The Checkerboard Model for the Eddy-dispersion in Laminar Flows Through Porous Media. Part II: Application to Ordered and Disordered 2-D Flow Systems

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Abstract

We report on a series of high-accuracy computational fluid dynamics band broadening simulations in three different 2-D flow systems: a 2-D pillar array and 2-D lumped packed bed geometries with different checkerboard velocity bias patterns. These media display a local maximum in the relationship between the eddy-dispersion plate height and the mobile phase velocity. The occurrence of such a dispersion maximum has not been reported before but appears to be a characteristic of regular chromatographic media with alternating velocity bias, at least in a 2-D geometries. This newly observed behavior can be fully understood and modelled using the checkerboard model established in part I of the present study.

1. Introduction

After briefly being challenged two decades ago by in-situ synthesized silica and polymer monolithic packings [1], and in the future maybe by perfectly ordered silicon pillar array columns [2] or 3D-printed columns, the packed bed of spheres is by far still the most commonly used format for liquid chromatography [3-7]. A characteristic feature of the packed bed is that its local structure is intrinsically heterogeneous, just as is the case for silica and polymer monolithic packings. This leads to lateral velocity biases spanning different lateral scales, each representing a substantial source of additional band broadening, commonly referred to as eddy-dispersion [8-11]. In its currently most commonly accepted definition, this is the band broadening in excess of that caused by the longitudinal diffusion (so called B-term band broadening) and the resistance to mass-transfer occurring at the single through-pore level (so called C-term band broadening). In other words, the eddy-dispersion can be defined as what remains of the band broadening after the B- and C-terms appearing in the general plate height model (see e.g., refs. [12] and [13] for exact expressions) are subtracted from the total observed plate height [7,14]:

\[ h_{\text{eddy}} = h - h_B - h_{\text{Cm}} - h_{\text{Cs}} \]  \hspace{1cm} (1)

There is also a clear consensus that the eddy-dispersion is an aggregate effect of dispersion phenomena occurring at different scales j=1,N, where the scale is typically related to the lateral width of the velocity bias zones (cf. Giddings’ classification of single through-pore/particle, short-range, long-range and transcolumn velocity biases):

\[ h_{\text{eddy}} = \sum_{j=1}^{N} h_{\text{eddy},j} \]  \hspace{1cm} (2)

wherein \( h_{\text{eddy},j} \) is the eddy-dispersion originating from scale j.

In part I of the present study, a new model for the eddy-dispersion in laminar flow systems has been established. The model assumes the locally fluctuating packing density in a random packing medium follows a checkerboard pattern. Whereas the Giddings model and finite parallel zone (FPZ)-eddy-dispersion models [8,15] used up till now in literature consider the transversal velocity biases (VB) as isolated regions or events, the new checkerboard model accounts for the fact that the band broadening experienced in a given VB zone can be (partially) rectified when moving into the next VB region, as the
length of each velocity bias zone can always be selected such that the sign of its bias $u_1-u_2$ is reversed
when entering a next velocity bias zone allowing species lagging behind after the passage to the first
zone to (partially) make up their delay. This rectification phenomenon plays an important role in the
range of large reduced velocities $\nu (=u.d_p/D_{mol})=$Peclet number in engineering literature). Based on a unit
dispersion cell that incorporates this internal VB rectification possibility, the checkerboard model levels
off to lower horizontal large $\nu$-asymptote than that predicted by the single step Giddings and finite
parallel zone (FPZ)-models (see Section 4.2 of part I). Considering the same A- and C-constant, the
checkerboard model predicts an eddy-dispersion contribution that can easily be only half that predicted
by the single step models.

