the Laplace model transformation. The observations on the packed particles evolving in WPB show that we do not have any preferential motion directions. We can extend this observation to the motion of the liquid element. Indeed, we can accept the equality of its transition probabilities: $p_{ij} = 1/3$; $i = 1,3$; $j = 1,3$. If we take into account this last consideration, together with a unitary value for the velocity evolution ($v_x = 1$ length units/s or $v_x = 1$ dm/s), we can assert that the model of the evolution of the liquid element flowing inside the MWPB is fully characterized. The solution of this model is carried out with its Laplace transformation of the differential equations of the model and by considering the corresponding univocity conditions. The result is given by Eqs. (4.190) and (4.191). As explained at the beginning of this section, $P_2(x,s)$ is missing here as a consequence of its elimination from the first state of the Laplace transformation of model differential equations:

$$\frac{dP_1(x,s)}{dx} = -\frac{(s+a)(3s+a)}{3s+2a}P_1(x,s) + \frac{a(s+a)}{3s+2a}P_3(x,s) \tag{4.190}$$

$$\frac{dP_3(x,s)}{dx} = \frac{(s+a)(3s+a)}{3s+2a}P_3(x,s) + \frac{a(s+a)}{3s+2a}P_1(x,s) \tag{4.191}$$

If we remove $P_3(x,s)$ from the assembly of relations (4.190) and (4.191), the result is:

$$\frac{d^2P_1(x,s)}{dx^2} = \frac{3as(s+a)^2}{3s+2a}P_1(x,s) \tag{4.192}$$

The general solution of this last differential equation is given by relation (4.193), where C_1 and C_2 are integration constants and λ^2 is expressed by relation (4.194):

$$P_1(x,s) = C_1e^{\lambda(s+a)} + C_2e^{-\lambda(s+a)} \tag{4.193}$$

$$\lambda^2 = \frac{3as}{3s + 2a} \tag{4.194}$$

Constants C_1 and C_2 are obtained from the univocity problem adapted to the Laplace transformation. The solution thus obtained is given below. In this relation, Λ is given by Eq. (4.196):

$$P_1(x, s) = \frac{1}{\Lambda}[(1 + \lambda)^2 e^{-\lambda x(s+a)} - (1 - \lambda)^2 e^{-2\lambda H_d + \lambda x(s+a)}] \tag{4.195}$$

$$\Lambda = (1 + \lambda)^2 - (1 - \lambda)^2 e^{-2\lambda H_d} \tag{4.196}$$

If we take into consideration the procedure that we used above to eliminate $P_3(x, s)$ from the system (4.190)–(4.191), we can obtain the following expression for $P_3(x, s)$:

$$P_3(x, s) = \frac{1}{\Lambda}[(1 - \lambda^2) e^{-\lambda x(s+a)} - (1 - \lambda^2) e^{-2\lambda H_d + \lambda x(s+a)}] \tag{4.197}$$

The residence time distribution function is found as a result of the addition of the probabilities showing the possibility for a liquid element to leave the MWPB (see also Section 4.3.1):

$$f(\tau, H_d) = P_1(H_d, \tau) + P_3(0, \tau) \tag{4.198}$$

The mean residence time for the liquid element evolution in a MWPB, can easily be obtained from the first derivative of the characteristic function of the residence time distribution:

$$\tau_{m0}(H_d) = -\varphi(0, H_d) \tag{4.199}$$

The analytical expression of our $\varphi(s, H_d)$ is obtained by coupling the basic formula of the characteristic residence time distribution function with the solutions of $P_1(x, s)$ and $P_3(x, s)$:

$$\varphi(s, H_d) = \int_0^\infty f(\tau, H_d) e^{-s\tau} d\tau = P_1(H_d, s) + P_3(0, s) \tag{4.200}$$

$$\varphi(s, H_d) = \frac{\mathrm{Ch}(\lambda H_d s) - \frac{1 - \lambda^2}{2\lambda}\mathrm{Sh}(\lambda H_d) - \frac{1 + \lambda^2}{2\lambda}\mathrm{Sh}(\lambda H_d s)}{\frac{1 + \lambda^2}{2\lambda}\mathrm{Sh}(\lambda H_d) + \mathrm{Ch}(\lambda H_d)} \tag{4.201}$$

A similar result for $\varphi(s, H_d)$ but with a different relation for parameter λ was obtained in application 4.3.1. The value of the derivative $\varphi'(0, H_d)$ is then obtained using the definition of the derivative in a point:

$$
\begin{aligned}
\varphi'(0,H_d) &= \lim_{s\to 0}\frac{\varphi(s,H_d)-\varphi(0,H_d)}{s-0} = \lim_{s\to 0}\frac{\varphi(s,H_d)-1}{s} = \\
&\lim_{s\to 0}\frac{\mathrm{Ch}(\lambda H_d s)-\lambda \mathrm{Sh}(\lambda H_d)-\mathrm{Ch}(\lambda H_d)-\dfrac{1+\lambda^2}{2\lambda}\mathrm{Sh}(\lambda H_d s)}{\dfrac{1+\lambda^2}{2\lambda}s\mathrm{Sh}(\lambda H_d)+s\mathrm{Ch}(\lambda H_d)} \\
&= \ldots = -\left(\frac{3}{2}H_d+\frac{H_d}{H_d+2}\right)
\end{aligned} \tag{4.202}
$$

It is easy to observe that the intensity of transition from one state to another (parameter a from relations (4.179)–(4.181)) does not influence the mean residence time characterizing the liquid evolution in the MWPB:

$$
\tau_{m0}(H_d) = -\varphi'(0,H_d) = -\left(\frac{3}{2}H_d+\frac{H_d}{H_d+2}\right).
$$

Coming back to the problem of liquid fraction in the MWPB, we observe that the replacement of Eq. (4.177) by (4.202) imposes homogenizing units because we previously established that the mean residence time of the liquid was calculated considering $v_x = 1$ in dm/s and, consequently, H_d was used in decimeters. Now considering H_d in meters, relation (4.177) becomes:

$$
\varepsilon_l = \left(\frac{30}{2}+\frac{10}{H_d+2}\right)q_{vl}\left[\frac{d_{p0}}{d_p}\right]^{\alpha}\left[\frac{q_{vl0}}{q_{vl}}\right]^{\beta} \tag{4.203}
$$

We complete the expression of MWPB liquid hold-up by considering $\alpha = 0.5$ and $\beta = 0.4$. These values are also used to hold-up the liquid in a countercurrent gas–liquid flow in a fixed packed bed. To complete the building of the MWPB liquid hold-up expression, we show the identified conditions corresponding to a standard defined MWPB. These conditions correspond to a spherical-shaped packing with $d_{p0} = 0.025$ m, $\rho_p = 300$ kg/m^3, fluidized by air and wetted by water with a flowing density of $q_{vl0} = 2.5{*}10^{-3}$ m^3/m^{2}s. Indeed, the final expression is:

$$
\varepsilon_l = 0.216\left(\frac{30H_d+8}{30H_d+6}\right)q_{vl}^{0.6}d_p^{-0.5} \tag{4.204}
$$

For other shapes of packing, we have to correct the previous relation with a coefficient ψ (shape factor). Relation (4.205) takes into account this correction:

$$
\varepsilon_l = 0.216\left(\frac{30H_d+8}{30H_d+6}\right)q_{vl}^{0.6}d_p^{-0.5}\psi^{-0.5} \tag{4.205}
$$

The final expression giving the mean residence time for the liquid evolution in a MWPB of spherical particles is written as follows:

$$
\tau_{ml} = 0.0143\left(\frac{30H_d}{2}+\frac{10H_d}{10H_d+2}\right)d_p^{-0.5}q_{vl}^{-0.4} \tag{4.206}
$$

Experimental validation. When a model cannot be verified by experiments, it can be considered as an excellent exercise which however does not have any practical significance. So as to validate the results of our stochastic model for a liquid flow in a MWPB, we will use data previously published [4.80, 4.82] for a model contacting bed of spherical particles, in which the gas and liquid fluids were respectively air and water. In these studies, the liquid residence time was estimated by measuring the response of a signal injected into the bed. The MWPB liquid hold-up was obtained by the procedure of instantly stopping the water and air at the bed input. The data obtained are reported in Figs. 4.18–4.20.

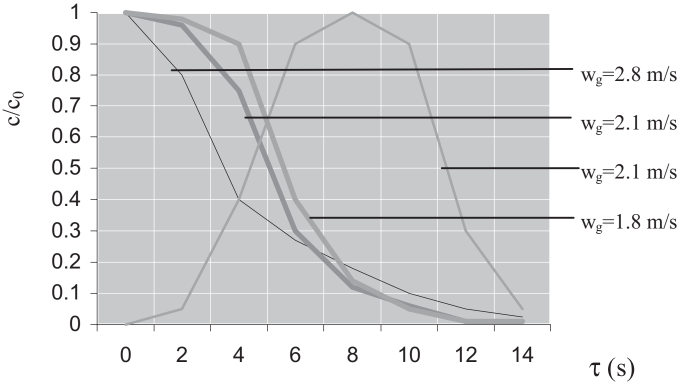


Figure 4.18 Response to signals in liquid for a WPB operated with air and water (packing of spherical particles with $d_p = 0.0275$ m and $\rho_p = 330$ kg/m^3, $q_{vl} = 12$ m^3/m^{2}h , $H_0 = 0.18$ m).

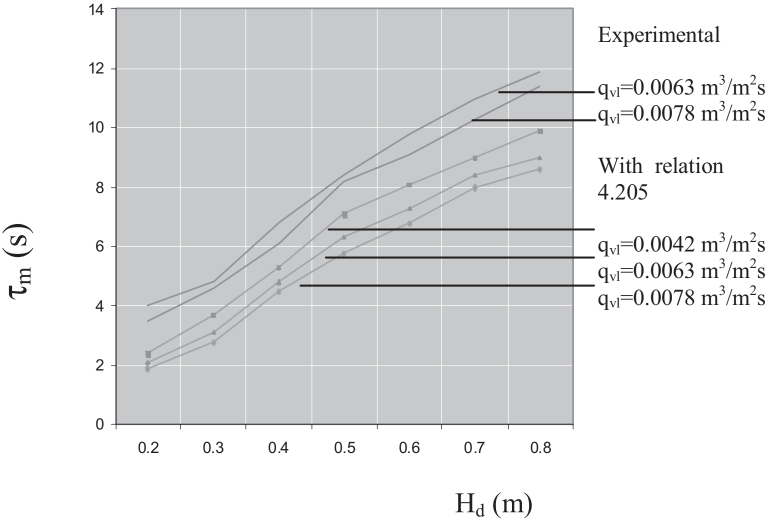


Figure 4.19 Liquid residence time for a MWPB operated with air and water (Spherical particles with $d_p = 0.0275$ m and $\rho_p = 330$ kg/m^3).

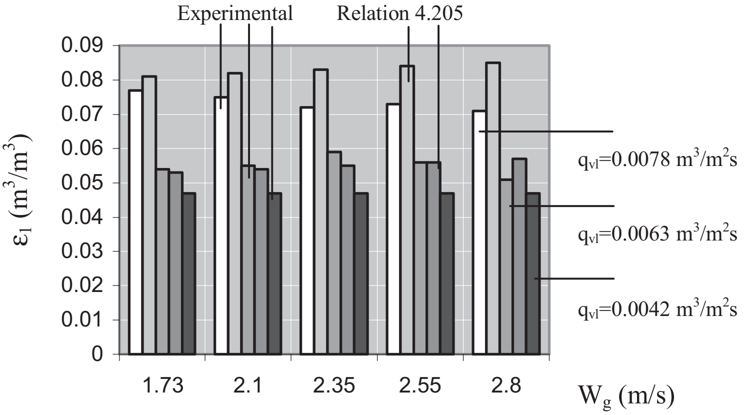


Figure 4.20 Liquid hold-up state for air and water operated MWPB. (Spherical particles with $d_p = 0.0275$ m and $\rho_p = 330$ kg/m^2, $H_0 = 0.18$ m).

Each point on the curves in Fig. 4.19 corresponds to the mean value of various experimental results. We can notice that, even if we have good trends, the experimental and calculated values do not match well. This can be ascribed to model inadequacies, especially with respect to the liquid exit conditions; in that case, we considered that the MWPB output had occurred at $x = 0$ and at $x = H_d$ when it was experimentally observed that the liquid exit dominantly occurs at $x = H_d$. This results in a decrease in the mean residence time computed values. If we look at Figs. 4.20 to 4.22, which have been obtained at different operating conditions, we can conclude that we do not have major differences between the computed and experimental values of liquid MWPB hold up; then we can consider the equality of the transition probabilities between the individual states of the stochastic model to be realistic.

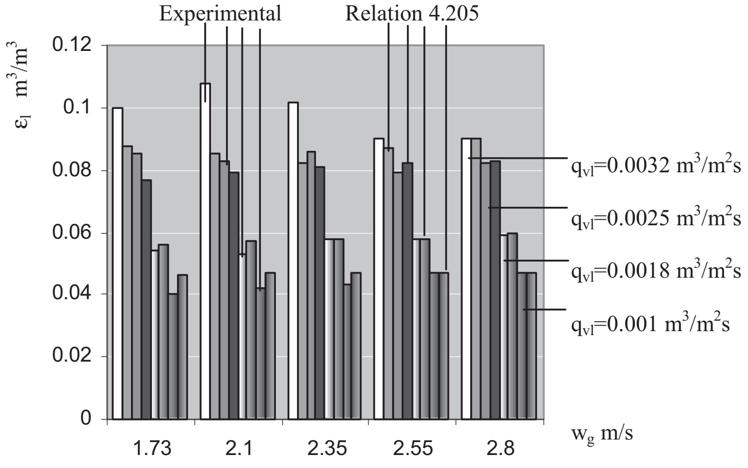


Figure 4.21 Liquid hold-up state for a MWPB operated with air and water. Packing particles of cylindrical shape with $d_p = 0.012$ m, $\rho_p = 430$ kg/m^3, $H_0 = 0.18$ m.

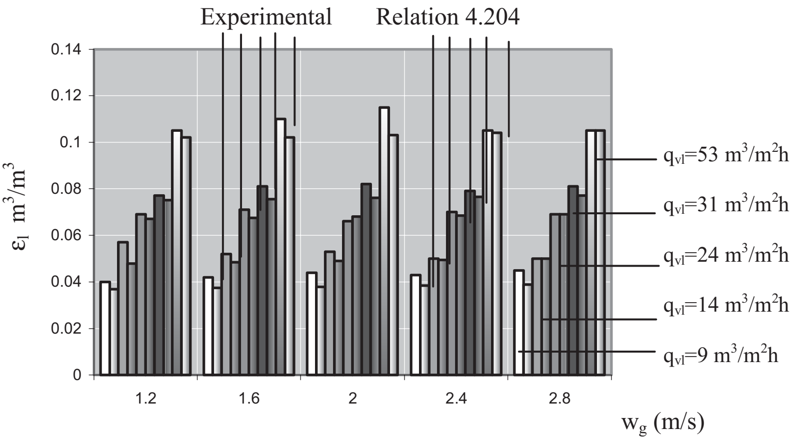


Figure 4.22 Liquid hold-up state for a WPB operated with air and water. Case of spherical particles with $d_p = 0.02$ m and $\rho_p = 220$ kg/m^3; $H_0 = 0.22$ m.

According to Fig. 4.21, where the particles used for the bed are cylindrical, as well as to Fig. 4.22 obtained from the experimental data published by Chen [4.83], we observe that the MWPB liquid hold-up does not depend on gas velocity as was found in Fig. 4.20. In order to justify the value of the evolution velocity of a liquid element ($v_x = 1$ dm/s) used in the simulations, we drew Figs. 4.23 and 4.24. Figure 4.23 has been drawn after the data published by Cains and Prausnitz [4.84]. It shows the evolution of the liquid velocity when water fluidizes spherical particles of glass.

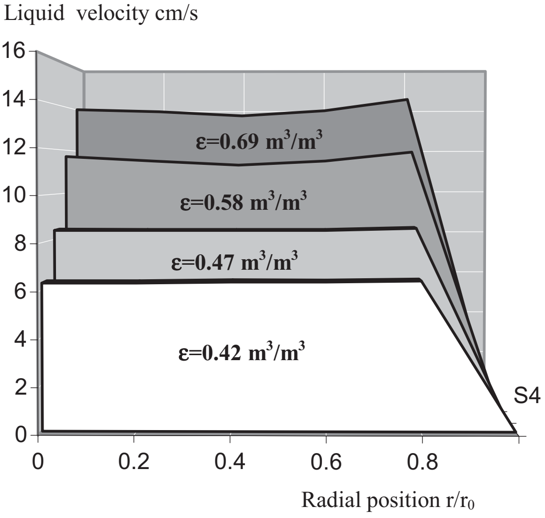


Figure 4.23 Liquid flow state for the fluidization of a bed of glass spheres with $d_p = 0.0032$ m.

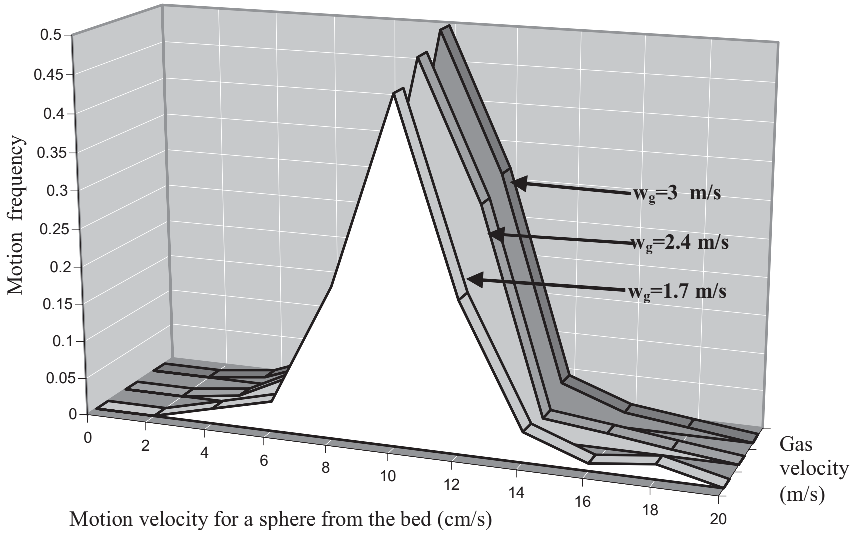


Figure 4.24 Velocity frequencies for the motion of a mobile sphere inside of a MWPB. Case: Air–water operated, spheres with $d_p = 0.0275$ m and $H_0 = 0.18$ m, $q_{vl} = 0.004$ m^3/m^2s.

In Fig. 4.24 we show the experimental data that present the frequency of the velocity states for the motion of some marked particles inside MWPB. For this purpose some particles of the packing have been coloured and their motion has been recorded by means of a high speed video-recorder [4.81]. From both figures it is obvious that the velocity range obtained is very near to the liquid element velocity considered for simulations. Indeed, if in the MWPB the most important quantity of the liquid covers the fluidized particles, the evolution of the liquid velocity has to be identical to the fluidized particle velocity. However, it is obvious that the physical properties of the liquid have to affect the residence time of the liquid element that evolves inside the MWPB. Indeed, if we have a liquid different from water we have to introduce the influence of its own physical properties on the system response. The solution to this problem can be obtained by derivation of the expression of the characteristic function of the liquid evolution as shown in Eq. (4.206). Here H_d^e is considered as an equivalent height of the MWPB corresponding to a unitary value of the velocity of displacement of the liquid element ($v_x = 1$ conventional length unit/s).

$$\varphi'(0, H_d^e) = -\left(\frac{3}{2}H_d^e + \frac{H_d^e}{H_d^e + 2}\right) \tag{4.207}$$

The transposition of the equivalent height of the mobile packed bed (H_d^e) to a normal working unit is carried out through a correction function, which is applied to a bed height corresponding to a MWPB operated with air and water. If we consider that the major contributions to the correction function expression are given by liquid density, viscosity and superficial tension, we can complete the relations (4.205) and (4.206), which are then rewritten as:

$$\varepsilon_l = 0.216\left(\frac{30H_d + 8}{30H_d + 6}\right) q_{vl}^{0.6} d_p^{-0.5} \psi^{-0.5} f(\eta_l, \sigma_l, \rho_l) \tag{4.208}$$

$$\tau_{ml} = 0.0143\left(\frac{30H_d}{2} + \frac{10H_d}{10H_d + 2}\right) d_p^{-0.5} q_{vl}^{-0.4} f(\eta_l, \sigma_l, \rho_l) \tag{4.209}$$

Some computed values of the function $f(\eta_l, \sigma_l, \rho_l)$ obtained by using the data reported by Masao et al. [4.85], are given in Table 4.3. The analysis of the data of Table 4.3 shows that the expression of the function $f(\eta_l, \sigma_l, \rho_l)$ can be written as follows:

$$f(\eta_l, \sigma_l, \rho_l = \eta_{rl}^{\alpha} \sigma_{rl}^{\beta} \rho_{rl}^{\gamma}) \tag{4.210}$$

Table 4.3 Some values of the function $f(\eta_l, \sigma_l, \rho_l)$ when the MWPB is operated with air and various liquids.

