



# Transverse dispersion in ordered pillar arrays as a Markov chain: Extension of the Galton-board model

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## Introduction

Band broadening in a chromatographic bed caused by the lateral differences in eluent velocity (e.g., due to wall effect) is inversely related to the rate of transverse mass transport in the bed. Therefore, several recent studies [1–3] have been devoted to the simulations and measurements of the solute transverse dispersion under conditions of laminar flow in sphere packings, silica monoliths, and arrays of non-porous cylindrical pillars. Unfortunately, only few models of the dispersion process in ordered pillar arrays are available [3].

Hexagonal array of pillars closely resembles the Galton board. Nevertheless, the simple Galton-board model of transverse dispersion [3, 4] fails to describe the experimental data. The aim of this presentation is to show how the Galton-board model can be modified in order to obtain a useful expression for the velocity dependence of the transverse dispersion coefficient in regular pillar arrays.

## The Galton-board model

Usually, solute dispersion is considered as a combination of two independent processes: molecular diffusion and advective (purely mechanical) dispersion. In the Galton-board model [4], the latter contribution is treated as a one-dimensional random walk consisting of independent steps of the length  $s$  and describing the imaginary streamline-splitting process shown in Fig. 1A. The steps in positive and negative directions of the  $y$ -axis, which is orthogonal to the direction of flow, are equally probable ( $P(+)=P(-)=0.5$ ). The average squared transverse displacement of the molecules from their original position  $\sigma_T^2$  after  $N$  steps of this random walk is given by

$$\sigma_T^2 = s^2 \cdot N. \quad (1)$$

The transverse dispersion coefficient  $D_T$  is calculated as

$$D_T = \frac{1}{2} \cdot \frac{\Delta \sigma_T^2}{\Delta t} = \frac{1}{2} \cdot s^2 \cdot \frac{\Delta N}{\Delta t}, \quad (2)$$

where  $t$  is time and symbol  $\Delta$  denotes the differences of the quantities. Expressing the step length  $s$  and the frequency of steps  $\Delta N/\Delta t$  through the geometrical parameters of the array (Fig. 1B) and the interstitial linear velocity of the mobile phase  $u$  leads to

$$s = \frac{w_{cell}}{2} \quad \rightarrow \quad D_T = \frac{w_{cell}^2}{4l_{cell}} \cdot u \quad \rightarrow \quad \frac{D_T}{D_m} = \beta \cdot v, \quad (3)$$

$$\frac{\Delta N}{\Delta t} = \frac{2u}{l_{cell}} \quad \rightarrow \quad \beta = \frac{w_{cell}^2}{4l_{cell}d_p}$$

where  $d_p$  is the pillar diameter,  $D_m$  is the molecular diffusion coefficient of the solute,  $v = ud_p/D_m$  is the reduced mobile phase velocity. For a fixed (hexagonal) arrangement of pillars, parameter  $\beta$  is a function of the array porosity (interpillar volume fraction)  $\varepsilon$  only:  $\beta \approx 0.1774$  and  $0.2510$  for  $\varepsilon = 0.4$  and  $0.7$ , respectively.

Assumption of the additivity of diffusive and advective contributions to  $D_T$  results in

$$\frac{D_T}{D_m} = \gamma + \beta \cdot v, \quad (4)$$

where  $\gamma$  is the diffusion obstruction factor. Linear Eq. (4) does not describe the experimental  $D_T/D_m(v)$  curves, which level off at high  $v$ .

## Extension of the Galton-board model

Actually, no purely mechanical contribution to  $D_T$  is possible in ordered pillar arrays under laminar flow conditions. The streamlines do not split (Fig. 2), and mass transfer between adjacent streamlines is diffusive. In the absence of diffusion, the solute molecules would simply follow the same streamlines they were initially placed in, proceeding in sequences of alternating steps (+ - + - ...) of the approximate length  $s$ . This would result in zero transverse dispersion. In reality, diffusion allows the molecules to cross the lines of zero transverse velocity (Fig. 2) and make consecutive steps in the same direction, such steps being necessary for the lateral solute spreading. Adopting the terminology used by Scheven [2] to describe transverse dispersion in random sphere packings, the above process can be called diffusively coupled mechanical dispersion.