In physical terms, the work in part I also showed that a patchwork of low and high permeability regions
gives rise to a velocity distribution that consists of two components: i) a checkerboard distribution of
high and low velocity regions coinciding with the permeability checkerboard and ii) an overlaying
preferential flow path. Mathematically, this is reflected in two distinct contributions (resp. $h_{\text{checker}}$ and
$h_{\text{pref}}$), such that the checkerboard model for the eddy-dispersion at scale $j$ can generally be written as:

$$h_{\text{eddy},j} = h_{\text{checker}} + h_{\text{pref}} = C_\nu \left[ 1 - \frac{C_\nu}{4A} \left( 1 - e^{-A/(C_\nu)} \right) \right] \left( 1 - e^{-A/C_\nu} \right) + C_{\text{pref}} \cdot \nu_t$$  \hfill (3)

with $\nu_t$ the reduced interstitial velocity based on the actual degree of transversal dispersion $D_{\text{trans}}$ (see
Section 4 of part I):

$$\nu_t = \frac{u \cdot d_p}{D_{\text{trans}}} = \frac{\nu}{\gamma_{\text{eff}} + \beta \cdot \nu}$$  \hfill (4)

wherein $\gamma_{\text{eff}}$ is the reduced effective diffusion ($\gamma_{\text{eff}}=D_{\text{eff}}/D_{mol}$) [ref] and $\beta$ is an empirical constant reflecting
the magnitude of the convective contribution to the transversal dispersion [16]. The last term in Eq. (3)
originates from the preferential flow path that inevitably develops in a flow-through medium with a
checkerboard pattern of alternating high and low packing density zones. As shown in Sections 3.3 and
3.4 of part I, this preferential flow path persists over a very long distance and therefore gives rise to a
pure C-term-like contribution.

The A- and C-constants appearing in Eq. (3) have exactly the same definition and meaning as in the
Giddings and FPZ-model. The A-constant relates to the band broadening effect emanating in the high $\nu$-
range from a single VB with relative velocity difference $\Delta \nu (=(u_1-u_2)/u_0)$. This is the so-called mechanic
dispersion [17], as this is the type of band broadening obtained under the limiting conditions (zero
diffusion) where the species permanently stay on the stay streamlines. The C-constant relates to the
same relative velocity difference $\Delta \nu$, but expresses its band broadening effect in the low $\nu$-range, where
there is ample time for the species to re-equilibrate between different streamlines. In a general form
[15], both constant depend on this relative velocity difference $\Delta \nu$ according to:

$$\Lambda = \frac{\alpha_1 \alpha_2 K}{(\alpha_1 + \alpha_2 K)^2} \cdot \Delta \nu^2 \cdot \lambda_{ax}$$  \hfill (5)
\[
C = \frac{2}{Sh} \cdot \frac{(\alpha_1 \alpha_2 K)^2}{(\alpha_1 + \alpha_2 K)^3} \cdot \left(\frac{\alpha_1}{K} + \frac{\alpha_2}{K}\right) \cdot \Delta v^2 \cdot \frac{\lambda_{\text{trans}}^2}{\gamma_{\text{trans}}} \cdot \frac{1}{1 + k''}
\]  

(6)

with \(\alpha_1\) and \(\alpha_2\) the volumetric fraction of zone 1 and zone 2 of the VB (note that \(\alpha_1 + \alpha_2 = 1\)) and \(K\) the volume-based retention equilibrium constant between both zones. Further, \(\lambda_{\text{ax}}\) and \(\lambda_{\text{trans}}\) respectively are the dimensionless axial length and transversal width of the VB zone and \(\gamma_{\text{trans}}\) is the dimensionless transversal diffusion coefficient, defined as \(\gamma_{\text{trans}} = D_{\text{trans}}/D_m\). Despite having the same definition and meaning, the expressions in Eqs. (5-6) are more elaborate than the A- and C-constant expressions introduced by Giddings. This is because the FPZ-model underlying Eqs. (5-6) allows for VB zones where the high and low velocity zone have different volumetric fractions (Giddings assumes \(\alpha_1 = \alpha_2 = 0.5\)) as well as for the existence of an equilibrium distribution between the two VB zones. Whereas Giddings assumed \(K=1\), two adjacent VB zones will generally contain a different volumetric fraction of particles of stationary phase, such that species will not distribute evenly at thermodynamic equilibrium between the two VB zones, thus giving rise to a \(K\)-value differing from unity. The appearance of the Sherwood number \(Sh\) as a geometrical constant implies the FPZ-model also allows to consider VB zones with a general shape. Note that \(Sh = 3\) for the simplest case of two-dimensional rectangles [13], which is also the shape assumed by Giddings.