$f(\eta_l, \sigma_l, \rho_l)$	**Water** $\rho_l = 1$ g/cm^3 , $\eta_l = 1$ CP, $\sigma_l = 72.8$ d/cm	**Ethanol** $\rho_l = 0.8$ g/cm^3, $\eta_l = 1.38$ CP, $\sigma_l = 22.5$ d/cm	**Glycerol 25%** $\rho_l = 1.07$ g/cm^3, $\eta_l = 1.33$ CP, $\sigma_l = 70.8$ d/cm	**Glycerol 65%** $\rho_l = 1.16$ g/cm^3, $\eta_l = 14.5$ CP, $\sigma_l = 67.5$d/cm
Spheres of 170 kg/m^3 $d_p = 0.02$ m, $w_g = 2$ m/s $q_{vl} = 0.0025$ m^3/m^{2}s	1	0.759	0.955	1.36
Spheres of 590 kg/m^3 $d_p = 0.028$ m, $w_g = 3$ m/s $q_{vl} = 0.006$ m^3/m^{2}s	1	0.801	0.983	1.31
	$\rho_{rl} = 1$ $\eta_{rl} = 1$ $\sigma_{rl} = 1$	$\rho_{rl} = 0.8$ $\eta_{rl} = 1.33$ $\sigma_{rl} = 0.303$	$\rho_{rl} = 1.07$ $\eta_{rl} = 1.33$ σ_r	$\rho_{rl} = 1.16$ $\eta_{rl} = 14.45$ $\sigma_{rl} = 0.981$

The data of this table also allow the identification of parameters $\alpha = 0.158$, $\beta = 0.484$ and $\gamma = -1.65$. Based on these values, we can then write slightly more complex relations for the liquid hold-up and liquid residence time in the MWPB:

$$\varepsilon_l = 0.216\left(\frac{30H_d + 8}{30H_d + 6}\right) q_{vl}^{0.6} d_p^{-0.5} \psi^{-0.5} \eta_{rl}^{0.158} \sigma_{rl}^{0.484} \rho_{rl}^{-1.65} \tag{4.211}$$

$$\tau_{ml} = 0.0143\left(\frac{30H_d}{2} + \frac{10H_d}{10H_d + 2}\right) d_p^{-0.5} q_{vl}^{-0.4} \eta_{rl}^{0.158} \sigma_{rl}^{0.484} \rho_{rl}^{-1.65} \tag{4.212}$$

4.6.1.1 **Gas Hold-up in a MWPB**

In Fig. 4.16 the gas is shown to be the continuous phase of the MWPB. In this configuration, many direction changes in the flow of gas elements originate from the presence and moving of the packing spheres. If we consider that these changes take place randomly, then we can carry out the particularization of the stochastic flow description of the gas elements. This description has been successfully used for the case of gas–liquid flow in a fixed and in a mobile packed bed [4.28, 4.81].

The gas element evolves inside the MWPB in 3 states: displacement in the $+x$ direction with velocity $+v_x$; displacement in the $-x$ direction with velocity $-v_x$; non-motion or displacement in the horizontal plane. The mathematical writing of the stochastic model is given by relations (4.182)–(4.187). In order to particularize this model to the case of gas element evolution inside the MWPB, we take into account the following considerations:

1. The sense of the x-axis is determined by the global gas flow direction and is inverse with respect to the liquid flow.
2. It is difficult to select the values for the probabilities of passage between process states.
3. The gas flowing element rapidly passes from one actual process state to another and tends to follow an elementary process type 1state.
4. Concerning the evolution of the velocity of the gas flowing element, the skip velocity is added or subtracted from the local gas flow velocity in the bed, when the gas flowing element skips in the $+x$ and $-x$ directions respectively.

With these considerations, the model that describes the gas element motion inside the MWPB can be described by the following assembly of relations:

$$\frac{\partial P_1(x,\tau)}{\partial \tau} + (w_g + v_x)\frac{\partial P_1(x,\tau)}{\partial x} = -(p_{12} + p_{13})aP_1(x,\tau) + p_{21}aP_2(x,\tau) + p_{31}aP_3(x,\tau) \tag{4.213}$$

$$\frac{\partial P_3(x,\tau)}{\partial \tau} + (w_g - v_x)\frac{\partial P_3(x,\tau)}{\partial x} = -(p_{31} + p_{32})aP_3(x,\tau) + p_{13}aP_1(x,\tau) + p_{23}aP_2(x,\tau) \tag{4.214}$$

$$\frac{\partial P_2(x,\tau)}{\partial \tau} + w_g\frac{\partial P_2(x,\tau)}{\partial x} = -(p_{21} + p_{23})aP_2(x,\tau) + p_{12}aP_1(x,\tau) + p_{32}aP_3(x,\tau) \tag{4.215}$$

$$\tau = 0 \ , \quad x = 0 \ , \ P_1(x,0) = P_2(x,0) = P_3(x,0) = 0 \tag{4.216}$$

$$\tau = 0 \ , \quad x = 0 \ , \ P_1(0,0) = 1 - u \quad P_2(0,0) = P_3(0,0) = u/2 \tag{4.217}$$

$$\tau > 0 \quad , \quad x = 0 \ , \quad P_1(0,\tau) = 0 \quad , \quad P_2(0,\tau) = 0 \ , \ P_3(0,\tau) = 0 \tag{4.218}$$

This stochastic model is in fact one type of turbulent motion model. For the univocity problem, we consider that a gas element can be influenced by any type of elementary process after its insertion into the MWPB at $x = 0$. The permanent velocity w_g, pushes the gas element outside the bed at $x = H_d$ and through any of the elementary processes. The presented model can be completed by considering the different frequencies induced by passing from one elementary process to another: $p_{11}a_{11} = \alpha_{11}$, $p_{12}a_{12} = \alpha_{12}$, $p_{13}a_{13} = \alpha_{13}$, etc.

The distribution of the residence time for the gas evolution inside the bed takes into account the statement above, which concerns the possibility for the gas to exit the bed through any of the elementary processes:

$$f(\tau, H_d) = P_1(\tau, H_d) + P_2(\tau, H_d) + P_3(\tau, H_d) \tag{4.219}$$

Theoretical and experimental results of the gas hold-up inside a MWPB show that the data converge only when the p_{11} values are greater than 0.7. Figure 4.25 presents a simulation of the presented model, which intends to fit some experimental data [4.82]. In the presented simulation, the initial values of $P_1(0,0)$, $P_2(0,0)$ and $P_3(0,0)$ injected into the model give an idea about the values of the transition probabilities; these are: $p_{11} = p_{21} = p_{31} = 0.7$, $p_{12} = p_{13} = p_{12} = p_{23} = p_{22} = p_{33} = p_{32} =$ 0.15. In Fig. 4.25 we can see that we have all the necessary data to begin the computation of the mean residence time of a gas element evolving inside the MWPB. Indeed, relation (4.176) can now be used to calculate the gas hold-up in the bed.

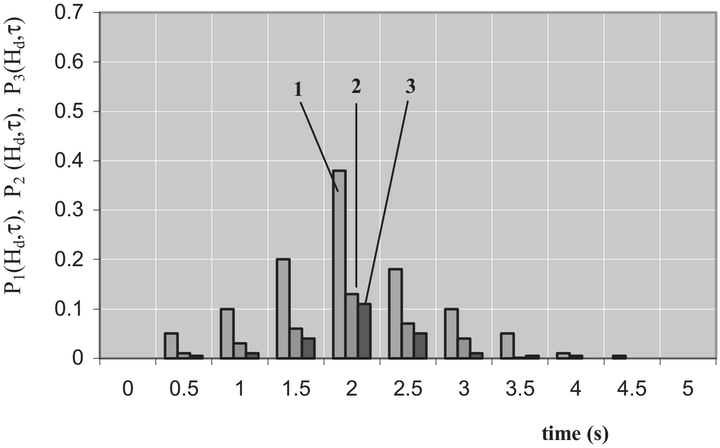


Figure 4.25 The gas exit from the MWPB in terms of probability of the elementary motion processes ($w_g = 2$ m/s, $v_x = 0.1$ m/s, $H_d = 0.9$ m, 1 – $P_1(0,0) = 0.7$, 2 – $P_2(0,0) =$ 0.15, 3 – $P_3(0,0) = 0.15$).

4.6.1.2 **Axial Mixing of Liquid in a MWPB**

The liquid flowing inside a MWPB can be described with a one-parameter dispersion flow model. As we show in Section 3.3, the axial mixing coefficient or, more correctly, the axial dispersion coefficient is the specific parameter for this model. Relation (3.112) contains the link between the variance of the residence time of liquid elements and the Peclet number. We can rewrite this relation so as to particularize it to the case of a MWPB. Here, we have the possibility to compute the variance of the residence time of the liquid through the stochastic model for the liquid flow developed previously in order to obtain the value of the axial dispersion coefficient:

$$\sigma^2 = \frac{2}{\mathrm{Pe}} - \frac{2}{\mathrm{Pe}^2}\left(1 - e^{-\mathrm{Pe}}\right) = \frac{\varphi''(0, H_d)}{[\varphi'(0, H_d)]^2} - 1 \tag{4.220}$$

$$\mathrm{Pe} = \frac{w_l H_d}{D_l} = \frac{H_d^2}{\tau_{ml} D_l} = -\frac{H_d^2}{\varphi'(0, H_d) D_l} \tag{4.221}$$

If we carefully observe the expression of the characteristic function of the residence time distribution for the evolution of a liquid element ($\varphi(s, H_d)$, relation (4.201)), we can notice that it is difficult to compute the expressions of the derivatives $\varphi'(0, H_d)$ and $\varphi''(0, H_d)$. Using the expansion of the hyperbolic sine and cosine respectively as multiplication series, we obtain the following simplified expression for the characteristic function:

$$\mathrm{Ch}(z) = \left(1 + \frac{4z^2}{\pi^2}\right)\left(1 + \frac{4z^2}{3^2\pi^2}\right)\left(1 + \frac{4z^2}{5^2\pi^2}\right)\ldots\ldots\left(1 + \frac{4z^2}{(2n+1)^2\pi^2}\right)\ldots \tag{4.222}$$

$$\mathrm{Sh}(z) = z\left(1 + \frac{z^2}{\pi^2}\right)\left(1 + \frac{z^2}{2^2\pi^2}\right)\left(1 + \frac{z^2}{3^2\pi^2}\right)\ldots\ldots\left(1 + \frac{z^2}{(2n+1)^2\pi^2}\right)\ldots \tag{4.223}$$

$$\varphi(s, H_d) = \frac{(2 + H_d) + (3 - H_d)s - 3H_d s^2 + 1.2H_d s^3}{(2 + H_d) + (3 + 3H_d + 1.2H_d^2)s} \tag{4.224}$$

Table 4.4 compares the residence time results obtained with the characteristic function given by the original equation (4.201) and with the simplified form (4.224). We can notice that the values obtained with the simplified form are good enough.

$$\begin{aligned} \varphi'(0, H_d) &= \lim_{s \to 0} \frac{\varphi(s, H_d) - \varphi(0, H_d)}{s - 0} = \\ &\lim_{s \to 0} \frac{1.2H_d s^3 - 3H_d s^2 - (1.2H_d^2 + 4H_d)s}{(1.2H_d^2 + 3H_d + 3)s^2 + 5(H_d + 2)s} = \\ &\lim_{s \to 0} \frac{3.6H_d^2 s^2 - 6H_d s - (1.2H_d^2 + 4H_d)}{(2.4H_d^2 + 6H_d + 6)s + (H_d + 2)} = -\frac{1.2H_d^2 + 4H_d}{H_d + 2} \end{aligned} \tag{4.225}$$

Table 4.4 Mean residence time of the liquid in a MWPB as a function of the bed height. First row – simplified characteristic function, second row – original characteristic function.

H_d (dm)	0.5	1	2	3	4
$-\varphi'(0,H_d)=\tau_{ml}=\dfrac{1.2H_d^2+4H_d}{H_d+2}$ (s)	0.91	1.73	3.2	4.57	5.87
$-\varphi'(0,H_d)=\tau_{ml}=\dfrac{3}{2}H_d+\dfrac{H_d}{H_d+2}$ (s)	0.95	1.83	3.5	5.1	6.67

The analytical computation for the first derivative of the characteristic function gives relation (4.226) where the functions $\alpha_i(H_d)$, $i=1,6$ are written with the relations (4.227)–(4.232):

$$\varphi'(s,H_d)=\frac{\alpha_1(H_d)s^3+\alpha_2(H_d)s^2+\alpha_3(H_d)s+\alpha_4(H_d)}{[\alpha_5(H_d)+\alpha_6(H_d)s]^2} \tag{4.226}$$

$$\alpha_1(H_d)=7.2H_d^2+7.2H_d^3+2.88H_d^4 \tag{4.227}$$

$$\alpha_2(H_d)=-(9H_d+1.8H_d^2) \tag{4.228}$$

$$\alpha_3(H_d)=-(12H_d+6H_d^2) \tag{4.229}$$

$$\alpha_4(H_d)=-(8H_d+6.4H_d^2+1.2H_d^3) \tag{4.230}$$

$$\alpha_5(H_d)=2+H_d \tag{4.231}$$

$$\alpha_6(H_d)=3+3H_d+1.2H_d^2 \tag{4.232}$$

For the second derivative $\varphi''(0,H_d)$ at point zero, we use the definition formula coupled with the l'Hospital rule for the elimination of the non-determination of 0/0 type. The result is:

$$\varphi''(0;Hd)=\frac{\alpha_3(H_d)\alpha_5(H_d)-2\alpha_4(H_d)\alpha_6(H_d)}{[\alpha_5(H_d)]^2} \tag{4.233}$$

Considering relations (4.220) and (4.221), we can observe that we have all the required elements to compute the axial dispersion coefficient. The theoretical computed values for the axial mixing coefficient for the case where the bed height has a practical importance are shown in Table 4.5. For the cases when the selection $v_x=1$ dm/s is not justified by the operational conditions, we replace H_d by H_d^e. We can introduce H_d^e through equation (4.210):

$$H_d^e=\eta_{rl}^{0.158}\sigma_{rl}^{0.484}\rho_{rl}^{-1.65}H_d \tag{4.234}$$

Table 4.5 Evolution of the Peclet number and of the axial dispersion coefficient with the height of the MWPB (theoretical computation).

H_d (dm)	$-\varphi'(0, H_d)$ (s)	$\varphi''(0, H_d)$ (s^2)	σ^2	Pe	$D_l * 10^2$ (m^2/s)
0.5	0.95	2.33	1.33	–	–
1	1.83	6.32	0.887	0.5	1.07
2	3.50	19.08	0.557	2.1	0.54
3	5.10	37.98	0.46	2.8	0.63
4	6.67	64.83	0.43	3.3	0.73
5	8.21	93.67	0.388	3.7	0.823
6	9.75	130.32	0.371	3.9	0.946
7	11.28	172.79	0.36	4.1	1.05
8	12.80	221.05	0.35	4.4	1.14
9	14.31	275.16	0.343	4.6	1.23
10	15.93	335.04	0.0336	4.7	1.34

Experimental testing. The experimental work for the determination of the liquid axial mixing inside the packed bed has been carried out with the introduction of an impulse of NaCl (12 g/l) on the input of a MWPB which operates with air and water [4.80, 4.81] and with the recording of the evolution with time of the signal state at the liquid output. We assume that the system can be described by the dispersion model and that its analytical solution is given by Eqs. (3.106) and (3.107). Using these equations as well as the experimental results, we can then calculate the Pe number and the D_l coefficient values. Figure 4.26 indirectly shows the evolution of the signal at the output through the electric tension of a Wheatstone bridge having the resistive detector placed in the output flow of liquid.

The experimental data processing has previously been presented in example 3.3.5.3. Equations (3.106) and (3.107) can be simplified in order to allow a rapid identification of Pe and D_l as follows:

$$\ln\frac{c(\theta)}{c_0} = -\left(\frac{Pe}{4}+\frac{4}{Pe}\lambda_1^2\right)\theta+\frac{Pe}{2}+ \ln\frac{2\lambda_1}{\left(1+\frac{Pe}{2}\right)\lambda_1\sin(2\lambda_1)-\left[\frac{Pe}{2}+\left(\frac{Pe}{2}\right)^2-\lambda_1^2\right]\cos(2\lambda_1)} = m\theta+n \tag{4.235}$$

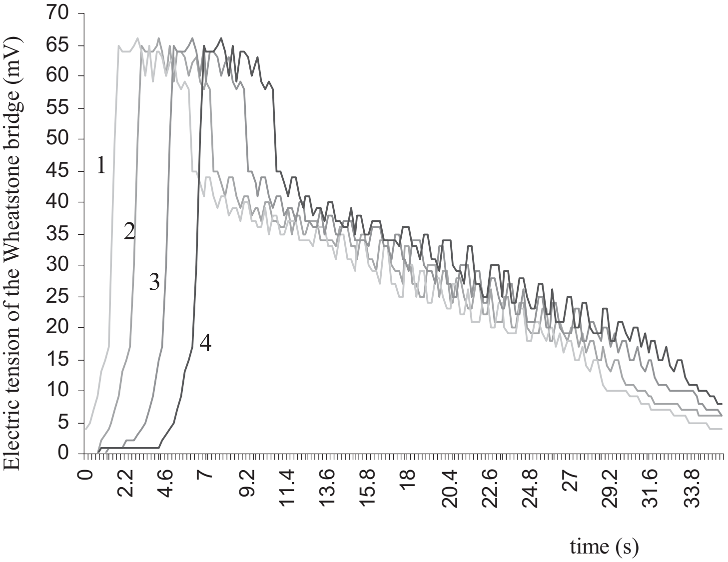


Figure 4.26 The output signal of the inverse unitary impulse of a solution of 12 g/l NaCl in the liquid of the MWPB.
(1 – $w_g = 1.31$ m/s, $q_{vl} = 0.0062$ m^3/m^{2}s, $H_0 = 0.18$ m , $d_p = 0.0275$ m , $\rho_p = 330$ kg/m^3;
2 – $w_g = 1.31$ m/s, $q_{vl} = 0.0031$ m^3/m^2 s, $H_0 = 0.18$ m , $d_p = 0.0275$ m , $\rho_p = 330$ kg/m^3;
3 – $w_g = 2.4$ m/s, $q_{vl} = 0.0062$ m^3/m^2 s, $H_0 = 0.18$ m , $d_p = 0.0275$ m , $\rho_p = 330$ kg/m^3 ;
4 – $w_g = 2.4$ m/s, $q_{vl} = 0.0031$ m^3/m^2 s, $H_0 = 0.18$ m , $d_p = 0.0275$ m , $\rho_p = 330$ kg/m^3).

$$\mathrm{tg}(2\lambda_1) = \frac{\frac{\mathrm{Pe}}{2}\lambda_1}{\lambda_1^2 - \left(\frac{\mathrm{Pe}}{4}\right)^2} \tag{4.236}$$

It is easy to notice that the values of the parameters m and n, from Eq. (4.235), will be estimated after the particularization of the least squares method for the dependence of $\ln\left(\frac{c(\theta)}{c_0}\right)$ vs θ

$$m = \frac{\mathrm{Pe}}{4} + \frac{4}{\mathrm{Pe}}\lambda_1^2 \tag{4.237}$$

$$n = \frac{\mathrm{Pe}}{2} + \ln\frac{2\lambda_1}{\left(1+\frac{\mathrm{Pe}}{2}\right)\lambda_1 \sin(2\lambda_1) - \left[\frac{\mathrm{Pe}}{2} + \left(\frac{\mathrm{Pe}}{2}\right)^2 - \lambda_1^2\right]\cos(2\lambda_1)} \tag{4.238}$$

The value of the Pe number is obtained by solving the system formed by Eqs. (4.237) and (4.238). Two examples of data processing [4.81] are given in Table 4.6. Figure 4.27 presents the evolution of the Peclet number with the gas velocity [4.81–4.83, 4.86]. A comparison between the published and computed stochastic dependence of Pe vs w_g is given for cases 1 and 2, [4.81] ($H_0 = 0.36$ m, $q_{vl} = 0.0031$ and 0.0071 m^3/m^2 s, $d_p = 0.0275$ m , $\rho_p = 330$ kg/m^3).

Table 4.6 Experimental data processing for the estimation of Pe and D_l.