This process can be treated as a two-state Markov chain [5], i.e., as a sequence of such trials (steps) that the probability of a particular outcome (one of the two chain states, which corresponds to a particular step direction; Fig. 3) is dependent on the outcome of the preceding trial and independent of the outcomes of all earlier trials. Fig. 2 suggests that the probability  $p$  to make a step in the same direction as the preceding step is smaller than the probability  $q = 1 - p$  to reverse the direction of motion, i.e.,  $p < 0.5 < q$ . To give another definition,  $p$  is the conditional probability to exit a rhombic unit cell of the array through the red boundary (Fig. 4; see the black arrows) after entering the cell through the other red boundary (or blue after blue), while  $q$  corresponds to the combinations "blue after red" and "red after blue". The value of  $\sigma_T^2$  after  $N$  steps of this Markov chain is given by [6, 7]:

$$\sigma_T^2 = s^2 \cdot \left( \frac{p}{q} \cdot N - \frac{(p-q)(1-(p-q)^N)}{2q^2} \right). \quad (5)$$

In derivation of Eq. (5), positive and negative directions are assumed to be equally probable for the first step. Fig. 5 shows that the function  $\sigma_T^2(N)$  becomes linear after sufficiently large number of steps depending on  $p$ . The asymptotic transverse dispersion coefficient is calculated as

$$D_T = \frac{1}{2} \cdot \lim_{N \rightarrow \infty} \frac{\Delta \sigma_T^2}{\Delta t} = \frac{1}{2} \cdot \frac{p}{q} \cdot s^2 \cdot \frac{\Delta N}{\Delta t}. \quad (6)$$

By analogy with Eq. (2), Eq. (6) leads to

$$\frac{D_T}{D_m} = \frac{p}{1-p} \cdot \beta \cdot v. \quad (7)$$

Eq. (7) differs from Eq. (3) only by the multiplier  $p/(1-p)$  that becomes unity at  $p = 0.5$ . Eq. (7) describes the main contribution to  $D_T$  at high  $v$  ( $>10$ ). Assumption of the additivity of pure diffusion and diffusively coupled mechanical dispersion results in

$$\frac{D_T}{D_m} = \gamma + \frac{p(v)}{1-p(v)} \cdot \beta \cdot v. \quad (8)$$

Importantly,  $p$  is velocity-dependent. With the increase in  $v$ , it should decrease since the time available for the solute to cross the zero-velocity lines (Fig. 2) decreases. At low  $v$ , the reasonable limiting value for  $p$  should be 0.5. The velocity-dependence of  $p$  accounts for the leveling-off of the experimental  $D_T/D_m$  vs.  $v$  curves at high  $v$ . Assuming the following simple expression for  $p(v)$ :

$$p = \frac{1}{2+a \cdot v}, \quad (9)$$

where  $a$  is a coefficient, leads to

$$\frac{D_T}{D_m} = \gamma + \frac{\beta \cdot v}{1+a \cdot v}. \quad (10)$$

The least squares fit of Eq. (10) to the simulation data from paper [1] is presented in Fig. 6A. Parameters of the fit are given in Table 1. The fit is rather satisfactory. The remaining non-ideality is due to the assumed simple form of Eq. (9) and intrinsic limitations of the model.

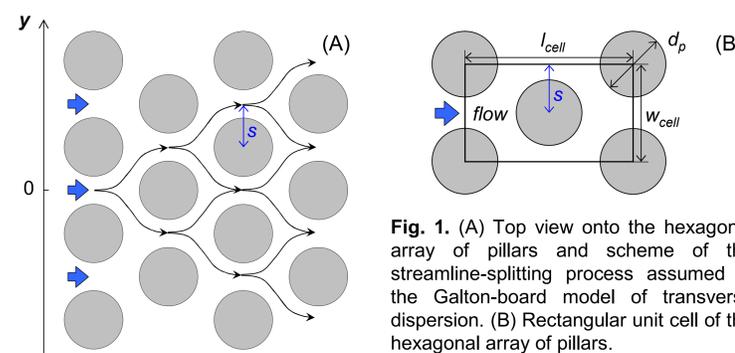


Fig. 1. (A) Top view onto the hexagonal array of pillars and scheme of the streamline-splitting process assumed in the Galton-board model of transverse dispersion. (B) Rectangular unit cell of the hexagonal array of pillars.