Experimental conditions $w_g = 2$ m/s, $q_{vl} = 0.0047$ m^3/m^2 s, $H_0 = 1.8$ dm, $H_d = 2.1$ dm, $d_p = 0.0275$ m, $\rho_p = 330$ kg/m^3					Experimental conditions $w_g = 2.4$ m/s, $q_{vl} = 0.0047$ m^3/m^2 s, $H_0 = 1.8$ dm, $H_d = 2.1$ dm, $d_p = 0.0275$ m, $\rho_p = 330$ kg/m^3			
N°	$c(\theta)/c_0$	θ	$\ln c(\theta)/c_0$		$c(\theta)/c_0$	θ	$\ln c(\theta)/c_0$	
	0	0	*	m = 1.29	0	0	*	m = 1.31
2	1	0.36	0	**Solutions:**	1	0.34	0	**Solutions:**
3	0.52	0.69	−0.69	$\lambda_1 = 0.608$	0.53	0.69	−0.65	$\lambda_1 = 0.618$
4	0.375	1.03	−0.98	Pe = 1.75	0.35	1.02	−1.04	Pe = 1.81
5	0.276	1.37	−1.35		0.26	1.38	−1.347	
6	0.23	1.71	−1.47	Stochastic	0.23	1.7	−1.47	Stochastic
7	0.11	2.05	−2.2	Pe = 2.4	0.12	2.04	−2.12	Pe = 2.55
8	0.05	2.4	−2.99		0.04	2.4	−3.2	
9	0.013	2.76			0.028	2.72		

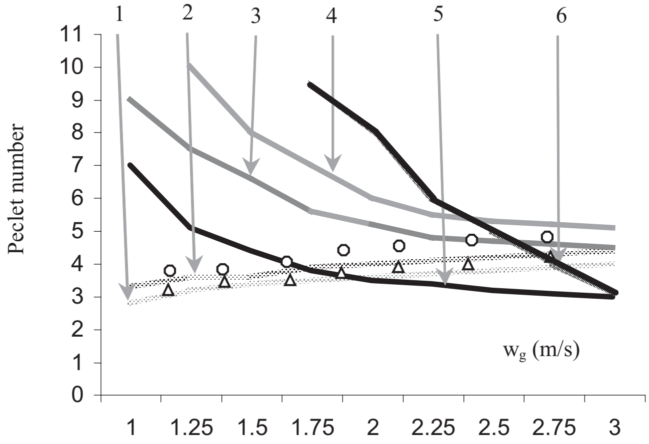


Figure 4.27 Variation of the Pe number with gas velocity. 1,2 – [4.81] $H_0 = 0.36$ m, $q_{vl} = 0.0031$ and 0.0071 m^3/m^2 s, $d_p = 0.0275$ m , $\rho_p = 330$ kg/m^3 ; 3,4 – [4.83] $H_0 = 0.16$ m, $q_{vl} = 0.0038$ and 0.016 m^3/m^2 s, $d_p = 0.016$ m , $\rho_p = 283$ kg/m^3; 5,6 – [4.86] $H_0 = 0.30$ m , $q_{vl} = 0.0025$ and 0.015 m^3/m^2 s $d_p = 0.0255$ m , $\rho_p = 173$ kg/m^3. ○ and △: calculated results for the cases 1 and 2.

Figure 4.28 illustrates the dependence of the axial mixing coefficient with the gas velocity for the examples given above. This graphic representation is derived form Fig. 4.27 according to the relation: $\mathrm{Pe} = \mathrm{H}_\mathrm{d}^2/(\tau_\mathrm{ml}\mathrm{D}_\mathrm{l}))$. Apparently, the stochastic model predictions of the liquid axial mixing versus gas velocity are in contradiction with the published data, especially at low gas velocity. This discordance can be explained if we consider that, at low gas velocity, we only have an incipient motion of the packing. Indeed, at low velocity, we can consider that we are near the conditions of a fixed packed bed, and the stochastic model which considers three states with the same probability: $\mathrm{p}_\mathrm{ij} = 1/3, \forall \mathrm{i} = 1,3; \mathrm{j} = 1,3$ is no longer sustained. At the same time, the calculated Pe values are slightly less than the experimental ones and then the experimentally obtained mixing is greater than when calculated by the model. However, it is important to notice the good trend observed for the axial mixing coefficient, which increases with the gas velocity as shown in Fig. 4.28.

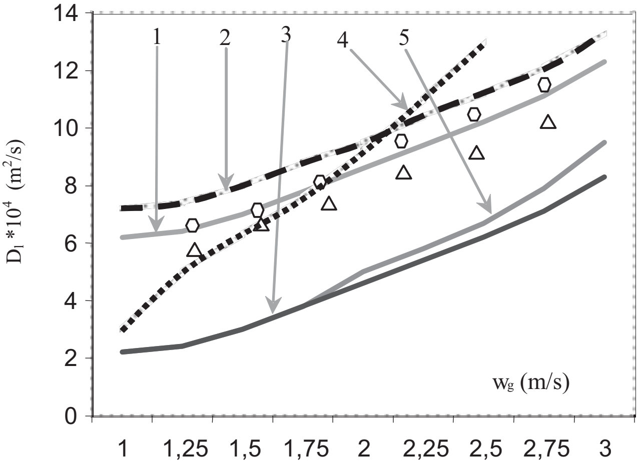


Figure 4.28 State of the axial mixing coefficient versus gas velocity. 1,2 – [4.81] $H_0 = 0.36$ m, $q_{vl} = 0.0031$ and 0.0071 m^3/m^2 s, $d_p = 0.0275$ m , $\rho_p = 330$ kg/m^3 ; 3,4 – [4.83] $H_0 = 0.16$ m, $q_{vl} = 0.0038$ and 0.016 m^3/m^2 s, $d_p = 0.016$ m , $\rho_p = 283$ kg/m^3; 5 – [4.86] $H_0 = 0.30$ m , $q_{vl} = 0.0025$ and 0.015 m^3/m^2 s $d_p = 0.0255$ m , $\rho_p = 173$ kg/m^3. ○ and △: calculated results for the cases 1 and 2.

Before closing this discussion about the axial mixing of liquid inside the MWPB, it is important to note the significance of the result generated by the stochastic model. Concretely, we can compute the values of the axial mixing parameters for liquid flow inside the mobile wetted bed by a procedure (assembly of relations (4.202), (4.220), (4.221), (4.229)–(4.233)) that requires only the computation of the bed height (H_d). This last parameter strongly depends on all the factors that characterize fluidization: the density and diameter of the spheres, liquid flow density, gas velocity, all momentum transport properties of gas and liquid (gas and liquid density, viscosity, liquid superficial tension, etc.). Therefore, the axial mixing parameters for the liquid flow in the MWPB are influenced by all these factors. For the computation of the height of the MWPB, we can use previously published relations [4.80–4.81]. In these relations, the minimum fluidization velocity appears as an important variable. The liquid flow density and the minimum gas flow velocity for the fluidization, determine the value of this variable.

4.6.1.3 **The Gas Fraction in a Mobile Flooded Packed Bed**

Figure 4.16 shows that, in a mobile flooded packed bed (MFPB), the gas flow bubbles through the bed which is composed of the assembly of liquid and solid packing. The spheres that represent the mobile packing are frequently fluidized in the liquid and are predominantly near the surface. In this MFPB, the bed's gas fraction strongly depends on the feed gas flow rate and consequently depends on the apparent gas velocity. As far as many other factors can influence the bed's gas fraction, a stochastic approach to this problem can be convenient. Therefore, this section will be devoted to establishing one stochastic model for the gas movement inside the bed and to its use in solving the dependence between the gas fraction and the various factors of the process. Experimental observations indicate that, in a liquid–solid system, the gas bubbles have a non-organized motion, which can be associated with a stochastic process. In addition, the phenomenon of bubble association is frequently observed in all cases of gas bubbling in a liquid or suspension or in a liquid with large suspended solids. Looking at the motion of a single bubble in this type of system, we can consider that the bubbles will change their velocity in response to: (i) an interaction with the liquid or with the solid; (ii) an interaction with the bubbles in their vicinity. When d_k-diameter bubbles interact with the surrounding liquid, their velocities v_k can be calculated by the following relation $v_k = \sqrt{\frac{4gd_k(\rho_l - \rho_g)}{3\zeta_k \rho_g}}$. Here, ζ_k shows the hydrodynamic friction-resistance coefficient related with the movement of the bubble k. With $f_k^0(x, v_k, \tau)$, we note the function of the velocity distribution with respect to the individual k-type bubbles. We define the multiplication $f_k^0(x, v_k, \tau)dx$ as the fraction of bubbles having velocity v_k that are positioned between x and $x + dx$ at the time τ. For an intense bubbling situation, the interaction of the bubbles with the liquid or with the solid coexists with the bubble–bubble interactions. For this motion type, the function of distribution of velocities is noted as $f(x, v_k, \tau)$. Indeed, from the given motion description we can identify two basic motion processes of bubbles (two elementary evolution states): bubbles interacting with only the neighborhood liquid, when their velocities remain unchanged; bubbles interacting with other bubbles, when we have an evolution of the velocities (the velocity of one bubble can skip from one state to other m possible states).

If the probability for a motion caused only by bubbles–liquid interactions is $p_a = \alpha\Delta\tau$, then the following: $1 - p_a = 1 - \alpha\Delta\tau$, gives the probability for a displacement due to the bubble–bubble interactions. When we have the last type of motion in the interval of time $\Delta\tau$, one bubble changes its velocity v_e to velocity v_k

with the probability p_{ek}. Based on this description, the probability balance (please see the model relation (4.20)) gives the following equation:

$$f_k(x, v_k, \tau + \Delta\tau) = (1 - \alpha\Delta\tau) \sum_{e=1}^{m} p_{ek} f_e(x - v_k\Delta\tau, v_e, \tau) + \alpha\Delta\tau f_k^0(x - v_k\Delta\tau, v_k, \tau) \tag{4.239}$$

Relation (4.239) shows that "k" bubbles (bubbles having velocity v_k) reach point x at time $\tau + \Delta\tau$ because of the interaction with the other types of bubbles (the probability for this event is $1 - \alpha\Delta\tau$) or because of the interaction with the composite liquid–solid medium (the probability for this event is $\alpha\Delta\tau$). At the same time, the bubbles that originate from the position $x - v_k\Delta\tau$ without interaction with the nearly bubbles keep their velocity; so the local distribution function of these individuals velocities is $f_k^0(x, v_k, \tau)$. Due to the stochastic character of the described process, the transition probabilities from the state "e" to all "k" states verify the unification condition. Consequently, the probability p_{kk} will be written as $p_{kk} = 1 - \sum\limits_{e=1, e \neq k}^{m} p_{ke}$ and relation (4.239) will be rewritten as follows:

$$\begin{aligned} f_k(x, v_k, \tau + \Delta\tau) = (1 - \alpha\Delta\tau) & \sum_{e=1, k \neq e}^{m} p_{ek} f_e(x - v_k\Delta\tau, v_e, \tau) + \\ & \left(1 - \sum_{e=1, e \neq k}^{m} p_{ke}\right) f_k(x - v_k\Delta\tau, v_k, \tau) + \\ & \alpha\Delta\tau f_k^0(x - v_k\Delta\tau, v_k, \tau) \end{aligned} \tag{4.240}$$

The determination of the transition probabilities (p_{ek}, $\forall$ k, e = 1, ...m) is a problem that requires careful analysis. Experimental observations show that, for bubbles moving in a liquid, two interaction rules can be accepted:

1. The assembly resulting from a bubble–bubble interaction, which takes the velocity of the bubble having the higher velocity:

$$\mathrm{Int}(v_e, v_k) = \max(v_e, v_k) \quad \forall\ e, k = 1, \ldots m \tag{4.241}$$

2. The assembly resulting from a bubble–bubble interaction, which takes a velocity higher than any of the individual velocities of the bubbles:

$$\mathrm{Int}(v_e, v_k) = \sup[\max(v_e, v_k)] \quad \forall\ e, k = 1, \ldots m \tag{4.242}$$

Expressions (4.241) and (4.242) describe the well known observed phenomena of accelerated bubbling.

To estimate the probabilities p_{ek} or p_{ke}, we consider the behaviour of one individual bubble having velocity v_k at position x. Their interactions with the bubbles having velocities v_e with $v_e \prec v_k$ are described with the term $-\sum\limits_{e=1,e\neq k}^{m} p_{ke}f_e(....)$ in relation (4.240). Because our “k” bubble has the highest velocity, we derive that its relative velocity with respect to the type “e” bubbles is $v_k - v_e$. For the period of time $\Delta\tau$, the covered space is $(v_k - v_e)\Delta\tau$ and the number of type “e” bubbles met by our “k” bubble is $f_e(x, v_e, \tau)(v_k - v_e)\Delta\tau$. At the same time, the probability for our bubbles to realize a linear velocity change depends on the interactions number $f_e(x, v_e, \tau)(v_k - v_e)\Delta\tau$. So, for the transition probability p_{ke}, we can establish:

$$p_{ke} = \beta f_e(x, v_e, \tau)(v_k - v_e)\Delta\tau \quad ; \ k, e = 1; 2, ...m \tag{4.243}$$

When $v_e > v_k$, the interactions of the bubbles having a v_k velocity with the bubbles having a v_e velocity are described in relation (4.240) by the term $\sum\limits_{e=1,e\neq k}^{m} p_{ek}f_e(....)$. After the analysis, updated here for the case of $v_e \prec v_k$, we obtain the following relation for the transition probabilities p_{ek}:

$$p_{ek} = \beta f_k(x, v_k, \tau)(v_e - v_k)\Delta\tau \ ; \ e, k = 1, 2, ...m \tag{4.244}$$

These two last relations respect the following interaction rule: (1) the assembly resulting from a bubble–bubble interaction takes the higher velocity higher of any of the individual velocities of the bubbles.

For the interaction rule of type (2), relations (4.243) and (4.244) become respectively (4.245) and (4.246) where $\sup(v_k)$ and $\sup(v_e)$ are velocities which are higher than v_k and v_e respectively:

$$p_{ke} = \beta f_e(x, v_e, \tau)(\sup(v_k) - v_e)\Delta\tau \quad ; \ k, e = 1; 2, ...m \tag{4.245}$$

$$p_{ek} = \beta f_k(x, v_k, \tau)(\sup(v_e) - v_k)\Delta\tau \ ; \ e, k = 1, 2, ...m \tag{4.246}$$

In order to transform Eq. (4.240) into a form that can be computed, we introduce the following considerations and definitions:

- the real effect of the bubbles interaction is:

$$\begin{aligned} &\lim_{\Delta\tau\to 0}\frac{1}{\Delta\tau}\left[\sum_{e=1}^{m} p_{ek}f_e(x - v_k\Delta\tau, v_e, \tau) - \sum_{e=1}^{m} p_{ke}f_k(x - v_k\Delta\tau, v_k, \tau)\right] \\ &= \beta\left[\sum_{e=1,v_e\succ v_k}^{m} f_e(...)(v_e - v_k)f_k(..) - \sum_{e=1,v_e<v_k} f_e(..)(v_k - v_e)f_k(...)\right] \\ &= \beta f_k(..)\sum_{e=1}^{m} f_e(...)(v_e - v_k) \end{aligned} \tag{4.247}$$

- the concentration of bubbles is linear along their trajectory:

$$b(x, \tau) = \sum_{e=1}^{m} f_e(x, v_e, \tau) = \sum_{e=1}^{m} f_k^0(x, v_e, \tau) \tag{4.248}$$

- the definition of the mean velocity ($\bar{v}(x,\tau)$) of bubbles along their trajectory is:

$$\bar{v}(x,\tau)=\frac{\sum\limits_{e=1}^{m} v_e f_e(x, v_e \tau)}{\sum\limits_{e=1}^{m} f(x, v_e, \tau)} \tag{4.249}$$

We can notice that relation (4.248) is a norma condition for the distribution functions $f_k^0(x, v_k, \tau)$ and $f_k(x, v_k, \tau)$. The probability balance of the motion of bubbles is developed by replacing relation (4.247) in Eq. (4.240) and by rearranging some terms:

$$\begin{aligned}
&\frac{f_k(x, v_k, \tau+\Delta\tau) - f_k(x - v_k\Delta\tau, v_k, \tau)}{\Delta\tau} = \\
&-\alpha\left[f_k(x - v_k\Delta\tau, v_k, \tau - f_k^0(x - v_k\Delta\tau, v_k, \tau\right] \\
&+\beta f_k(x, v_k, \tau)\sum_{e=1}^{m} f_e(x, v_e, \tau)(v_e - v_k) + O_1(\Delta\tau) \\
&+\beta f_k(x - v_k\Delta\tau, v_k, \tau)\sum_{e=1}^{m} f_e(x - v_k\Delta\tau, v_e, \tau)(v_e - v_k) + O_2(\Delta\tau)
\end{aligned} \tag{4.250}$$

Here $O_1(\Delta\tau)$ and $O_2(\Delta\tau)$ have negligible values. By introducing the Taylor expansion of functions $f_k(x - v_k\Delta\tau, v_k, \tau)$ into relation (4.250), we obtain the following assembly of relations:

$$f_k(x - v_k\Delta\tau, v_k, \tau) = f_k(x, v_k, \tau) - v_k\Delta\tau\frac{\Delta f_k(x, v_k, \tau)}{\Delta x} + \ldots.. \tag{4.251}$$

$$\frac{\partial f_k}{\partial\tau} + v_k\frac{\partial f_k}{\partial x} = -\alpha(f_k - f_k^0) + \beta f_k\sum_{e=1}^{m} f_e(v_e - v_k) \tag{4.252}$$

The final form of the stochastic model of the gas bubbling in the liquid–solid system is written by coupling Eq. (4.252) with Eqs. (4.248) and (4.249):

$$\begin{aligned}
\frac{\partial f_k(x, v_k, \tau)}{\partial\tau} + v_k\frac{\partial f_k(x, v_k, \tau)}{\partial x} = &-\alpha[f_k(x, v_k, \tau) - f_k^0(x, v_k, \tau)] + \\
&\beta f_k(x, v_k, \tau)b(x, \tau)[\bar{v}_k - v(x, \tau)] \quad k = 1, ..m
\end{aligned} \tag{4.253}$$

When the number of the elementary states of the process (m) is important, the discrete model (4.253) can be written in a continuous form:

$$\frac{\partial f(x, v, \tau)}{\partial\tau} + v\frac{\partial f(x, v, \tau)}{\partial x} = -\alpha[f(x, v, \tau) - f^0(x, v, \tau)] + \beta f(x, v, \tau)b(x, \tau)[v - \bar{v}(x, \tau)] \tag{4.253'}$$

Here we have:

$$b(x,\tau) = \int_0^\infty f(x,v,\tau)dv = \int_0^\infty f^0(x,v,\tau)dv \tag{4.254}$$

$$\bar{v}(x,\tau) = \frac{\int_0^\infty vf(x,v,\tau)dv}{\int_0^\infty f(x,v,\tau)dv} \tag{4.255}$$

Taking into consideration the physical meaning of $f_k(x, v_k, \tau)$ and $f(x, v, \tau)$ and deriving $f(x, v, \tau)dxdv$, we define the number of the bubbles positioned at time τ between x and $x + dx$ and that gives the velocities in the interval $(v, v + dv)$. Relation (4.253) shows that: (i) the number of bubbles with velocity v decreases with the fraction $\alpha f(x, v, \tau)$ due to their interaction with the neighbouring medium; (ii) the number of bubbles with velocity v increases with the fraction $\alpha f^0(x, v, \tau)$ due to their interaction with the neighbouring medium; (iii) for $v > \bar{v}$ the number of the bubbles with velocity v increases respectively for $v < \bar{v}$ decreases due to the interactions with other bubbles.

The complete unsteady state stochastic model of the bubbling process is given coupling the assembly of relations (4.253)–(4.255) with the univocity conditions. The numerical analysis (checking) of this model can easily produce interesting data for the cases of bubbles coalescence and bubbles breaking. One interesting solution of this model corresponds to the case of a homogenous steady state bubbling which can be obtained with relation (4.253) and considering $\partial/\partial\tau = \partial/\partial x = 0$ and $1 + \frac{\beta}{\alpha}(\bar{v} - v) > 0$. Here $f(x, v, \tau)$ becomes $f(v)$:

$$f(v) = \frac{f^0(v)}{1 + \frac{\beta}{\alpha}(\bar{v} - v)b} \tag{4.256}$$

With the same conditions but considering $1 + \frac{\beta}{\alpha}(\bar{v} - v) = 0$, the solution for $f(v)$ is given by the new relation below written; this fact is equivalent to $v = \bar{v} + \alpha/(b\beta)$ which is the univocity condition for the model given by relations (4.253)–(4.255):

$$f(v) = \frac{f^0(v)}{1 + \frac{\beta}{\alpha}(\bar{v} - v)b} + \gamma b\delta\left[1 + \frac{\beta}{\alpha}(\bar{v} - v)b\right] \tag{4.256'}$$

This expression (bubble velocities distribution) shows that two types of flows participate in the bubbling process: the first type, introduced by the first term Eq. (4.256′), is the regular flow; the second flow type is called singular flow and is contained in the term where the Dirac function $\delta[1 + \frac{\beta}{\alpha}(\bar{v} - v)b]$ appears. The singular flow becomes unimportant when we have: (i) a velocity distribution in a restricted domain around $\bar{v}$; (ii) a slow concentration of bubbles. Both cases are coupled when we can consider that $\gamma \to 0$ in relation (4.256′). If we multiply the left and right terms of equation (4.256′) by v and then integrate it for all velocities of the bubbles, we obtain relations (4.257)–(4.258). Here we used $\bar{v} = \int_0^\infty vf(v)dv / \int_0^\infty f(v)dv$ for the identification of the mean bubble velocity and for the variance of the velocities around the mean velocity:

$$\sigma^2 = \int_0^\infty (\bar{v} - v)vf(v)dv / \int_0^\infty f(v)dv = \int_0^\infty v(\left[1 + \frac{\beta}{\alpha}(\bar{v} - v)b\right] f(v)dv = \int_0^\infty vf^0(v)dv \quad (4.257)$$

$$\bar{v} - \frac{\beta}{\alpha}\sigma^2 b = \bar{v}^0 \quad (4.258)$$

Equation (4.258) gives the mean bubble velocity which is described through the apparent gas velocity $\bar{v} = w_g/\varepsilon_g$, whereas the linear bubble concentration is given through the bubble diameter and the gas fraction $b = \left(\frac{6}{\pi}\right)^{1/3} \frac{\varepsilon_g^{1/3}}{d_{mb}}$. With these two last expressions we can write that:

$$w_g = \frac{\bar{v}^0 \varepsilon_g}{1 - k\varepsilon_g^{1/3}} \quad (4.259)$$

where $k = \left(\frac{6}{\pi}\right)^{1/3} \frac{\beta\sigma^2}{\alpha\bar{v}d_{mb}}$ contains all the unknown factors introduced during model building. Here, σ^2 depends on $\bar{v}$. Indeed, it appears of interest to describe a case where σ^2 becomes independent with respect to $\bar{v}$. In relation (4.259), when $\varepsilon_g \rightarrow 1$, we have a limit case where $k = 1$ and the relation between the gas fraction and the gas apparent velocity becomes:

$$w_g = \frac{\bar{v}^0 \varepsilon_g}{1 - \varepsilon_g^{1/3}} \quad (4.260)$$

To compute the mean bubble velocity ($\bar{v}^0$), it is necessary to know the mean bubble diameter and some physical properties of the medium in which the bubbles evolve.

Experimental checking. Figure 4.29 compares the theoretical calculations and experimental results for the evolution of $\varepsilon_g/(1 - \varepsilon_g^{1/3})$ with $w_g/\bar{v}^0$ for a MFPB. The bed height has been fixed at 0.25 m. Two liquid–solid systems with solid fractions of 0.1 and 0.3 m^3/m^3 have been chosen. A 0.0275 m diameter spheres of density 980–1030 kg/m^3 were selected as mobile packing. Air and water are the working fluids. The gas fraction results from bed expansion when gas flows through the liquid–solid system.

The computation of the mean bubble velocity was based on the bubble diameter resulting from the bubble forming at each submerged orifice from the gas bubbling arrangement. In Fig. 4.29, we can observe that the stochastic model gives a good trend with respect to the experimental results, even if some discordance appears, especially at small values of the gas fraction. In all cases, the model underestimates the experimental results, the underestimation is between 5 and 15% for values of w_g/v^0 greater than 0.3.

The problem of bubble motion in a liquid is fundamental in chemical reaction engineering because about 25% of all chemical reactions occur in bi-phase systems. As we have shown, the gas–liquid two-phase flow prevailing in a bubble column is extremely complex. It is dominated by a rich variety of logical configurations and exhibits inherent unsteadiness. As a consequence, the modelling of this flow is an attractive subject and constitutes an excellent subject for stochastic modelling.

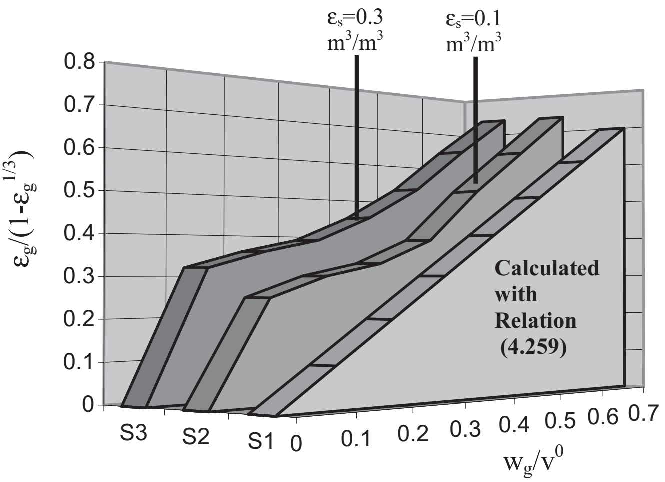


Figure 4.29 Gas hold-up versus gas velocity for a MFPB.

4.6.2
Species Movement and Transfer in a Porous Medium

Frequently we define a porous medium as a solid material that contains voids and pores. The notion of "pore" requires some observations for an accurate description and characterization. If we consider the connection between two faces of a porous body we can have opened and closed or blind pores; between these two faces we can have pores which are not interconnected or with simple or multiple connections with respect to other pores placed in their neighborhood. In terms of manufacturing a porous solid, certain pores can be obtained without special preparation of the raw materials whereas designed pores require special material synthesis and processing technology. We frequently characterize a porous structure by simplified models (Darcy's law model for example) where parameters such as volumetric pore fraction, mean pore size or distribution of pore radius are obtained experimentally. Some porous synthetic structures such as zeolites have an apparently random internal arrangement where we can easily identify one or more cavities; the connection between these cavities gives a trajectory for the flow inside the porous body (see Fig. 4.30).

The diameter or the radius of the pores is one of the most important geometric characteristic of porous solids. In terms of IUPAC nomenclature, we can have macropores (mean pore size greater than 5×10^{-8} m), mesopores (between 5×10^{-8} and 2×10^{-9} m) and micropores (less than 2×10^{-9} m). The analysis of species transport inside the porous structure is very important for the detailed description of many unit operations or applications; among them we can mention: suspension filtration, solid drying and humidification, membrane processes (dialysis, osmosis, gaseous permeation ......), flow in catalytic beds, ion exchange, adsorp-

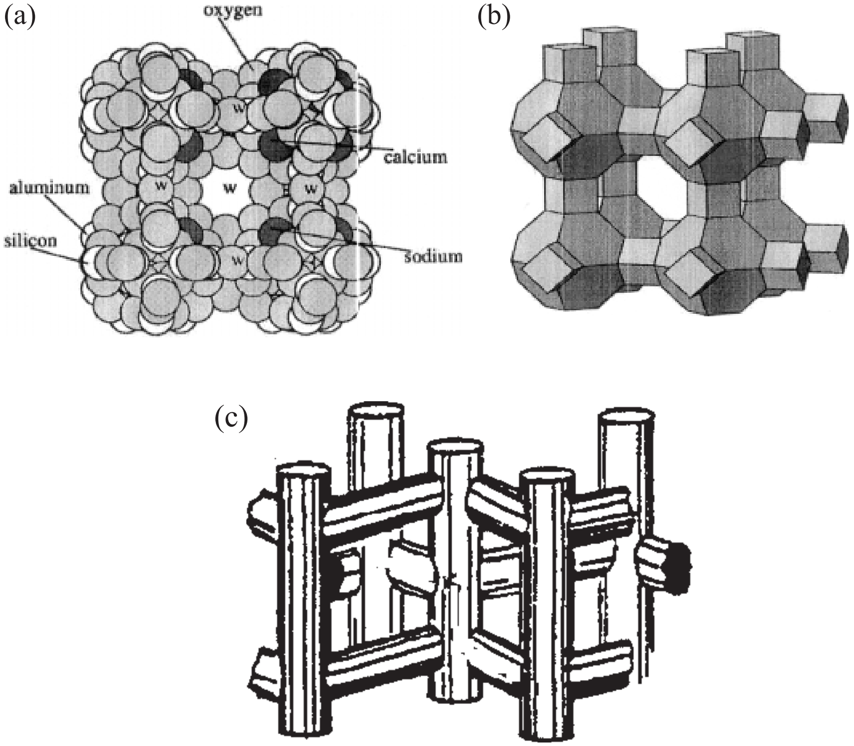


Figure 4.30 Structure of a zeolite material. (a) Internal view – atoms, (b) internal view of windows, (c) central-cavities and windows.

tion, solid–liquid extraction, the dispersion of therapeutic species inside an animal or human body, species penetration in porous soils etc.

The most used methods for the characterization of flow and species transport inside a porous body include the identification of the characteristics of the pores of the porous structure and the particularisation of classic transport equations to this case. These equations are generally associated with equations describing the solid–fluid interaction, adsorption, capillary condensation and flow due to the capillary forces etc. Concerning the species displacement (flow) problem inside a porous structure, we can consider the following classification:

- For pores with a radius between 10^{-3} and 10^{-7} m, the theory of Poiseuille flow is valid; so the mean force for fluid flow between two planes is expressed by the pressure difference; this can be a consequence of differential actions of external and capillary or/and gravitational forces.
- For pores having a mean radius between 10^{-8} and 10^{-9} m, we explain the porous body flow by the Knudsen theory; here the diffusion coefficient and, consequently, the flow, strongly depend on

the molecular weight of the species (two or more species moving inside the porous body will present different displacement velocities);

- For pores smaller than 10^{-9} m, a molecular sieving effect can be present and the movement of one or more species inside the porous solid occurs due to the molecular interactions between the species and the network of the porous body; here, for the description of species displacement, the theory of molecular dynamics is frequently used. The affinity between the network and the species is the force that controls the molecular motion; at the same time, the affinity particularities, which appear when two or more species are in motion inside the porous structure, explain the separation capacity of those solids. We can use a diffusive characterisation of species motion inside a porous solid by using the notion of conformational diffusion.

Porous solids generally have a pores size distribution and in many cases this results in a complicated transport mechanism which is a combination of the different mechanisms described above. This is also the case when the pores size are ranged near the boundaries between these different mechanisms.

All these different mechanisms of mass transport through a porous medium can be studied experimentally and theoretically through classical models (Darcy's law, Knudsen diffusion, molecular dynamics, Stefan–Maxwell equations, dusty-gas model etc.) which can be coupled or not with the interactions or even reactions between the solid structure and the fluid elements. Another method for the analysis of the species motion inside a porous structure can be based on the observation that the motion occurs as a result of two or more elementary evolutions that are randomly connected. This is the stochastic way for the analysis of species motion inside a porous body. Some examples that will be analysed here by the stochastic method are the result of the particularisations of the cases presented with the development of stochastic models in Sections 4.4 and 4.5.

4.6.2.1 **Liquid Motion Inside a Porous Medium**

The classic and stochastic methods used for the analysis of liquid flow inside a porous medium are strongly related. These interactions are given by the relationships between the parameters of both types of models. We show here that the analysis of the flow of a liquid through a porous medium, using a stochastic model, can describe some of the parameters used in deterministic models such as:

- parameters from Darcy's law;
- parameters that appear in the equation of flow continuity in a porous medium;
- parameters used by the models explaining the flow mechanism inside a porous solid.

Apparently the parameters of stochastic models are quite different from those of classic (deterministic) models where the permeability, the porosity, the pore radius, the tortuosity coefficient, the specific surface, and the coefficient of the effective diffusion of species represent the most used parameters for porous media characterization. Here, we will present the correspondence between the stochastic and deterministic parameters of a specified process, which has been modelled with a stochastic and deterministic model in some specific situations.

4.6.2.1.1 Stochastic Modelling of Dispersion of a Liquid in a Porous Body

The dispersion of a liquid that flows inside a porous medium is the macroscopic result of some individual motions of the liquid determined by the pore network of the solid structure. These motions are characterised by the local variations of the velocity magnitude and direction. Accepting the simplified structure of a porous structure shown in Fig. 4.31, the liquid movement can be described by the motion of a liquid element in a $+x$ direction (occurring with the probability p) compared to the opposite motion or $-x$ displacement (here q gives the probability of evolution and Δx represents the length portion of the pore which is not in contact with the nearby pores). Indeed, the balance of probability that shows the chances for the liquid element to be at time τ in x position can be written as follows:

The probability to have the fluid element at time τ in position x	=	The probability to have the fluid element at time $\tau - \Delta\tau$ in position $x - \Delta x$ with an evolution along $+x$ for the next $\Delta\tau$ time	+	The probability to have the fluid element at time $\tau - \Delta\tau$ in position $x + \Delta x$ with an evolution along $-x$ for the next $\Delta\tau$ time	(4.261)

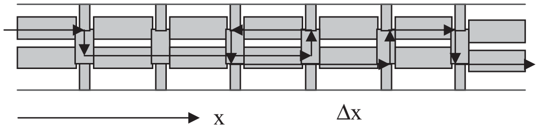


Figure 4.31 Fluid movement inside a uniform porous body.

When we express relation (4.261) mathematically we have:

$$P(x,\tau) = pP(x-\Delta x, \tau-\Delta\tau) + qP(x+\Delta x, \tau-\Delta\tau) \tag{4.262}$$

The Taylor expansions of $P(x+\Delta x, \tau-\Delta\tau)$ and $P(x-\Delta x, \tau-\Delta\tau)$ are used as their right term:

$$\frac{\Delta P(x,\tau)}{\Delta\tau} + (p-q)\frac{\Delta x}{\Delta\tau}\frac{\Delta P(x,\tau)}{\Delta x} = \frac{\Delta x^2}{2\Delta\tau}\frac{\Delta^2 P(x,\tau)}{\Delta x^2} \tag{4.263}$$

The term $(p - q)\dfrac{\Delta x}{\Delta \tau}$ has a velocity dimension ($L\,T^{-1}$) and physically represents the net velocity of the liquid moving in the flow direction (w). The ratio $\dfrac{\Delta x^2}{2\Delta \tau}$ has the dimension of a diffusion coefficient ($L^2\,T^{-1}$) and is recognized as the dispersion coefficient (D). With these observations we can rewrite relation (4.263) in order to obtain Eq. (4.264) which is the equation that characterizes the dispersive flow in one dimension (for instance see Section 3.35).

$$\frac{\partial P(x,\tau)}{\partial \tau} + w\frac{\partial P(x,\tau)}{\partial x} = D\frac{\partial^2 P(x,\tau)}{\partial x^2} \tag{4.264}$$

It is not difficult to observe that, using this simple stochastic model of liquid flow inside the porosity, we obtain that the parameters of the model, such as the net flow velocity (w) and the dispersion coefficient (D), are determined by the porous structure. This last parameter is considered here through the value of Δx (length of one pore which is not in contact with nearby pores).

In order to solve the model equation, we must complete it with the univocity conditions. In some cases, relations (3.100)–(3.107) can be used as solutions for the model particularized for the process. The equivalence between both expressions is that $c(x,\tau)/c_0$ appears here as $P(x,\tau)$. Extending the equivalence, we can establish that $P(x,\tau)$ is in fact the density of probability associated with the repartition function of the residence time of the liquid element that evolves inside a uniform porous structure.

In the scientific literature, we can find a large quantity of experimental results where the flow characterization inside a porous medium has shown that the value of the dispersion coefficient is not constant. Indeed, for the majority of porous structures the diffusion is frequently a function of the time or of the concentration of the diffusing species. As far as simple stochastic models cannot cover these situations, more complex models have been built to characterize these dependences. One of the first models that gives a response to this problem is recognized as the *model of motion with states having multiple velocities.*

With this model, the liquid element evolves inside a porous solid with random motions having the velocities $v_i, i = 1,..m$. These random skips of velocity from one state to another can be explained by random changes in pore sections and pore interconnections. This description can be completed with the consideration that here the elementary connection between the states (from one velocity or flow to another) becomes a Markov type connection: $p_{ij} = p^*_{ij} a\Delta\tau = \alpha_{ij}\Delta\tau$. We can observe that, for a randomly chosen length of time, the component of the process remains unchanged (the motion of the liquid with velocity v_i); after this length of time, the liquid element changes its velocity by skipping to another elementary state of process and again it keeps this new value (v_j) constant during this new length of time. For this stochastic description, the balance of probabilities gives relation (4.265). Here $P_i(x,\tau + \Delta\tau)$ represents the density of the probability that shows the possibility of the existence of the liquid element at time $\tau + \Delta\tau$ in the position x with the evolution $v_i, i = 1,...m$.

$$P_i(x,\tau+\Delta\tau)=\sum_{j=1}^{m}p_{ji}P_j(x-v_i\Delta\tau) \quad , \ i=1,...m \tag{4.265}$$

If we go back to Section 4.4, then we discover that the model presented herein is identical to the model presented at the beginning of Section 4.4.2. Based on the analogy principle, we can extend the treatment of this previous model (Section 4.4.3) to the model in progress. Consequently, the assembly of relations (4.265) takes the following form:

$$\frac{\partial P_i(x,\tau)}{\partial\tau}=-v_i\frac{\partial P_i(x,\tau)}{\partial x}-\left(\sum_{j=1,j\neq i}^{m}\alpha_{ij}\right)P_i(x,\tau)+\sum_{j=1,j\neq i}^{m}\alpha_{ji}P_j(x,\tau) \tag{4.266}$$

Equation (4.266) shows that the time evolution of the fraction of the fluid (or fluid elementary particles) that reaches position x with velocity v_i at time τ is determined by the following types of particles (i) particles having velocity v_i and leaving position x; (ii) particles having velocity v_i and reaching position x ; (iii) particles reaching position x and changing their velocity from v_j to v_i. For the particular case where we have two evolution states for the fluid velocity ($v_1=+v$, $v_2=-v$) the general model (4.266) is written as the set of relations (4.267). Here, the consideration of $\alpha_{12}=\alpha_{21}=\alpha$ shows that we have a case of isotropic porous solid:

$$\begin{aligned}\frac{\partial P_1(x,\tau)}{\partial\tau}&=-v\frac{\partial P_1(x,\tau)}{\partial x}-\alpha P_1(x,\tau)+\alpha P_2(x,\tau)\\ \frac{\partial P_2(x,\tau)}{\partial\tau}&=v\frac{\partial P_2(x,\tau)}{\partial x}-\alpha P_2(x,\tau)+\alpha P_1(x,\tau)\end{aligned} \tag{4.267}$$

This model is of interest because it can be easily reduced to a hyperbolic form of the transport model of one property. With some particular univocity conditions, this hyperbolic model accepts analytical solutions, which are similar to those of an equivalent parabolic model. The hyperbolic model for the transport of a property is obtained by coupling the equation $P(x,\tau)=P_1(x,\tau)+P_2(x,\tau)$ to relations (4.267) and then eliminating the terms $P_1(x,\tau)$ and $P_1(x,\tau)$. The result can be written as:

$$\frac{\partial P(x,\tau)}{\partial\tau}+\frac{1}{2\alpha}\frac{\partial^2P(x,\tau)}{\partial\tau^2}=\frac{v^2}{2\alpha}\frac{\partial^2P(x,\tau)}{\partial x^2} \tag{4.268}$$

$P(x,\tau)$ gives the probability of having the liquid element flowing inside the porous solid, in position x at time τ. By a simple analysis of the hyperbolic model for the property transport, (relation (4.268)) we can conclude that, in the case when parameter α has a high value, the term $\frac{1}{2\alpha}\frac{\partial^2P(x,\tau)}{\partial\tau^2}$ can be negligible with respect to other terms. The result is the conversion of the hyperbolic model into a parabolic model. For the transport in one dimension, this model is given by the partial differential equation:

$$\frac{\partial P(x,\tau)}{\partial\tau}=\frac{v^2}{2\alpha}\frac{\partial^2P(x,\tau)}{\partial x^2} \tag{4.269}$$

Now, we can have a special univocity case that considers the following unitary impulse as presented in the example of Section 4.2.1 as signal to the flow input inside the porous solid:

$$P(x,0_-)=\begin{cases}0 & \text{for } x\le 0\\ \hline 0 & \text{for } x\succ 0\end{cases},\ P(x,0_+)=\begin{cases}1 & \text{for } x\le 0\\ \hline 0 & \text{for } x\succ 0\end{cases} \tag{4.270}$$

The solution for the coupling of the model equation (4.269) with the above specified conditions (relations (4.270)) can be reached using the solution given by Crank [4.87] for the response given by a similar model to a unitary impulse input:

$$P(x,\tau)=\int\limits_{-\infty}^{0}P^{imp}(|x-\xi|,\tau)d\xi=-\int\limits_{\infty}^{x}P^{imp}(\eta,\tau)d\eta=\int\limits_{x}^{\infty}P^{imp}(\eta,\tau)d\eta \tag{4.271}$$

For the particularization of this last equation to our problem, we have to take into account the following observations: (i) P(x, τ) is normalized (its values are included in the interval [0, 1]); (ii) P(x, τ) is symmetric with respect to the plane x = 0. So we can write:

$$P(x,\tau)=\frac{1}{2}-\int\limits_{0}^{x}P^{imp}(\eta,\tau)d\eta\quad\text{for}\quad x>0$$

$$P(x,\tau)=\frac{1}{2}+\int\limits_{x}^{0}P^{imp}(\eta,\tau)d\eta\quad\text{for}\quad x<0 \tag{4.272}$$

The same particularization procedure is used to establish a solution for the hyperbolic model (4.268) coupled to conditions (4.270). The solutions for $P^{imp}(x,\tau)$, which correspond to the parabolic and hyperbolic models, are presented in Section 4.2.1 (for instance see relations (4.36) and (4.37)). The results for the probabilities $P(x,\tau)$ are given by the following relations:

$$\begin{aligned} x>0\ ;\quad P(x,\tau)&=\frac{1}{2}-\int\limits_{0}^{x}\sqrt{\frac{\alpha}{2v^2\tau}}\exp\left(-\frac{\alpha\eta^2}{2v^2\tau}\right)d\eta\\ &=\frac{1}{2}-\int\limits_{0}^{\frac{x}{\sqrt{2v^2\frac{\tau}{\alpha}}}}\frac{1}{\sqrt{\pi}}e^{-z^2}dz=\frac{1}{2}-\frac{1}{2}\operatorname{erf}\left(\frac{x}{\sqrt{2v^2\frac{\tau}{\alpha}}}\right)\\ x<0\ ;\quad P(x,\tau)&=\frac{1}{2}+\frac{1}{2}\operatorname{erf}\left(\frac{x}{\sqrt{2v^2\frac{\tau}{\alpha}}}\right)\end{aligned} \tag{4.273}$$

The solution for the hyperbolic model is given by Eqs. (4.274). For negative values of x (x < 0) the computation for the model solutions is developed by the same procedure given above:

$$x > 0 \;\; ; \;\; P(x,\tau) = \frac{1}{2} - \int\limits_0^x \frac{\alpha e^{-\alpha\tau}}{2v}\left[I_0\left(\alpha\tau\sqrt{1-\frac{\eta^2}{v^2\tau^2}}\right) + \frac{1}{\sqrt{1-\frac{\eta^2}{v^2\tau^2}}} I_1\left(\alpha\tau\sqrt{1-\frac{\eta^2}{v^2\tau^2}}\right)\right] d\eta$$

$$= \frac{1}{2}e^{-\alpha\tau}\left[I_0\left(\frac{\alpha}{v}\sqrt{v^2\tau^2-x^2}\right) + 2\sum_{n=1}^{\infty}\left(\frac{v\tau - x}{v\tau + x}\right)^{\frac{n}{2}} I_n\left(\frac{\alpha}{v}\sqrt{v^2\tau^2-x^2}\right)\right] \quad \text{for} \;\; 0 \prec x \prec v\tau$$

$$P(x,\tau) = 0 \;\; \text{for} \;\; x \succ v\tau \tag{4.274}$$

With the hyperbolic and parabolic models, we can describe the evolution for the existence probability $P(x,\tau)$, which is shown in Fig. 4.32. Major differences between both models can be observed at small values of time.