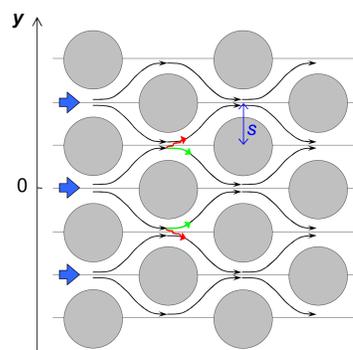


Fig. 2. Scheme of the main streamlines in a laminar flow through the ordered pillar array. Thin horizontal lines are the lines of zero transverse eluent velocity. Green arrows indicate the more probable changes of the direction of lateral motion of the molecules following the streamlines. Each red arrow illustrates the diffusive transfer necessary to make a less probable random step in the same direction as the previous step.

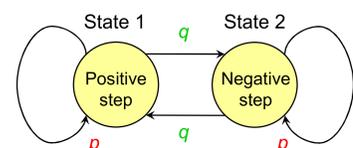


Fig. 3. Directed graph of the two-state Markov chain that models transverse dispersion in the ordered pillar array. Probabilities of transitions between the states are  $p$  and  $q$ ,  $p + q = 1$ , and  $p < q$ .

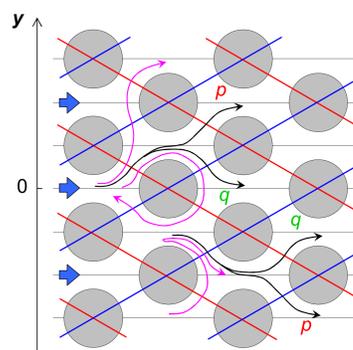


Fig. 4. Division of the hexagonal array of pillars into rhombic unit cells to define probabilities  $p$  and  $q$ . Black arrows indicate preferential paths of the solute at high  $v$ . Purple arrows exemplify the paths that cannot be neglected at low  $v$  (see "Limitations..." section for discussion).

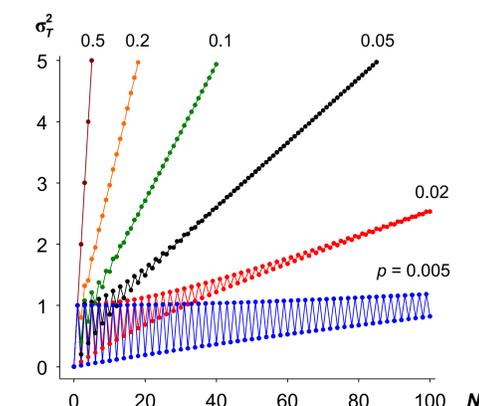


Fig. 5. Dependences of the average squared transverse displacement  $\sigma_T^2$  on the number of steps  $N$  in the considered Markov chain (Eq. (5)) for various values of probability  $p$ . The step length  $s = 1$ .

## Limitations and adjustment of the model

Treatment of the diffusively coupled mechanical dispersion as the Markov chain described by Fig. 3 requires that only such trajectories of the molecules as those shown by the black arrows in Fig. 4 be possible. This situation can be safely assumed at high  $v$ . However, at low  $v$  such trajectories as those exemplified by the purple arrows in Fig. 4 cannot be neglected, and the sum  $p + q$  becomes smaller than unity. This necessitates considering more complicated Markov chains. Further, it is more difficult to define the frequency of steps at low  $v$ . Division of the overall dispersion coefficient into purely diffusive and diffusively coupled mechanical terms is controversial as well.