The hyperbolic model shows a fast evolution of the probability $P(x.\tau)$ at the spatial distance $x = y\tau$ with respect to $x = 0$ or more precisely at $x/\lceil v^2\tau/\alpha\rceil^{0.5} = 1/2\exp(-\alpha\tau)$. At moderate or large time, we cannot observe a difference between the predicted values of $P(x.\tau)$ from the models. This is due to the rapid decrease with time of the magnitude of the rapid evolution of the predicted probability $P(x.\tau)$ in the hyperbolic model. It is important to specify that the hyperbolic model keeps a fast evolving probability $P(x.\tau)$ for all possible univocity conditions at small time. It is difficult to demonstrate experimentally the prediction of the stochastic hyperbolic model for the liquid dispersion inside a porous solid because the predicted skip is very fast $P(x.\tau)$ and not easily measurable.

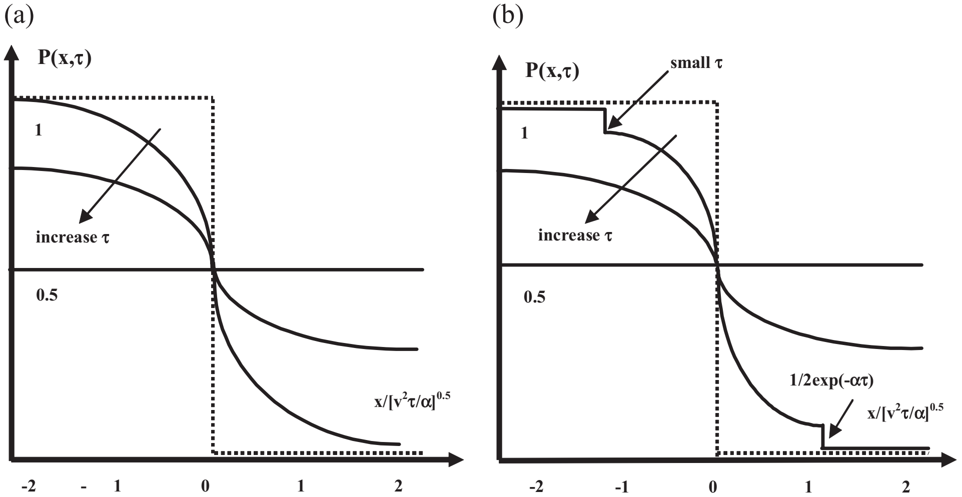


Figure 4.32 Differences between the parabolic and hyperbolic models for the calculation of the evolution of $P(x,\tau)$. (a) Parabolic model, (b) hyperbolic model.

In the characterization of porous membranes by liquid or gaseous permeation methods, the interpretation of data by the hyperbolic model can be of interest even if the parabolic model is accepted to yield excellent results for the estimation of the diffusion coefficients in most experiments. This type of model is currently applied for the time-lag method, which is mostly used to estimate the diffusion coefficients of dense polymer membranes; in this case, the porosity definition can be compared to an equivalent free volume of the polymer [4.88, 4.89].

Coming back to the stochastic analysis of the elementary particle motion inside the porous solid, we can notice that this analysis introduces a consistent explanation of the parameters participating in the coefficient of diffusion or dispersion, which is written as $D = \lim_{\Delta x \to 0, \Delta\tau \to 0} \frac{(\Delta x)^2}{2\Delta\tau} = \frac{v^2}{2\alpha}$. Indeed, it is determined by the motion velocity of the species and by the frequency of the changes of direction of the velocity. Because v and α have specific values for each individual species–porous structure couple, then the diffusion is the mechanism which allows separating out such species when they permeate through a porous membrane.

The particularization of the limit theorem of the second type to model (4.267) (for instance see also Section 4.5.1.2, relations (4.132)–(4.134)) shows that the stochastic model of the process becomes asymptotic with the parabolic model. Indeed, we can identify the expressions $Q = \begin{pmatrix} -\alpha & \alpha \\ \alpha & -\alpha \end{pmatrix}$, $\overline{V}_1 = 0$, $\overline{V}_{11} = \frac{v^2}{2\alpha}\frac{\partial^2}{\partial x^2}$ that transform model (4.267) into model (4.269). The deviation of the original stochastic model to a parabolic one is not a definitive argument to eliminate the use of the hyperbolic model for the practical interpretation of some experimental data on membrane permeation.

In porous solids made of larger elements such as fixed packed beds, where the characteristic dimension of the packing is d (for example the diameter of a packed solid), the frequency of the velocity change is $\alpha = v/d$ (after each flow through an element of the packed bed, the local fluid velocity v changes its direction). Now if we use this value of α in the dispersion coefficient, we obtain the famous relation $Pe = (vd)/D = 2$, which gives the value of the dispersion coefficient when a fluid flows through a packed bed [4.90].

This stochastic model of the flow with multiple velocity states cannot be solved with a parabolic model where the diffusion of species cannot depend on the species concentration as has been frequently reported in experimental studies. Indeed, for these more complicated situations, we need a much more complete model for which the evolution of flow inside of system accepts a dependency not only on the actual process state. So we must have a stochastic process with more complex relationships between the elementary states of the investigated process. This is the *stochastic model of motion with complete connections*. This stochastic model can be explained through the following example: we need to design some flowing liquid trajectories inside a regular porous structure as is shown in Fig. 4.33. The porous structure is initially filled with a fluid, which is non-miscible with a second fluid, itself in contact with one surface of the porous body. At the start of the process, the second fluid begins to flow inside the well-structured porosity by means of a process with the following characteristics:

- in a given time only a small portion of the liquid inside the porosity is in a moving state;
- the points where the liquid gets into and out of the porous solid are randomly distributed with time;
- we cannot exclude the possibility for the liquid element to come back to a previous position;
- the present motion of the liquid element depends on its previous state;
- at each spatial position and timing for the liquid motion, we can identify four elementary states of the motion: $k=1$ forward lead; $k=2$ backward lead; $k=3$ left lateral movement; $k=4$ right lateral movement;
- the change in liquid velocity occurs not only when the flowing liquid changes direction;
- the length of the step of the liquid movement is randomly distributed.

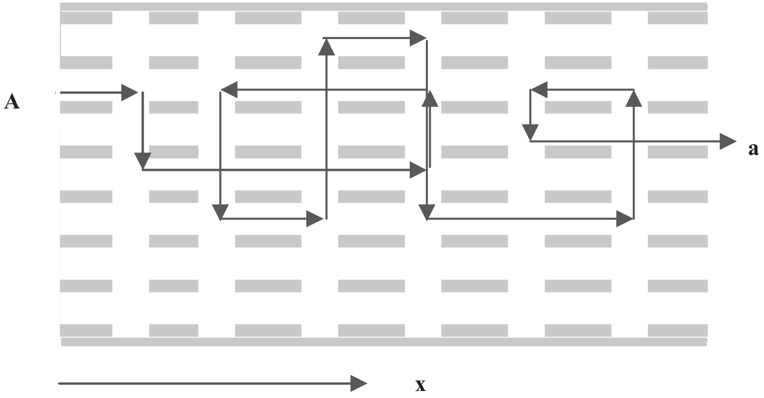


Figure 4.33 The trajectory of a liquid element flowing inside a regular porous structure.

If we combine all the aspects above with the descriptions of basic stochastic processes, then we can conclude that we have the case of a stochastic process with complete and random connections (see Section 4.4.1.1).

If a liquid element is initially in an i position moving with a k type of motion, the probability that shows its coming to a j position as a result of n motion steps is given by:

$$P_k^*(n,i,j) = \sum_{e\in K}\sum_{a\in Z} p_{ke}(i)p_k(a)P_k^*(n-1,i+a,j) \quad (4.275)$$

In relation (4.275), we recognize $p_{ke}(i)$, which represents the transition probability from a type k motion into a type e motion at position i. By $p_k(a)$, we express the distribution of the length of steps related with type k motion.

For this case, the random system with complete connections $[(A,\mathbf{A}),(B,\mathbf{B}),u,P]$ presents the following particularisations: $A = B = ZxK$, $u(S_n,E_{n+1}) = u((i,k),(a,e)) = (i+a,e)$ and $P(S_n...E_1,S_1, S_0) = P((i,k);(a,e)) = p_e(a)p_{ke}(i)$.

The probability of the type k motion for the liquid element which gets to the j position, in a period of time given by the n evolution steps, is given by:

$$P_k(n,j) = \sum_{e\in K}\sum_{a\in Z} p_{ek}(j-a)p_k(a)P_k(n-1,j-a) \tag{4.276}$$

For a practical computation, these two last equations need: (i) one procedure that gives the transition probabilities from e to k state at each $j-a$ position $(p_{ek}(j-a))$; (ii) some practical relations that express, for $k = 1$, $k = 2$, etc., the distributions of the step lengths $(p_k(a))$. It is not difficult to establish that the transition probabilities $p_{ek}(j-a)$ depend strongly on the totality of the previous trajectory. As a consequence, the fluid flowing trajectory is continuously updated step by step.

4.6.2.1.2 Stochastic Models for Deep Bed Filtration

Deep bed filtration is used to clarify suspensions with a small content of solids. This process, which is usually applied for water treatment, is based on the flowing of a fluid through a deep bed of granular solids such as sand. During the flowing inside the granular bed, interaction forces between one particle from the suspension and one particle from the granular bed occur. This interaction allows the particle from the suspension to latch onto the particle of the bed. This elementary process occurs in many points placed through all the granular bed. The quantity of the solid retained in one element of the system cannot exceed the quantity held-up by the open spaces of the granular bed. When this retained quantity approaches the quantity determined by the bed porosity we can assert that the bed is clogged. After clogging, we can regenerate the granular bed by a counter current liquid fluidization but, depending on the type of bed filtration, other regeneration processes can be used. For this filtration case, the quantity of particles retained by the bed increases with time and, consequently, the filtrate flow rate decreases if we do not increase the filtration pressure difference.

In addition to the traditional deep bed filtration, other interesting examples of different processes and techniques can be described by the same basic principle: (i) the tangential micro-filtration and ultra-filtration where a slow deep filtration produces the clogging of the membrane surface; (ii) some processes of impregnation of porous supports with a sol in order to form a gel which, after precipitation, will form a membrane layer. Here the sol penetration inside the support is fundamental for the membrane quality.

The modelling of the deep bed filtration based on the description of the trajectory of a suspension particle and on the deposition on a bed of solid has been extensively published. However, until now, the majority of the results generated by these models were not satisfactory, because the models generally consider simplifications with respect to the action of the forces that cause the deep bed filtration. While reviewing the forces occurring in the deep bed filtration, the complexity of this operation can easily be noticed. Figure 4.34, which aims to indirectly present those forces, shows the movement of one particle of the suspension around one particle of the granular bed. Among the most important forces considered in deep bed filtration we have:

- The inertial force, that expresses the tendency of the microparticle to keep moving when it is under the influence of the hydrodynamic trajectory imposed by the flow around one element of the fixed bed. The action of this force is given by the number $\mathrm{In} = (\rho_p d^2 w_f)/(18\eta d_s)$; here d is the microparticle diameter, $d_s = D/2$ represents the diameter of the element of the granular bed, ρ_p gives the density of the microparticle which is expected to deposit, η is the viscosity of the flowing liquid and w_f measures the real local liquid velocity.
- The gravitational force characterizing the settling capacity of the microparticle from the suspension flowing inside the porosity. This is given by the Stokes number, $\mathrm{St} = [g(\rho_p - \rho)d^2]/(18\eta w_f)$, which is a ratio between the Stokes settling velocity and the local velocity for the flowing suspension.
- The diffusion force, giving the local action of the Brownian motion on the deposition of the microparticle. A modified Peclet

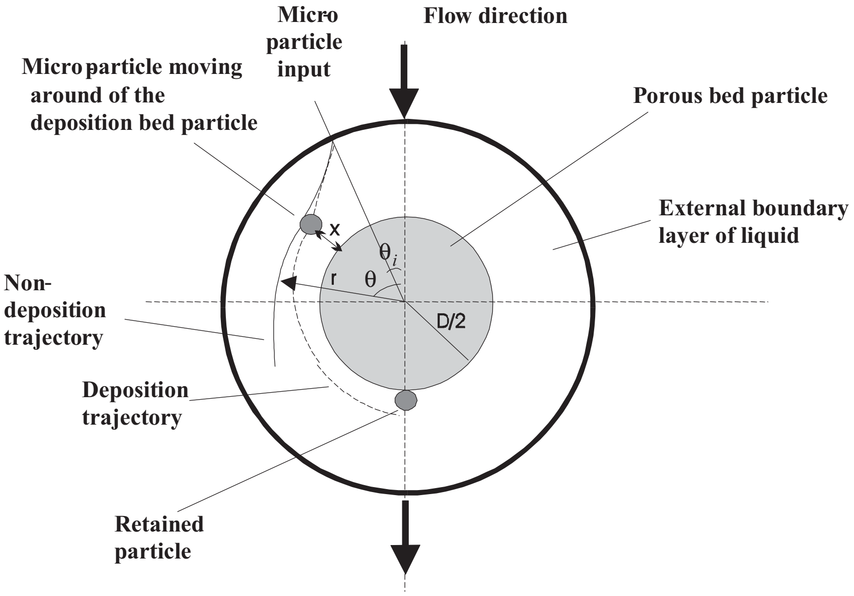


Figure 4.34 Scheme of the microparticle retention by one particle of a fixed bed.

number, $Pe = (3\pi\eta d d_s w_f)/(kT)$, is then considered. It is the ratio between the Stokes and Brownian forces, which together influence the microparticle movement;

- the laminar flow force characterizing the action of the flowing liquid on the microparticle; when the flowing field around the element of the porous structure is not uniform, an undesired rotation movement will be induced for the microparticle. The effect of the laminar flow force can be considered by means of the Reynolds number ($Re = (w_f d_s \rho)/\eta$).

The common action of these four forces results in the global mechanism that produces the approach of microparticles to deposition elements of the porous solid. At distances shorter than 1 μm, other forces come into play and produce the fixation of microparticles onto elements of the porous structure. Among these forces we have:

- The electrostatic force that appears when microparticles and the deposition element of the bed have electric charges; when the electric charges of both entities have identical signs, we have a repulsive force, the value of which is predicted by relation (4.277). The suspensions including ionized substances contain an excellent source of charged microparticles.

$$F_R^{(x)} = \frac{\exp\left[-kd\left(\frac{2x}{d} - 2\right)\right]}{1 + \exp\left[-kd\left(\frac{2x}{d} - 2\right)\right]} \tag{4.277}$$

- The Van der Waals force that is caused by the molecular vibrations of the material composing microparticles and deposition elements. This is an attraction force that strongly depends on the interparticles distance and on the wavelength ($\bar{\lambda}$) that characterizes the assembly microparticle–deposition element. Relation (4.278) gives a qualitative indication of the value of this force. In this relation, $F(u)$ gives a function which decreases rapidly with the distance (x).

$$F_{vw}^{(x)} = \frac{1}{\left(\frac{2x}{d} - 2\right)^2} F\left(\frac{\frac{2x}{d} - 2}{\bar{\lambda}}\right) \tag{4.278}$$

- The hydrodynamic adhesion force that expresses the resistance occurring when microparticles latch onto deposition elements. It is caused by the liquid that must be extracted out of the space between two particles when both microparticles adhere. This force allows the slowing down of microparticles adhesion and offers a possibility for drowning it in the flowing suspension.
- The detachment force that realizes the detachment of the assembly microparticle–deposition element; when the number of the

retained microparticles on one deposition element is important, this force is very active. This force is not a short distance action force.

As far as these forces, which present various origins and specificities, determine an assembly of very complex interactions between the suspension of microparticles and the deposition elements of the porous solid it is impossible to build a completely phenomenological model for deep bed filtration. Nevertheless, various empirical models have been developed by simplifying the assumptions concerning the description of interactions. Among these models, we have the famous filtration coefficient model or the Mint model [4.81]. This filtration coefficient noted as $\lambda(\lambda_0, c_{ss})$ depends on its initial value (λ_0) and on the local concentration of the retained solid around the bed deposition elements (c_{ss}). It is defined as the fraction of the solid retained from the suspension in an elementary length of the granular bed:

$$\lambda(\lambda_0, c_{ss}) = -\frac{dc_{vs}}{c_{vs}} \frac{1}{dx} \tag{4.279}$$

In Fig. 4.35, the mass balance of solid in an elementary volume is given when the suspension flow is considered as a plug flow. This figure allows the establishment of relationships between the local concentration of the solid in suspension and the retained solid in the bed.

The mass balance of the retained solid is described by Eq. (4.280). The Mint deterministic model results from the coupling of this relation with the definition of the filtration coefficient. The result is written in Eq. (4.281) for the start time of the filtration and in Eq. (4.282) for the remaining filtration time. Here α is the detachment coefficient of the retained particle; its dimension is T^{-1}.

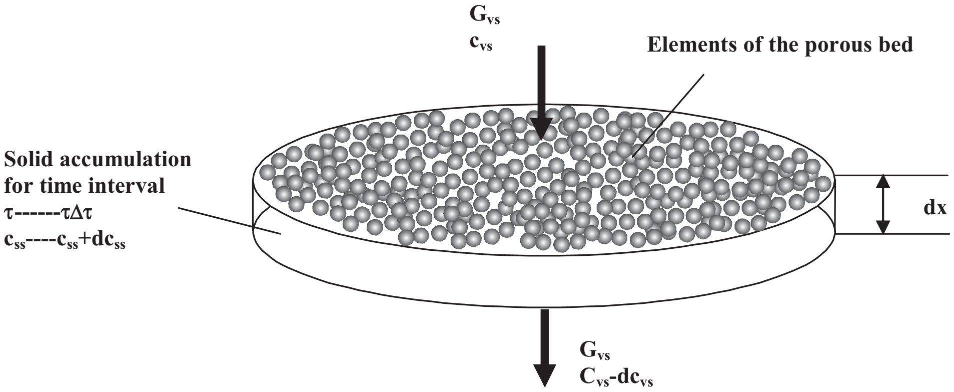


Figure 4.35 Scheme for the mass balance of the retained solid in deep bed filtration.

$$-\frac{dc_{vs}}{dx}=\frac{A}{G_{vs}}\frac{\partial c_{ss}}{\partial \tau}=\frac{1}{w_f}\frac{\partial c_{ss}}{\partial \tau} \tag{4.280}$$

$$\frac{\partial c_{ss}}{\partial \tau}=w_f\lambda_0 c_{vs} \quad ; \quad \tau=0 \tag{4.281}$$

$$\frac{\partial c_{ss}}{\partial \tau}=w_f\lambda_0 c_{vs}-\alpha c_{ss} \quad ; \quad \tau \succ 0 \tag{4.282}$$

Relation (4.283), obtained by coupling Eq. (4.282) and (4.280), presents the time derivation results in (4.284). Replacing the term $\partial c_{ss}/\partial \tau$ in (4.284) by (4.280) results in the famous Mint model equation (4.285). Relations (4.286) and (4.287) are the most commonly used univocity conditions of this model: (i) before starting filtration, the bed does not contain any retained solid; (ii) during filtration, the bed is fed with a constant flow rate of suspension, which has a constant concentration of solid.

$$\frac{\partial c_{vs}}{\partial x}=\lambda_0 c_{vs}-\frac{\alpha}{w_f}c_{ss} \tag{4.283}$$

$$\frac{\partial^2 c_{vs}}{\partial x\partial \tau}=\lambda_0\frac{\partial c_{vs}}{\partial \tau}-\frac{\alpha}{w_f}\frac{\partial c_{ss}}{\partial \tau}=0 \tag{4.284}$$

$$\frac{\partial^2 c_{vs}}{\partial x\partial \tau}+\lambda_0\frac{\partial c_{vs}}{\partial \tau}+\alpha\frac{\partial c_{vs}}{\partial x}=0 \tag{4.285}$$

$$\tau=0 \qquad x\geq 0 \qquad c_{vs}=0 \tag{4.286}$$

$$\tau\geq 0 \qquad x=0 \qquad c_{vs}=c_{v0} \tag{4.287}$$

Relations (4.288)–(4.290) give one solution for the Mint model. It is not difficult to verify that this solution cannot cover the requirement of relation (4.281). The given solution is a series with a rapid convergence due to the strong evolution of the chain T_n. A good result will consequently be obtained by limiting the sum of Eq. (4.288) to four or five terms:

$$\frac{c_{vs}}{c_{v0}}=\sum_{n=1}^{\infty}\exp(-\lambda_0 x)\frac{(\lambda_0 x)^{n-1}}{(n-1)!}T_n\exp(-\alpha\tau) \tag{4.288}$$

$$T_n=T_{n-1}-\frac{(\alpha\tau)^{n-2}}{(n-2)!} \tag{4.289}$$

$$T_1=\exp(\alpha\tau) \tag{4.290}$$

A second solution to this model is given by Eq. (4.291), which is an assembly of i-order Bessel functions with real argument $I_i((\lambda_0 x\alpha\tau)^{1/2})$:

$$\frac{c_{vs}}{c_{v0}} = \exp(-(\lambda_0 x + \alpha\tau)) \sum_{i=1}^{\infty} \left(\frac{\alpha\tau}{\lambda_0 x}\right)^{i/2} I_i\left[(\lambda_0 x\alpha\tau)^{1/2}\right] \tag{4.291}$$

In the Mint model, we have to take into account the following considerations: (i) the initial filtration coefficient λ_0, which is a parameter, presents a constant value after time and position; (ii) the detachment coefficient, which is another constant parameter; (iii) the quantity of the suspension treated by deep filtration depends on the quantity of the deposited solid in the bed; this dependency is the result of the definition of the filtration coefficient; (iv) the start of the deep bed filtration is not accompanied by an increase in the filtration efficiency. These considerations stress the inconsistencies of the Mint model: 1. valid especially when the saturation with retained microparticles of the fixed bed is slow; 2. unfeasible to explain the situations where the detachment depends on the retained solid concentration and /or on the flowing velocity; 3. unfeasible when the velocity of the mobile phase inside the filtration bed, varies with time; this occurrence is due to the solid deposition in the bed or to an increasing pressure when the filtration occurs with constant flow rate. Here below we come back to the development of the stochastic model for the deep filtration process.

A *stochastic model of deep bed filtration* [4.5] identifies two elementary processes for the evolution of the micro-particle in the filtration bed:

1. A type I process that considers the motion of microparticles occurring with a velocity $v_1 = v$; this velocity is induced by the surrounding flowing fluid (physically this type of process corresponds to the non-deposition of the microparticle);
2. A type II process that shows the possibility for the microparticle to deposit; from the viewpoint of the motion, the velocity of this process is $v_2 = 0$.

The stochastic model accepts a Markov type connection between both elementary states. So, with $\alpha_{12}\Delta\tau$, we define the transition probability from type I to type II, whereas the transition probability from type II to a type I is $\alpha_{21}\Delta\tau$. By $P_1(x,\tau)$ and $P_2(x,\tau)$ we note the probability of locating the microparticle at position x and time τ with a type I or respectively a type II evolution. With these introductions and notations, the general stochastic model (4.71) gives the particularization written here by the following differential equation system:

$$\begin{cases} \dfrac{\partial P_1(x,\tau)}{\partial\tau} = -v\dfrac{\partial P_1(x,\tau)}{\partial x} - \alpha_{12}P_1(x,\tau) + \alpha_{21}P_2(x,\tau) \\ \dfrac{\partial P_2(x,\tau)}{\partial\tau} = -\alpha_{21}P_2(x,\tau) + \alpha_{12}P_1(x,\tau) \end{cases} \tag{4.292}$$

For the transformation of the stochastic model into a form, such as the Mint model, that allows the computation of $c_{vs}(x,\tau)/c_{v0}$, we consider that this ratio gives a measure of the probability to locate the microparticle in the specified position: $P(x,\tau) = P_1(x,\tau) + P_2(x,\tau)$. We can simplify our equations by eliminating probabilities $P_1(x,\tau)$ and $P_2(x,\tau)$ with the use of this last definition and the relations of system (4.292). The result is the following interesting partial differential equation:

$$\frac{\partial^2 P(x,\tau)}{\partial \tau^2} + v\frac{\partial^2 P(x,\tau)}{\partial x \partial \tau} + v\alpha_{21}\frac{\partial P(x,\tau)}{\partial x} + (\alpha_{21}+\alpha_{12})\frac{\partial P(x,\tau)}{\partial \tau} = 0 \tag{4.293}$$

By considering the combined variable $z = x - v\tau/2$, we remove the mixed partial differential term from Eq. (4.293). The transformation obtained is the hyperbolic partial differential equation (4.294). This equation represents a new form of the stochastic model of the deep bed filtration and has the characteristic univocity conditions given by relations (4.295) and (4.296). The univocity conditions show that the suspension is only fed at times higher than zero. Indeed, here, we have a constant probability for the input of the microparticles:

$$\begin{aligned}&\frac{\partial^2 P(z+v\tau/2,\tau)}{\partial \tau^2} - \frac{v^2}{4}\frac{\partial^2 P(z+v\tau/2,\tau)}{\partial z^2} + \frac{v}{2}(\alpha_{21}-\alpha_{12})\frac{\partial P(z+v\tau/2,\tau)}{\partial z} + \\ &(\alpha_{21}+\alpha_{12})\frac{\partial P(z+v\tau/2,\tau)}{\partial \tau} = 0\end{aligned} \tag{4.294}$$

$$\tau = 0 \quad , \quad x > 0 \quad , \quad z = x \quad P(z,\tau) = 0 \tag{4.295}$$

$$\tau > 0 \quad , \quad x = 0 \quad , \quad z > 0 \quad P(z,\tau) = P_0 \tag{4.296}$$

In this stochastic model, the values of the frequencies skipping from one state to another characterize the common deep bed filtration. This observation allows the transformation of the above-presented hyperbolic model into the parabolic model, given by the partial differential equation (4.297). With the univocity conditions (4.295) and (4.296) this model [4.5] agrees with the analytical solution described by relations (4.298) and (4.299):

$$\frac{v^2}{4(\alpha_{21}+\alpha_{12})}\frac{\partial^2 P\left(z+\frac{v\tau}{2},\tau\right)}{\partial z^2} = \frac{v}{2}\left(\frac{\alpha_{21}-\alpha_{12}}{\alpha_{21}+\alpha_{12}}\right)\frac{\partial P\left(z+\frac{v\tau}{2},\tau\right)}{\partial z} + \frac{\partial P\left(z+\frac{v\tau}{2},\tau\right)}{\partial \tau} = 0 \tag{4.297}$$

$$x - \frac{v\alpha_{12}}{\alpha_{21}+\alpha_{12}} < 0 \quad , \quad \frac{P(x,\tau)}{P_0} = \frac{1}{2}\left\{1 + \operatorname{erf}\left[\frac{x - \frac{v\alpha_{12}}{\alpha_{21}+\alpha_{12}}\tau}{\sqrt{\frac{v^2}{\alpha_{21}+\alpha_{12}}}}\right]\right\} \tag{4.298}$$

$$x - \frac{v\alpha_{12}}{\alpha_{21}+\alpha_{12}} > 0 \quad , \quad \frac{P(x,\tau)}{P_0} = \frac{1}{2}\left\{1 - \operatorname{erf}\left[\frac{x - \frac{v\alpha_{12}}{\alpha_{21}+\alpha_{12}}\tau}{\sqrt{\frac{v^2}{\alpha_{21}+\alpha_{12}}}}\right]\right\} \tag{4.299}$$

It is well known that only experimental investigation can validate or invalidate a model of a process. For the validation of the model developed above, we use the experimental data of the filtration of a dilute $Fe(OH)_3$ suspension (the concentration is lower than 0.1 g $Fe(OH)_3$ /l) in a sand bed with various heights and particle diameters. The experiments report the measurements at constant filtrate flow rate and give the evolution with time of the concentration of $Fe(OH)_3$ at the bed output when we use a constant solid concentration at the feed. Figure 4.36 shows the form of the time response when deep bed filtration occurs. The concentration of the solid at the exit of the bed is measured by the relative turbidity (exit turbidity/input turbidity*100). The small skips around the mean dependence, which appear when the clogging bed becomes important, characterize the duality between the retention and dislocation of the bed-retained solid. This dislocation shows that the Mint model consideration with respect to the detachment coefficient is not acceptable, especially when the concentration of the bed-retained solid is high.

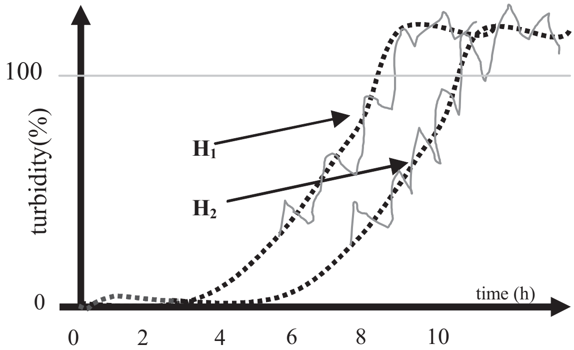


Figure 4.36 Response curves for the deep bed filtration of a suspension of $Fe(OH)_3$ in water.

The data from Fig. 4.36, that show the evolution of $c_{vs}(H, \tau)/c_{vo}$ versus time, have been used to identify the model parameters α_{12} and α_{21}. Here, H is the height of the fine sand granular bed used as porous filter. We have also selected the following process factors: the porous bed height (H), the mean diameter of the particles in the sand granular bed (d_g), the filtrate flow rate (G_v), the content of $Fe(OH)_3$ in the water (noted here as C_0 and c_{v0} in the model) and the fluid temperature as an indirect consideration of the liquid viscosity (t). Table 4.7 shows the results of these computations.

We can immediately observe that the assumption of the height values for the parameters α_{12} and α_{21} is excellently covered by the experimental starting data. Secondly, we find that all the process factors influence all the values of the parameters of the stochastic model.

Table 4.7 Influence of the factors of the process on the parameters of the stochastic model.

Deep bed filtration factor	Factor value	Stochastic model parameters	
		α_{12}	α_{21}
H [cm]			
t = 20 °C	2	1.14	326
G_v = 20 cc/min	3	0.592	458.9
d_g = 0.5–0.3 mm	5	0.262	420.22
C_0 = 6.75 mg/l	6	17.66	9611.41
t [°C]			
H = 6 cm	20	17.95	9805.1
G_v = 20 cc/min	30	2.6	2748.14
d_g = 0.5–0.31 mm	35	22.71	1347.5
C_0 = 6.75 mg/l	40	4.337	3028
G_v [cm^3/min]			
H = 6 cm	20	3.054	3020.66
t = 30 °C	30	13.34	6698.96
d_g = 0.5–0.31 mm	40	62.08	22605.24
C_0 = 6.75 mg/l	50	118.2	42908.68
C_0[mg/l] Fe(OH)$_3$			
H = 6 cm			
t = 30 °C	6.75	111.7	40493
d_g = 0.5–0.31 mm	13.49	82.7	28999.5
G_v = 50 cm^3/min	26.98	34.18	10294.41
d_g [mm]			
H = 6 cm	0.31–0.2	754.98	355456.89
C_0 = 6.75 mg/lFe(OH)$_3$	0.5–031	110.65	39773
T_f = 30 °C	0.63–0.5	22.409	8795.98
G_v = 50 cm^3/min	0.85–0.63	23.82	6449.82

Using a regression analysis, the following dependences have been obtained:

$$\alpha_{12} = 67.75 + 3.003\mathrm{Gv} - 2.872\mathrm{C}_0 - 256.28\mathrm{dg}$$

$$\alpha_{21} = 3.081 \cdot 10^4 + 1111\mathrm{Gv} - 1268\mathrm{C}_0 - 1.023 \cdot 10^5\mathrm{dg}$$

It is important to notice that these relations show the independence of the parameters of the stochastic model with respect to the height of the porous bed. With the identified values of α_{12} and α_{21}, we can now simulate the deep bed filtration process by computing Eqs. (4.298) and (4.299), which show how the dimensionless $c_{vs}(H,\tau)/c_{vo} = P(H,\tau)/P(0,\tau)$ evolve with time.

Figure 4.37 gives the combination of the simulation results obtained with the model and with an assembly of experimental data. We have to notice that the values of the factors for the relations that give the transition frequencies must respect the dimensional units from Table 4.7. These relations make it possible to formulate the optimisation of the filtration problem and then to establish the combination of factors allowing deep bed filtration at minimum financial cost.

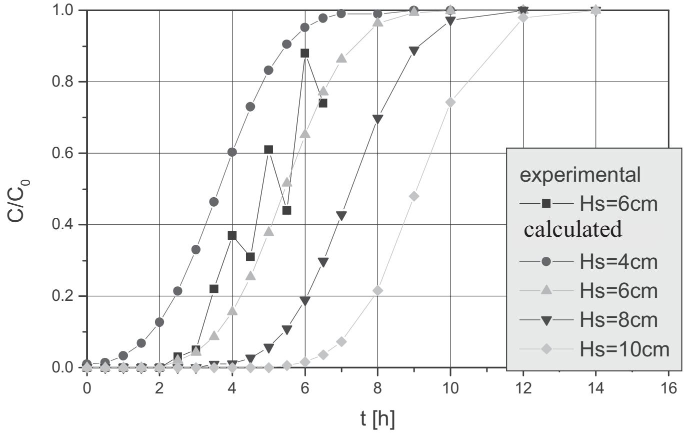


Figure 4.37 Simulated and experimental time dependence of the dimensionless solid concentration in the suspension at the bed output. (G_v = 50 cm^3/min, C_0 = 6.75 mg Fe(OH)$_3$/l, T = 30 °C, d_g = 0.4 mm.)

If we want to make a more complete stochastic model, it is recommended to consider a process with three elementary states which are: the microparticles motion in the direction of the global flow, the microparticles fixation by the collector elements of the porous structure and the washing of the fixed microparticles. In this case, we obtain a model with six parameters: α_{12}, α_{13}, α_{21}, α_{23}, α_{31}, α_{32}. This is a rather complicated computation.

The discussed stochastic model presents the capacity to be converted into a steady state model; in addition, an interesting asymptotic transformation can also be carried out. For the conversion of the model into a steady state one, we consider a time interval $\Delta\tau$, where the probabilities for the system to change by means of a type 1 or type 2 evolution process are given by $\alpha_1\Delta\tau$ and $\alpha_2\Delta\tau$ respectively and the transition probabilities of the process are described by $p_{12} = \alpha_{12}\Delta\tau$ and $p_{21} = \alpha_{21}\Delta\tau$. Indeed, the model (4.292) will be expressed as follows:

$$\begin{cases} \dfrac{\partial P_1(x,\tau)}{\partial \tau} = -v\dfrac{\partial P_1(x,\tau)}{\partial x} - \alpha_1 P_1(x,\tau) + \alpha_{21} P_2(x,\tau) \\ \dfrac{\partial P_2(x,\tau)}{\partial \tau} = -\alpha_2 P_2(x,\tau) + \alpha_{12} P_1 \leq (x,\tau) \end{cases} \tag{4.300}$$

With $P_1(x,\tau) + P_2(x,\tau) = P(x,\tau)$, we obtain relation (4.301) and its corresponding steady state (4.302):

$$\begin{gathered} \frac{\partial^2 P(x,\tau)}{\partial \tau^2} + v\frac{\partial^2 P(x,\tau)}{\partial x \partial \tau} + v\alpha_2 \frac{\partial P(x,\tau)}{\partial x} + (\alpha_2 + \alpha_1)\frac{\partial P(x,\tau)}{\partial \tau} + \\ (\alpha_1\alpha_2 - \alpha_{12}\alpha_{21})P(x,\tau) = 0 \end{gathered} \tag{4.301}$$

$$v\alpha_2 \frac{dP(x)}{dx} + (\alpha_1\alpha_2 - \alpha_{12}\alpha_{21})P(x) = 0 \tag{4.302}$$

When the particularization condition $x = 0, P(x) = P_0 = 1$ is used for the differential equation (4.302), its solution respects relation (4.303). The correspondence with concentrations $c_{vs}(x)$ and c_{v0} is presented by means of relation (4.304).

$$P(x) = P_0 \exp\left(-\frac{\alpha_1\alpha_2 - \alpha_{12}\alpha_{21}}{v\alpha_2}\right) = P_0 \exp\left(-\frac{\alpha x}{v}\right) = \exp\left(-\frac{\alpha x}{v}\right) \tag{4.303}$$

$$c_{vs}(x) = c_{v0} \exp\left(-\frac{\alpha x}{v}\right) \tag{4.304}$$

It is important to notice the didactic importance of this last relation, because the deep bed filtration process cannot operate at steady state.

The asymptotic transformation of the discussed stochastic model (see relation 4.292 and Section 4.5.1.2) is carried out with the identification of the operators:

$$V_1(1) = -v\partial/\partial x \quad , \quad V_1(2) = 0 \quad , \quad Q = \begin{pmatrix} -\alpha_{12} & \alpha_{12} \\ \alpha_{21} & -\alpha_{21} \end{pmatrix} \quad , \quad \overline{V}_1 = -\frac{v\alpha_{21}}{\alpha_{12} + \alpha_{21}} \frac{\partial}{\partial x}.$$

The resulting asymptotic model is described by the following equation and the univocity conditions given by relations (4.295) and (4.296):

$$\frac{\partial P(x,\tau)}{\partial \tau} + \frac{v\alpha_{21}}{\alpha_{12} + \alpha_{21}} \frac{\partial P(x,\tau)}{\partial x} = 0 \tag{4.305}$$

We can observe that the asymptotic model of the deep bed filtration has no term concerning the dispersion of the flowing fluid. At the same time, it is important to emphasize the fact that this model, considered as its deterministic equivalent, is frequently used for the characterization of fluids seeping into the soil.

4.6.2.2 Molecular Species Transfer in a Porous Solid

When a fluid flows through a porous solid or a porous bed, the species forming the fluid can present some affinities with the solid particles. The affinity of species with respect to the contacting solid, which here form what is called a stationary phase, can be the result of different phenomena such as adsorption, ion exchange, steric exclusion and absorption.

The separation of species by affinity is the principle of chromatographic processes, as shown schematically in Fig. 4.38. At time $\tau = 0$, we introduce a small quantity of A and B species mixture (probe injection) at the column input in a carrier fluid flowing inside a fine granular bed of porous medium. The motion of species A and B caused by the flowing carrier creates the conditions necessary for their separation. If species A and B present a sorption phenomenon on the granular solid, the separation will take place as a consequence of a specific adsorption–desorption process repeated along the porous bed. On the contrary, the carrier must be inert with respect to the interactions with the granular bed. Figure 4.38 shows that the separation of A and B is not complete at all the local points placed in the first part of the length of the granular bed. So, it is important to emphasize that complete separation of A and B is attained only if the combination of the bed

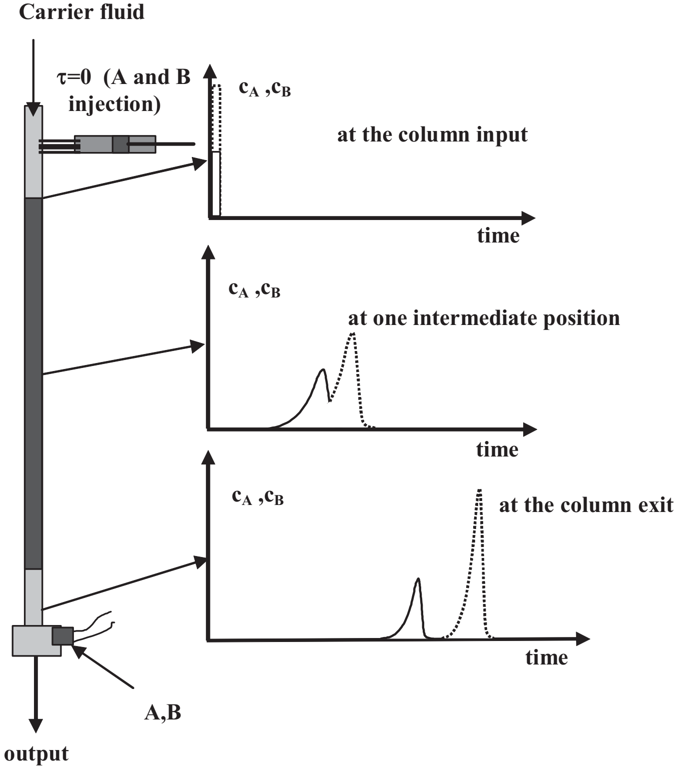


Figure 4.38 The principle of separation by chromatography.

length and the carrier velocity results in a good residence time. This residence time must comply with the time needed for the separation of A and B, which depends on the individual adsorption–adsorption process.

If we introduce a discrete feed of A and B, characterized by a reasonable interval of time between two inputs, and a discrete collection of A-carrier and B-carrier outputs into Fig. 4.38, then we will have a chromatographic separator.

When the carrier is a liquid, the instrumentation includes a pump, an injector, a column, a detector and a recorder or a data acquisition system, connected to a computer. The heart of the system is the column where the separation occurs. Since the stationary phase is composed of micrometric porous particles, a high-pressure pump is required to move the mobile phase through the column. The chromatographic process begins by injecting the solute into the top of the column by an impulse type injection. The separation of the components occurs during the elution of the mobile phase through the column.