Nevertheless, a useful expression for  $D_T/D_m(v)$  can be obtained by introducing a multiplier  $\varphi(v) = c \cdot (1 - \exp(-b \cdot v))$  to the second term of Eq. (10):

$$\frac{D_T}{D_m} = \gamma + c \cdot (1 - \exp(-b \cdot v)) \cdot \frac{\beta \cdot v}{1+a \cdot v}, \quad (11)$$

where  $b$  and  $c$  are coefficients. The multiplier  $\varphi(v)$  with  $c > 1$  increases the contribution of the second term to  $D_T/D_m$  at high  $v$  and decreases it at low  $v$ .

Eq. (11) fits the simulation data [1] well (Fig. 6B and Table 1). The inflection point of the  $D_T/D_m$  vs.  $v$  curves (seen in linear coordinates) is taken into account by Eq. (11). The product  $c \cdot \beta$  varies only slightly for different  $\varepsilon$  and can be used as a single new coefficient. Fixing  $c \cdot \beta$  at 0.260 does not impair the fitting quality and only slightly changes the other parameters (Table 1).

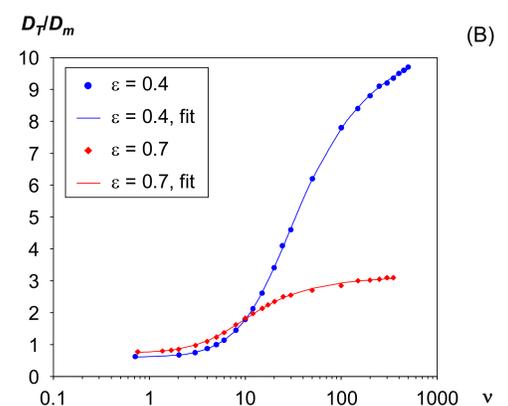
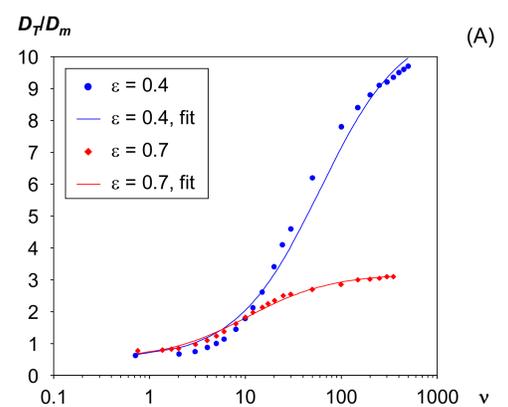


Fig. 6. Plot showing the least squares fit of (A) Eq. (10) and (B) Eq. (11) to the simulation data [1]. The data points were replotted from Fig. (14) in Ref. [1]. Note that  $v$  was defined using the domain size of the array  $d_{dom}$  in Ref. [1] and was recalculated to  $d_p$ -based  $v$  here. The point  $v = 0$  unseen in logarithmic coordinates was also used for fitting.

Table 1. Parameters of the least squares fit of the equations proposed in this study to the data from Ref. [1]

Equation	$\varepsilon$	$\gamma$	$a$	$b$	$c$	$r^2$	$c \cdot \beta$
(10)	0.4	0.526	0.017	n.a.	n.a.	0.991	n.a.
	0.7	0.507	0.094	n.a.	n.a.	0.989	n.a.
(11)	0.4	0.595	0.028	0.082	1.552	>0.999	0.275
	0.7	0.728	0.108	0.199	1.030	0.999	0.259
(11) with $c \cdot \beta = 0.260$	0.4	0.603	0.027	0.089	n.a.	>0.999	fixed
	0.7	0.727	0.108	0.198	n.a.	0.999	fixed

## Conclusions

Using the concept of Markov chains, a way was proposed to extend the probabilistic Galton-board model of transverse dispersion in order to make this model more consistent with the mechanism of advective-diffusive mass transport in laminar flow through regular pillar arrays. The limitations of the extended model were discussed. A relatively simple four-parameter equation that describes the available dispersion data well was suggested. The equation can be used as a part of the expression for the wall-induced contribution to the plate height of confined ordered arrays of non-porous pillars.

## References

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## Acknowledgements

Konstantin Smirnov is grateful to Prof. Gert Desmet (Vrije Universiteit Brussel, Brussels, Belgium) for the discussion that promoted this study.