The majority of chromatographic separations as well as the theory assume that each component elutes out of the column as a narrow band or a Gaussian peak. Using the position of the maximum of the peak as a measure of retention time, the peak shape conforms closely to the equation: $C = C_{max} \exp[-(t - t_R)^2 / 2\sigma^2]$. The modelling of this process, by traditional descriptive models, has been extensively reported in the literature.

As has been explained previously in this chapter, the building of a stochastic model starts with the identification of the individual states of the process.

For a chromatographic separation, each i species has three individual elementary evolutions (here we consider i = 2,…N because i = 1 corresponds to the carrier which is not retained by the granular bed):

1. motion with velocity +v in the sense of carrier flow (type 1 process);
2. adsorption on the solid (a type 2 process; the fixation on the solid stops the species motion);
3. motion with velocity −v.

If we consider that the connecting process is Markovian, then we can write the balance of the probabilities for $P_1^{(j)}(x,\tau)$, $P_2^{(j)}(x,\tau)$ and $P_3^{(j)}(x,\tau)$. Here $\alpha_i^{(j)}\Delta\tau$ gives the probabilities for j species to change their i evolution state. Through $\alpha_{ik}^{(j)}\Delta\tau$ (i = 1, 3; k = 1, 3) we consider the transition probabilities of species j between states i and k. With the statements above, we can write the following balance relations:

$$\begin{aligned} P_1^{(j)}(x,\tau) = {} & (1-\alpha_1^{(j)}\Delta\tau)P_1^{(j)}(x-\Delta x,\tau-\Delta\tau) + \alpha_{21}^{(j)}\Delta\tau P_2^{(j)}(x,\tau-\Delta\tau) + \\ & \alpha_{31}^{(j)}\Delta\tau P_3^{(j)}(x+\Delta x,\tau-\Delta\tau) \end{aligned} \tag{4.306}$$

$$\begin{aligned} P_2^{(j)}(x,\tau) = {} & (1-\alpha_1^{(j)}\Delta\tau)P_2^{(j)}(x,\tau-\Delta\tau) + \alpha_{12}^{(j)}\Delta\tau P_1^{(j)}(x,\tau-\Delta\tau) + \\ & \alpha_{32}^{(j)}\Delta\tau P_3^{(j)}(x,\tau-\Delta\tau) \end{aligned} \tag{4.307}$$

$$P_3^{(j)}(x,\tau) = (1-\alpha_3^{(j)}\Delta\tau)P_3^{(j)}(x+\Delta x,\tau-\Delta\tau) + \alpha_{13}^{(j)}\Delta\tau P_1^{(j)}(x+\Delta x,\tau-\Delta\tau) + \alpha_{23}^{(j)}\Delta\tau P_2^{(j)}(x,\tau-\Delta\tau) \tag{4.308}$$

Using the Taylor expansion of the probabilities $P_i^{(j)}(x \pm \Delta x, \tau - \Delta\tau)$ at Δx and $\Delta\tau \to 0$ for processing these balances, the results on the stochastic differential model are given by the relations of the assembly (4.309)

$$\begin{cases} \dfrac{\partial P_1^{(j)}(x,\tau)}{\partial\tau} = -v\dfrac{\partial P_1^{(j)}}{\partial x} - \alpha_1^{(j)}P_1^{(j)} + \alpha_{21}^{(j)}P_2^{(j)}(x,\tau) + \alpha_{31}^{(j)}P_3^{(J)} \\ \dfrac{\partial P_2^{(j)}(x,\tau)}{\partial\tau} = -\alpha_2^{(j)}P_2^{(j)} + \alpha_{12}^{(j)}P_1^{(j)}(x,\tau) + \alpha_{32}^{(j)}P_3^{(J)} \\ \dfrac{\partial P_3^{(j)}(x,\tau)}{\partial\tau} = v\dfrac{\partial P_1^{(j)}}{\partial x} - \alpha_3^{(j)}P_3^{(j)} + \alpha_{13}^{(j)}P_1^{(j)}(x,\tau) + \alpha_{23}^{(j)}P_2^{(J)} \end{cases} \tag{4.309}$$

Since these equations do not have an acceptable form for the description of the chromatographic separation, we have used them to build up the Lapidus model [4.92] by considering only one positive motion for the carrier fluid. Indeed, we will introduce $P_3^{(j)}(x,\tau) = 0$ into the general model. The result is given by the assembly of equations (4.310):

$$\begin{cases} \dfrac{\partial P_1^{(j)}(x,\tau)}{\partial\tau} = -v\dfrac{\partial P_1^{(j)}}{\partial x} - \alpha_1^{(j)}P_1^{(j)} + \alpha_{21}^{(j)}P_2^{(j)}(x,\tau) \\ \dfrac{\partial P_2^{(j)}(x,\tau)}{\partial\tau} = -\alpha_2^{(j)}P_2^{(j)} + \alpha_{12}^{(j)}P_1^{(j)}(x,\tau) \end{cases} \tag{4.310}$$

Now we have to particularize the obtained model by considering that the retention of species j occurs by one adsorption–desorption process. So, if the j species desorbs from the solid, it has to appear in the mobile phase. We can express this consideration mathematically with $\alpha_1^{(j)} = \alpha_{12}^{(j)}$ and respectively $\alpha_2^{(j)} = \alpha_{21}^{(j)}$. Now the model can be written as follows:

$$\begin{cases} \dfrac{\partial P_1^{(j)}(x,\tau)}{\partial\tau} = -v\dfrac{\partial P_1^{(j)}}{\partial x} - \alpha_{12}^{(j)}P_1^{(j)}(x,\tau) + \alpha_{21}^{(j)}P_2^{(j)}(x,\tau) \\ \dfrac{\partial P_2^{(j)}(x,\tau)}{\partial\tau} = -\alpha_{21}^{(j)}P_2^{(j)}(x,\tau) + \alpha_{12}^{(j)}P_1^{(j)}(x,\tau) \end{cases} \tag{4.311}$$

$$\tau = 0 \ , \ \ x > 0 \ , \ \ P_1^{(j)}(x,\tau) = P_2^{(j)}(x,\tau) = 0 \tag{4.312}$$

$$\tau = 0_+ \ , \ x = 0 \ , \ P_1^{(j)}(x,\tau) = P_{10}^{(j)} \ , \ P_2^{j)}(x,\tau) = 0 \ , \ \sum_j P_{10}^{(j)} = 1 \tag{4.313}$$

With the univocity conditions given in relations (4.312) and (4.313), the stochastic model becomes ready to be used in simulation.

If we agree with the absorption–desorption equilibrium of the j species at each point of the bed and considering that the absorption–desorption process obeys the well known Langmuir isotherm, then we can write: $\alpha_{12}^{(j)} = \beta_{12}^{(j)}(1 - P_2^{(j)}(x, \tau)) = \beta_{12}^{(j)} P_1^{(j)}(x, \tau)$ and the following local relation is obtained:

$$P_2^{(j)}(x, \tau) = \frac{\beta_{12}^{(j)} P_1^{(j)}(x, \tau)}{\alpha_{21}^{(j)} + \beta_{12}^{(j)} P_1^{(j)}(x, \tau)} \tag{4.314}$$

With these considerations, we can transform Eq. (4.311) from the stochastic model (4.311)–(4.313):

$$\begin{cases} \dfrac{\partial P_1^{(j)}(x, \tau)}{\partial \tau} = -v\dfrac{\partial P_1^{(j)} x, \tau)}{\partial x} - \beta_{12}^{(j)} P_1^{(j)}(x, \tau)(1 - P_2^{(j)}(x, \tau) + \alpha_{21}^{(j)} P_2^{(j)}(x, \tau) \\ \dfrac{\partial P_2^{(j)}(x, \tau)}{\partial \tau} = -\alpha_{21}^{(j)} P_2^{(j)} + \beta_{12}^{(j)} P_1^{(j)}(x, \tau)(1 - P_2^{(j)}(x, \tau) \quad j = 1, \ldots N_c \end{cases} \tag{4.315}$$

This model given by the system of equations (4.315) together with the conditions (4.312) and (4.313) can easily generate the chromatographic curves that are presented in Fig. 4.38. For this purpose, we simulate the state of existence probability of each species along the chromatographic bed. For two species, the sums $P^{(1)}(x, \tau) = P_1^{(1)}(x, \tau) + P_2^{(1)}(x.\tau)$ and $P^{(2)}(x, \tau) = P_1^{(2)}(x, \tau) + P_2^{(2)}(x.\tau)$ respectively show the state of species 1 and species 2 along the chromatographic bed. Indeed, we can identify the parameters of the stochastic model if we consider here the conventional identification $P^{(1)}(x, \tau) = c^{(1)}(x, \tau)/c^{(1)}(0, \tau)$, where $c^{(1)}(x, \tau)/c^{(1)}(0, \tau)$ has been established experimentally.

An interesting transformation of the stochastic model can be carried out when the derivate $\dfrac{\partial P_1^{(j)}(x, \tau)}{\partial \tau}$ is smaller than $\dfrac{\partial P_2^{(j)}(x, \tau)}{\partial \tau}$. This situation corresponds to the case when the variation of a fraction of the j species in the mobile phase is smaller than the fraction of the j species in the solid phase. To obtain this transformation, we operate in two steps: (i) we derivate again the first equation from system (4.311) with respect to time; (ii) with this derivate and the equation remaining from system (4.311), we eliminate probability $P_2^{(j)}(x, \tau)$. The result is:

$$\frac{\partial P_1^{(j)\prime} x, \tau)}{\partial x \partial \tau} + \frac{\alpha_{12}}{v}\frac{\partial P_1^{(j)}(x, \tau)}{\partial \tau} + \alpha_{21}\frac{\partial P_1^{(j)}(x, \tau)}{\partial x} = 0 \tag{4.316}$$

The univocity conditions can be obtained from Eq.(4.311) which, at $\tau = 0$, results in the problem described by Eq. (4.317), which presents solution (4.318). This last relation represents the initial condition from the univocity problem of model (4.316):

$$v\frac{\partial P_1^{(j)}(x, 0)}{\partial x} - \alpha_{21}^{(j)} P_1^{(j)}(x, 0) \quad , \quad P_1^{(j)}(0, 0) = P_{10}^{(j)} \tag{4.317}$$

$$P_1^{(j)}(x, 0) = P_{10}^{(j)} e^{-\left(\frac{\alpha_{12} x}{v}\right)} \tag{4.318}$$

Other conditions of the univocity problem, give the probabilities to have j species at the bed input. For an impulse at the input we have $P_1^{(j)}(0,0) = P_{10}^{(j)}$ and $P_1^{(j)}(0,\tau) = 0$. With all these conditions we can build the relation (4.319), which gives the explicit solution to this transformed model [4.33]. Here, the Bessel function $I_0(y)$ is introduced with relation (4.320):

$$P_1^{(j)}(x,\tau) = P_{10}^{(j)} e^{-\left(\frac{\alpha_{12}^{(j)} x}{v}\right)} \left[e^{-\left(\frac{\left(\alpha_{12}^{(j)}\right)^2 \tau}{\alpha_{21}}\right)} I_0\left(2\sqrt{\frac{\left(\alpha_{12}^{(j)}\right)^2 x\tau}{\alpha_{21}^{(j)}}}\right) + \frac{v}{\alpha_{12}^{(j)} x} \int_0^{\frac{\left(\alpha_{12}^{(j)}\right)^2 x\tau}{\alpha_{31}^{(j)}}} e^{-\frac{v\tau}{\alpha_{12}^{(j)} x}} I_0(2\sqrt{\tau} d\tau) \right] \tag{4.319}$$

$$I_0(y) = \sum_{k=0}^{\infty} \frac{(y/2)^{2k}}{(k!)^2} \tag{4.320}$$

This solution describes the evolution of the concentration of the j species in the carrier fluid from the input to the output of the chromatographic bed. Once the parameters are estimated, this solution can be used for the evaluation of the bed height (length of chromatographic column) needed for one actual separation (given values for $c_{10}^{(j)}$).

4.6.3
Stochastic Models for Processes with Discrete Displacement

In this type of process, the flow pattern inside a device is considered to occur in separated compartments. Each compartment is characterized by its own volume, input and exit flow rates. The circulation between all compartments is given in the scheme showing the flow topology of application 4.1.2 (Fig. 4.2). The system studied here corresponds in detail to the scheme shown in Fig. 4.39. Here we have species in motion inside a porous medium with active sites (as for example catalytic sites); species skip randomly from one site (or agglomeration) to another and inside the site they randomly interact with the site components. One agglomeration can support one or more visits of the flowing species and the time needed for one skip is low in comparison with the residence time inside one agglomeration. The model presented can easily be used to describe the visit of a very important person to a reception where the participants are distributed in various groups; considering that our VIP agrees with the protocol, he must visit each group; the time spended by the VIP with each group is established proportionally with the number of members of the group.

This type of model with compartment flow pattern can easily be applied in many chemical engineering devices such as chemical reactors, mechanical stirrers, absorption, rectification and liquid-liquid extraction columns [4.18, 4.19, 4.94]. Nevertheless, the practical applications of these models present some difficulties because of their high number of parameters. For example, in the application of Section 4.12 (the numerical application of the mechanical stirring of a liq-

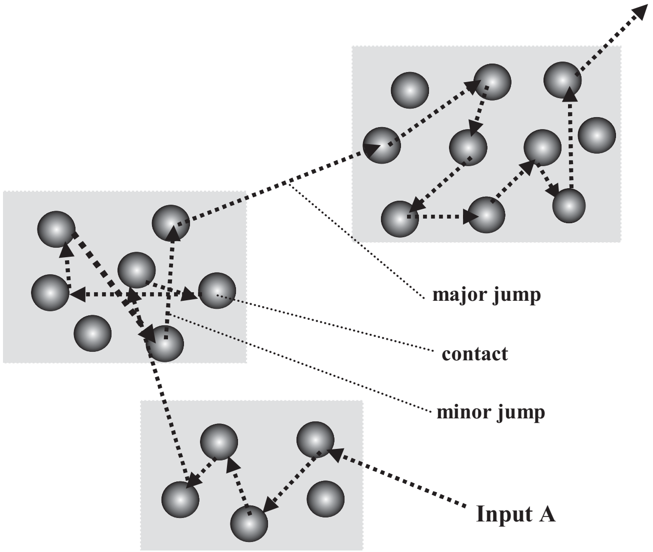


Figure 4.39 Scheme showing the motion of species A in a randomly organized porous body.

uid) the volume of cells, the flow rates and the fluid current topology are some of the parameters necessary for the model translation as simulator. Despite this major difficulty, these models remain very prolific for the production of theoretical data. In addition, these models can also be easily modified when we introduce some new conditions or when we change one or more of the existing conditions.

If we observe this type of modelling from the point of view of the general theory of the stochastic models, we can presume that it is not very simple. Indeed, the specific process which takes place in one compartment k = 1, 2, 3...., N, defines the possible states of a fluid element (the elementary processes of the global stochastic process) and the transition describing the fluid element flowing from one compartment to another represents the stochastic connections. Consequently, p_{ik} $i = 1, 2.....,N$ are the transition probabilities from the i to the k compartment and $P_k(\tau)$ is the probability of having, at time τ, the fluid element inside the k compartment. With these notations, the probability balances for $P_k(\tau + \Delta\tau)$ can be written as follows:

$$P_k(\tau + \Delta\tau) = \sum_{i=1}^{N} p_{ik} P_i(\tau) \tag{4.321}$$

Because, when $\tau = n\Delta\tau$, the discrete case is usually applied, relation (4.321) becomes:

$$P_k(n + 1) = \sum_{i=1}^{N} p_{ik} P_i(n) \tag{4.322}$$

During the time interval $\Delta\tau$, the fluid element exits compartment i and flows into compartment k, which it cannot leave. This is the condition for the selection of one realistic value of this time interval. So, for one cellular topology with N – 1 cells, the number N defines the output from the system. It is not difficult to observe then that we have:

$$\sum_{j=1}^{N} P_j(N) = 1 \tag{4.323}$$

The multiplication $P_k(n)\Delta\tau$ gives the existence probability or the probability to have the fluid element in compartment k in the interval of time defined by $n\Delta\tau$ and $(n+1)\Delta\tau$. In other words, it is the response of compartment k to an impulse signal. For $k = N$, we can observe that the probability $P_N(n)\Delta\tau$ makes it possible for the fluid element to leave the cells assembly in the same interval of time $\tau = n\Delta\tau$ and $\tau + \Delta\tau = (n+1)\Delta\tau$. Furthermore, because $P_{N-1}(n)$ gives the distribution of the residence time for our assembly of compartments, then we can conclude that the response to one step impulse can be written as:

$$F(\tau) = F(n\Delta\tau) = P_N(n) = \sum_{n=0}^{n} P_{N-1}(n)\Delta\tau \tag{4.324}$$

With this response, it is easy to obtain some important parameters characterizing the flow in the cellular assembly: the mean residence time (τ_m), the variance around the mean residence time (σ^2) and the flow intensity function ($\lambda(n)$):

$$\tau_m = \frac{\sum\limits_{n=1}^{\infty} nP_{N-1}(n)\Delta\tau}{\sum\limits_{n=1}^{\infty} P_{N-1}(n)} \tag{4.325}$$

$$\sigma^2 = \sum_{n=1}^{\infty} (n\Delta\tau - \tau_m)^2 P_{N-1}(n) \tag{4.326}$$

$$\lambda(n) = \frac{P_{N-1}(n)}{1 - P_N(n)} \tag{4.327}$$

The basic relation of our stochastic model (relation (4.322)) can be written as the vectorial equation (4.328), where E(n) gives the vector of the system state (relation (4.329)) and the matrix P (relation (4.330)) contains the transition probabilities:

$$E(n+1) = P * E(n) \tag{4.328}$$

$$E(n) = [P_1(n), P_2(n), P_3(n), \ldots P_{N-1}(n), P_N(n)] \tag{4.329}$$

$$P = \begin{bmatrix} p_{11} & p_{12} & - & p_{1N-1} & p_{1N} \\ p_{21} & p_{22} & - & - & p_{2N} \\ - & - & - & - & - \\ p_{N-11} & p_{N-12} & - & p_{N-1N-1} & - \\ p_{N1} & p_{N2} & - & p_{N-1N} & p_{NN} \end{bmatrix} \tag{4.330}$$

In actual applications, the vector of the system state is used to observe the system evolution through characteristic parameters such as species concentrations, temperature, pressure, etc.

4.6.3.1 The Computation of the Temperature State of a Heat Exchanger

In this example, we can use a deterministic model based on the particularization of the unsteady state heat balance and transfer equations. The particularization can be carried out considering either the whole exchanger or a part of it. The model that can present different degrees of complication is determined by the heat exchanger construction and by the models of flow used for the hot and cold fluids.

If we consider plug flow models for both fluids, the heat exchanger dynamics can be described using the following model:

$$\frac{\partial t_1}{\partial \tau} + w_1 \frac{\partial t_1}{\partial x} = -\frac{4k}{d\rho_1 c_{p1}}(t_1 - t_2) \tag{4.331}$$

$$\frac{\partial t_2}{\partial \tau} + w_2 \frac{\partial t_2}{\partial x} = -\frac{4k}{d\rho_2 c_{p2}}(t_1 - t_2) - \frac{4k_e}{D\rho_2 c_{p2}}(t_2 - t_e) \tag{4.332}$$

$$\tau = 0 \ , \quad x > 0 \ , \quad t_1 = f_1(x) \ , \quad t_2 = f_2(x) \tag{4.333}$$

$$\tau > 0 \ , \quad x = 0 \ , \quad t_1 = g_1(\tau) \ , \quad t_2 = g_2(\tau) \tag{4.334}$$

$$\frac{1}{k} = \frac{1}{\alpha_1} + \frac{\delta_p}{\lambda_p} + \frac{1}{\alpha_2} \ , \quad \frac{1}{k_e} = \frac{1}{\alpha_e} + \frac{\delta_{pe}}{\lambda_{pe}} + \frac{1}{\alpha_2} \ ,$$

$$\alpha_1 = h(w_1, \rho_1, c_{p1}, \lambda_1) \ , \ \alpha_2 = h(w_2, \rho_2, c_{p2}, \lambda_2) \tag{4.335}$$

The nomenclature of the equations above is: t_1 and t_2 – temperature of fluid 1 and fluid 2 respectively, w_1 and w_2 – mean velocities for hot and cold fluid, ρ_1 and ρ_2 – fluid densities, c_{p1} and c_{p2} – fluid sensible heats, d and D – specific diameters of the basic pipe and mantle of the heat exchanger, α_1 and α_2 – partial heat transfer coefficients around the basic pipe, δ_p and δ_{pe} – thickness of the basic pipe and the mantle, λ_p and λ_{pe} – thermal conductivities of the basic pipe and mantle walls, k and k_e – total heat transfer coefficients, t_e – external temperature of the heat exchanger.

This model has the remarkable characteristic of considering the heat loss in the external media with the term $\frac{4k_e}{D\rho_2 c_{p2}}(t_2 - t_e)$. The evolutions $t_1(x,\tau)$ and $t_2(x,\tau)$ result from the numerical integration of the model; for this purpose we need the analytical or discrete expressions for the functions $f_1(x), f_2(x), g_1(\tau)$ and $g_2(\tau)$.

The stochastic model of this problem is obtained after introducing a cellular structure and a flow topology. The partition of the heat exchanger into individual cells is carried out as follows:

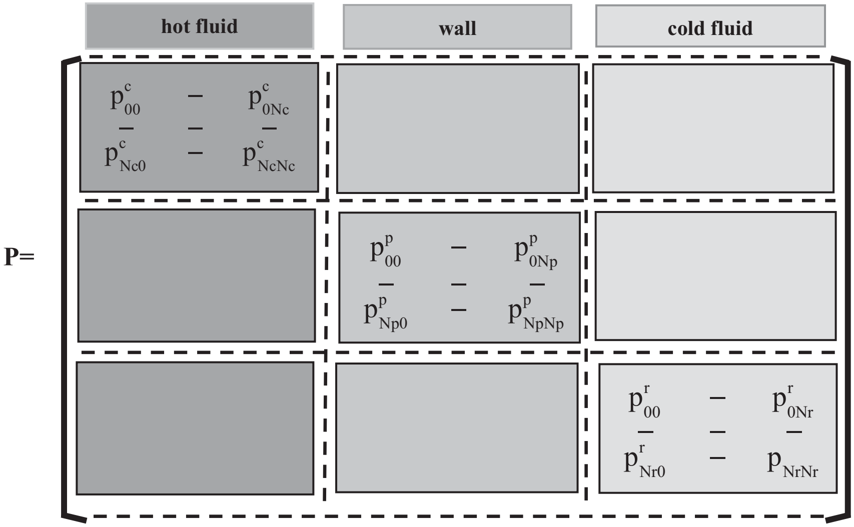
1. The exchanger contains N_C perfectly mixed cells exposed to the hot fluid flow and N_r cells of the same type where a cold fluid exists; frequently $N_c = N_r = N$ but this fact is not obligatory;
2. The inter-fluid walls can be divided into N_p cells where a cell separates one or more hot cells from one or more cold cells;
3. The thermal capacity is symbolized as $C_{Cj}, j = 1, N_c$, $C_{ri}, i = 1, N_r$ and $C_{pk}, k = 1, N_p$, for the hot, cold and inter-fluid wall cells respectively whereas, the heat flows corresponding to a cold or hot J cell are: $(G_{cij}c_{cj}(t_i{'} - t_r)$, $G_{rij}c_{cj}(t_i{''} - t_r)$; $\alpha_{cj}A_j(t_j{'} - t_{pj}{'})$ and $\alpha_{rj}A_j(t_{pj}{''} - t_j{''}))$; those are considered as q^c_{ij}, q^r_{ij} when the temperature differences are unitary.
4. If, for the interval of time $\Delta\tau$, one or many i cells coupled to a j cell change their temperature, then the temperature of the j cell will change too.
5. The heat transfer from a cell i to a cell j occurs in a time interval $\Delta\tau$ with the probability p_{ij}.

As far as the explanation above allows one to express the studied system with the necessary objects of a cellular stochastic model, we can now describe the temperature changes inside the exchanger with a discrete Markov evolution that starts with an input cell of the hot or cold fluid. Indeed, relations (4.328) or (4.329) can now be particularized giving the expressions below whereas the matrix of the transition probabilities is described with relation (4.338).

$$t_j(n+1) = \sum_{i=1}^{N} t_i(n)p_{ij} \tag{4.336}$$

$$T(n+1) = T(n)P \tag{4.337}$$

As explained above in our actual application, we have to begin by identifying the cellular structure and flow topology, consequently we have first carefully established the cellular structure after the heat capacities of different fluids or materials: $C_{ci} = m_{ci}c_{ri}, i = 1, N_c$; $C_{rj} = m_{rj}c_{rj}, j = 1, N_r$; $C_{pk} = m_{pk}c_{pk}, k = 1, N_p$.



(4.338)

The elements of p_{jj} type, which characterize the capacity of the heat carrier to be in a j cell during a time $\Delta\tau$, are obtained by considering the perfect mixing inside the cell. With this consideration, we introduce the fact that the carrier residence time follows a Poisson distribution:

$$p_{jj} = 1 - \frac{\sum\limits_{i=1, i\neq j}^{N} q_{ij}}{C_j}\Delta\tau \tag{4.339}$$

For our stochastic process, the probabilities $p_{ij}, i \neq j$ result from the Markov connections which are described as follows:

$$p_{ij} = \frac{q_{ij}}{C_j}\Delta\tau \tag{4.340}$$

The probabilities characterizing the hot or cold fluid input into the cellular system, or $p_{j0},\ j \neq 0$, are calculated with relation (4.340) but considering $C_0 \to \infty$. So, all $p_{j0}, j \neq 0$ are null and, consequently $p_{00} = 1$. The transition probabilities obey the norm conditions, which require the verification of the equality: $\sum\limits_{i=0}^{N} p_{ij} = 1, \forall j = 1, N$.

As we have shown at the beginning of this section, the application purpose consists in the establishment of a procedure for the thermal dynamics of the hot or cold fluid, when we have a rapid temperature change at the heat exchanger input. The topology of the heat exchanger of this example is shown in Fig. 4.40. If we consider, as an initial condition, that both fluids have the same temperature, we will not have a heat flow between the cells of the cellular assembly. Now, if we take into account a particular operation case where $V_1 = V_2 = 0.5 * V$, $C_1 = C_2 = 0.5C, G_{v1}\rho_1 c_{p1} = G_{v2}\rho_2 c_{p2}$, then we can compare the stochastic solution to an analytical solution of the deterministic model. The relation (4.341), which indicates the heat flow rate between both fluids, has been written with the intention of presenting the physical meaning of q_{12} and q_{21}. Indeed, when $t_1'' = t_2'' = t_r$, we do not have any heat flow inside the exchanger and the system state for $\tau = 0$ is represented by $\Delta T_1 = \Delta T_2 = 0$.

$$\begin{aligned} Q_{12} &= kA(t_1'' - t_2'') = kA(t_1' - t_r)\frac{t_1'' - t_r}{t_1' - t_r} - kA(t_1' - t_r)\frac{t_2'' - t_r}{t_1' - t_r} \\ &= q_{12}\Delta T_1 - q_{21}\Delta T_2 \end{aligned} \tag{4.341}$$

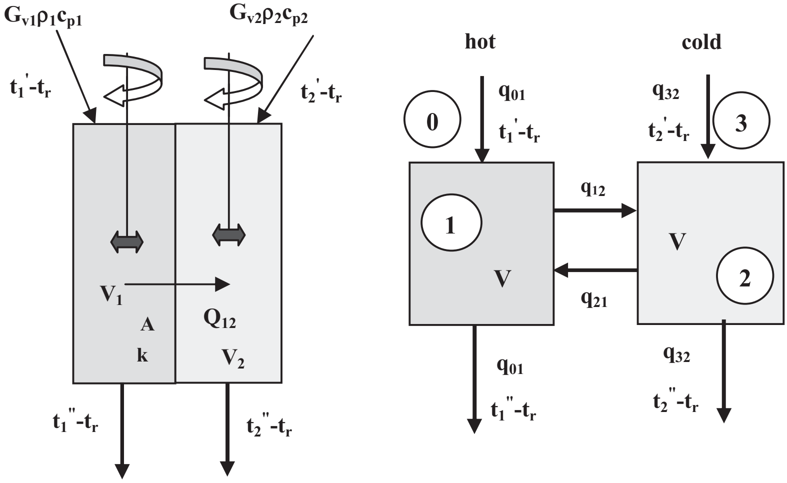


Figure 4.40 A simple heat exchanger and its cellular representation.

With the topology shown in Fig. (4.40) the matrix of the transition probabilities can be written as shown below:

$$P = \begin{bmatrix} p_{00} & p_{01} & p_{02} & p_{03} \\ p_{10} & p_{11} & p_{12} & p_{13} \\ p_{20} & p_{21} & p_{22} & p_{23} \\ p_{30} & p_{31} & p_{32} & p_{33} \end{bmatrix} \tag{4.342}$$

If we consider the relations (4.339) and (4.340) respectively for p_{ij}, we obtain:

$$\begin{aligned} &p_{00} = 1, p_{10} = q_{10}/C_0 = 0, p_{20} = q_{20}/C_0 = 0, p_{30} = q_{30}/C_0 = 0, \\ &p_{01} = q_{01}/C_1 == (G_{v1}\rho_1 c_{p1})/(V_1\rho_1 c_{p1}) * \Delta\tau == (G_{v1}/V) * \Delta\tau = \alpha, \\ &p_{02} = 0\ , p_{03} = 0\ , p_{11} = 1 - [(q_{01} + q_{21})/C_1]\Delta\tau = \\ &p_{21} = p_{12} = \alpha, p_{22} = 1 - (q_{32} + q_{12}) = 1 - 2\alpha, \\ &p_{23} = 0, p_{13} = 0\ , p_{32} = (q_{32}/C_2) * \Delta\tau = \alpha, p_{33} = 1. \end{aligned}$$

And the matrix giving the temperature change of the cells is written as follows:

$$T(1) = T(0)P = [1 \quad 0 \quad 0 \quad 0] * \begin{bmatrix} 1 & \alpha & 0 & 0 \\ 0 & 1-2\alpha & \alpha & 0 \\ 0 & \alpha & 1-2\alpha & 0 \\ 0 & 0 & 0 & 1 \end{bmatrix} = [1 \quad \alpha \quad 0 \quad 0],$$

$$T(2) = T(1)P = [1 \quad \alpha \quad 0 \quad 0] * \begin{bmatrix} 1 & \alpha & 0 & 0 \\ 0 & 1-2\alpha & \alpha & 0 \\ 0 & \alpha & 1-2\alpha & 0 \\ 0 & 0 & 0 & 1 \end{bmatrix} = [1 \quad 2\alpha - 2\alpha^2 \quad 0\alpha \quad 0] \ldots$$

The natural temperature values are:

$$\begin{aligned} &(t''_1(1) - t_r) = (t_1''(0) - t_r) + \alpha(t_1' - t_r); \\ &(t_2''(1) - t_r) = (t_2''(0) - t_r) + 0(t_1' - t_r); \\ &(t_1''(2) - t_r) = (t_1''(1) - t_r) + (2\alpha - 2\alpha^2)(t_1' - t_r); \\ &(t_2''(2) - t_r) = (t_2''(1) - t_r) + \alpha(t_1' - t_r), \text{etc......} \end{aligned}$$

The results above are obtained from:

$$T_1(1) = T_1(0)(1+\alpha) \Leftrightarrow \frac{t_1''(1) - t_r}{t_1' - t_r} = (1+\alpha)\frac{t_1''(0) - t_r}{t_1' - t_r}, \text{etc......}$$

It is not difficult to show that the analytical solution of the deterministic model is given in relations (4.343) and (4.344) [4.94], where the parameter λ is

$$\lambda = \frac{KA}{G_{v1}\rho_1 c_{p1}} = \frac{KA}{G_{v2}\rho_2 c_{p2}}$$

$$\Delta T_1 = \frac{1}{1+2\lambda}\left\{1 + \lambda - \frac{1}{2}(1+2\lambda)\exp(-\tau) - \frac{1}{2}\exp[-(1+2\lambda)\tau]\right\} \tag{4.343}$$

$$\Delta T_2 = \frac{1}{1+2\lambda}\left\{\lambda - \frac{1}{2}(1+2\lambda)\exp(-\tau) + \frac{1}{2}\exp[-(1+2\lambda)\tau]\right\} \tag{4.344}$$

Figure 4.41 compares the data predicted by the deterministic model with the stochastic model. In this figure, we have to specify that: (i) for $\lambda = 0$, the value of the corresponding α in the transition matrix of the probabilities results from the simplification $q_{12} = q_{21} = 0$; (ii) the case being analyzed corresponds to a rapid increase in the temperature of fluid 1 in the exchanger input; so t_1 is the highest temperature.

The extension of the stochastic method for actual exchangers depends strongly on the correctness of the projected cellular topology and on the reality of the estimated transition probabilities. Figure 4.42 shows an example of an actual heat

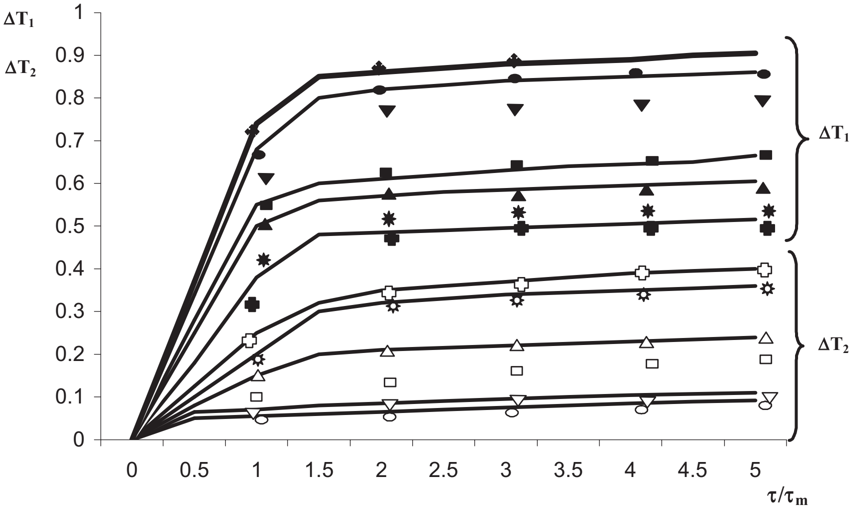


Figure 4.41 Dynamic evolution of the heat exchanger from figure 4.39.
Analytical solution – continuous lines; Stochastic solution – discrete points:
$\lambda = 0$ (✜), $\lambda = 0.1$ (○,●), $\lambda = 0.2$(▽,▼), $\lambda = 0.4$ (□,■), $\lambda = 1$ (△,▲), $\lambda = 0$(✸,✚); $\lambda = 5$(✣,✡).

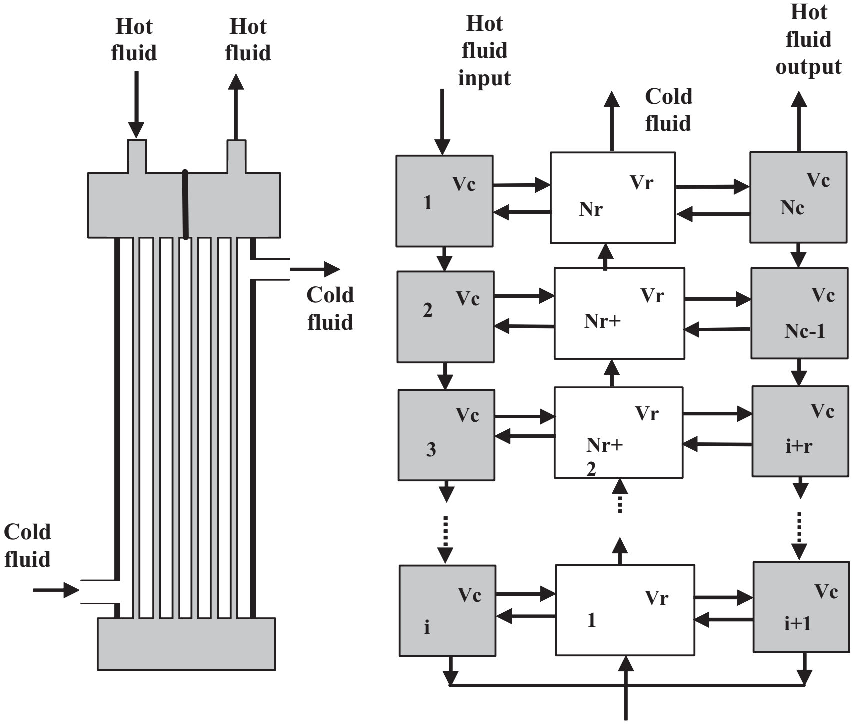


Figure 4.42 Stochastic topological scheme of a heat exchanger with two configurations for the flow pattern of the hot fluid (countercurrent and co-current).

exchanger and its division into cells. It is the case of a tubular heat exchanger, where the hot fluid passes through the exchanger twice (in countercurrent and in co-current). The walls separating the fluids have not been divided into cells; because we considered that the heat accumulated by the walls was insignificant with respect to the heat transferred between the hot and cold fluids. In such example, the respective volumes of the heat exchanger cells are *a priori* different and result in a much more complex situation when compared with the previous example discussed in this chapter.

4.6.3.2 **Cellular Stochastic Model for a Countercurrent Flow with Recycling**

The example presented in this section is a system where two countercurrent fluids flow through N identical cells; Fig. 4.43 describes this system schematically. In this simplified case, we consider that, at each cell level, we have a perfect mixing flow and that for a "k" cell, the actual transition probabilities are p_{kk}, p_{kk-1} and p_{kk+1}. Indeed, these probabilities are expressed as:

$$p_{kk-1} = \frac{aG_v\Delta\tau}{V} \ , \quad p_{kk+1} = \frac{(1+a)G_v\Delta\tau}{V} \ , \quad p_{kk} = 1 - (p_{kk-1} + p_{kk+1}) \qquad (4.345)$$

When we have the same fraction of recycling in the system and when the cells have the same volume, we can rewrite relation (4.345) as:

$$p_{kk-1} = \frac{a_k G_v\Delta\tau}{V_{k-1}} \ , \quad p_{kk+1} = \frac{(1+a_k)G_v\Delta\tau}{V_k} \ , \quad p_{kk} = 1 - (p_{kk-1} + p_{kk+1}) \qquad (4.345)$$

We can observe that the first and the last cell of the system are in contact with only one cell: cell number 2 and number N – 1 respectively. So, in the matrix of the transition probabilities, the values p_{13} and p_{N-2N} will be zero. It is easily noticed that, if we have a complete matrix of the transition probabilities, then we can compute the mean residence time, the dispersion around the mean residence time and the mixing intensity for our cells assembly. The relations (4.324)–(4.326) are used for this purpose.

$$P = \begin{bmatrix} p_{11} & p_{12} & 0 & 0 & - & 0 & 0 \\ p_{21} & p_{22} & p_{23} & 0 & - & 0 & 0 \\ 0 & p_{32} & p_{33} & p_{34} & - & 0 & 0 \\ 0 & 0 & p_{43} & p_{44} & p_{45} & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & p_{N-1N} & p_{NN} \end{bmatrix} \qquad (4.346)$$

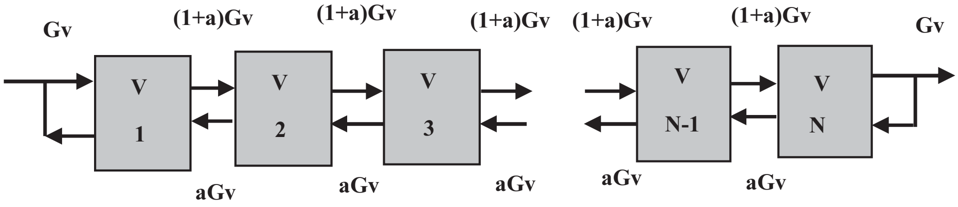


Figure 4.43 Countercurrent and recycle flow model.

If, besides hydrodynamics and mixing, we want to consider other phenomena, such as a chemical reaction, we have to separate the probabilities characterizing each particular phenomenon:

- $p_{jk} = \alpha_{jk}\Delta\tau$ – gives the probability for the species to skip from cell j to cell k in the time $\Delta\tau$;
- $p_{ke} = \alpha_{ke}\Delta\tau$ – gives the probability for the species to quit the system during the time interval $\Delta\tau$ (this probability exists when the k cell presents an open output);
- $p_{kr} = \alpha_{kr}\Delta\tau$ – is the probability that quantifies the species transformation as a result of its chemical interaction inside the k cell at $\Delta\tau$.

With this notation and considering the definition of $P_k(\tau)$ already given, the probability balance, with respect to the k cell for the time interval between τ and $\tau + \Delta\tau$ can be written as:

$$P_k(\tau + \Delta\tau) = \left[1 - \left(\sum_{j,j\neq k} \alpha_{kj}\Delta\tau\right)\right][1 - (\alpha_{ke} + \alpha_{kr})\Delta\tau]P_k(\tau) + \left(\sum_{j,j\neq k} \alpha_{jk}\Delta\tau\right)P_j(\tau) \tag{4.347}$$

If we consider that $\Delta\tau$ is very small, we obtain the concluding form of our cellular stochastic model. It describes the cellular countercurrent flow with recycling and chemical reaction:

$$\frac{dP_k(\tau)}{d\tau} = -(\alpha_{ke} + \alpha_{kr})P_k(\tau) - \left(\sum_{j,j\neq k} \alpha_{kj}\right)P_k(\tau) + \left(\sum_{j,j\neq k} \alpha_{jk}\right)P_J(\tau)\ ;$$

$$k = 1, N\ ;\ j = 1, N \tag{4.348}$$

Each term from the right side of this representative equation of the model has a particular meaning. The first term shows that the number of the reactant species molecules in the k cell decreases as a result of the consumption of species by the chemical reaction and the output of species from the cell. The second term describes the reduction of the number of molecules as a result of the transport to other compartments. The last term gives the increase in the number of the species in the k compartment because of the inputs from the other cells of the assembly. With reference to the mathematical formalism, our model is described by an ordinary system of differential equations. Indeed, for calculations we must specify the initial state of the probabilities. So, the vector $P_k(0), k = 1, N$ must be a known vector. The frequencies $\alpha_{ke}, \alpha_{kr}, \alpha_{kj}, \alpha_{jk}$ will be established by means of the cellular assembly topology and kinetic data. It is evident that the frequency α_{kr} will be related to the reaction process taking place in the cell.

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