The \((1+k'')\)-factor appears in Eq. (6) to express that the C-term contribution is eventually determined by the velocity of the retained species \((v/1+k'')\), with \(v\) the reduced interstitial velocity. Note that if Eq. (3) would have been written as a function of \(v_0\), the \(t_0\)-based reduced velocity, this zone retention factor \(k''\) [13,18] should be replaced by \(k'\), the more commonly used phase retention factor (see [7] or [13] for the difference between \(k'\) and \(k''\)). Please also note these retention factors are unrelated to the equilibrium constant \(K\) appearing in Eqs. (5) and (6), as this one relates to an equilibrium distribution between two VB zones comprising a mixture of particles and mobile phase, whereas the equilibrium constant appearing in \(k'\) and \(k''\) relates to the equilibrium distribution between the pure mobile phase (or zone) and the pure stationary phase (or zone).

Making the same simplifying assumption as Giddings (\(\alpha_1 = \alpha_2 = 0.5\) and \(K=1\)), Eqs. (5) and (6) respectively become:

\[
A = \frac{1}{4} \cdot \Delta v^2 \cdot \lambda_{\text{ax}}
\]

(7)

\[
C = \frac{1}{12} \cdot \Delta v^2 \cdot \frac{\lambda_{\text{trans}}^2}{\gamma_{\text{trans}}} \cdot \frac{1}{1 + k''}
\]

(8)

Eq. (6) also contains the geometrical and dynamic parameters required to establish an explicit expression for \(C_{\text{pref}}\), the third geometrical constant appearing in Eq. (3). This parameter should reflect the contribution of the preferential flow path running along the VB interfaces and is of the pure C-term type band broadening type, as it relates to a flow system (cf. Fig. 5b of part I) consisting of two parallel zones remaining in contact over an (infinitely) long distance and with a persisting difference in velocity.
Denoting the fraction of the VB zones covered by the preferential flow path with \( \alpha_{\text{pref}} \), we can take \( \alpha_1 = \alpha_{\text{pref}} \) and \( \alpha_2 = 1 - \alpha_{\text{pref}} \). Further, we again take \( K = 1 \) (no difference in retention properties between preferential flow path region and rest of VB), and assume the preferential flow path occupies a 2D-rectangular strip as represented in Fig. 5b of part I. Consequently, we again have \( Sh = 3 \). Further denoting the relative velocity difference between the preferential flow path and the rest of the VB zones as \( \Delta v_{\text{pref}} \),

we can derive from Eq. (6) that:

\[
C_{\text{pref}} = \frac{2}{3} \alpha_{\text{pref}}^2 \left( 1 - \alpha_{\text{pref}} \right)^2 \Delta v_{\text{pref}}^2 \frac{\lambda_{\text{trans}}^2}{4} \left( 1 + k'' \right) \tag{9}
\]

Note that the factor 4 appearing under the \( \lambda_{\text{trans}} \)-factor reflects that the relevant unit cell to describe the effect of the preferential flow path only extends over half the transversal width of the VB unit cell (cf. difference between Fig. 5a and Fig. 5b of part I).

In the present part, the checkerboard model from part I is applied to the eddy-dispersion observed when computing the band broadening using computational fluid dynamics data (CFD) in three different flow systems:-

- \( \text{i)} \) 2D pillar array columns (non-porous, non-retentive pillars)
- \( \text{ii)} \) porous 2-D medium with ordered checkerboard packing density pattern
- \( \text{iii)} \) porous 2-D medium with randomly disordered checkerboard packing density pattern

The advantage of this numerical CFD approach is that the dispersion can be determined very accurately because the measurement accuracy can be boosted by invoking very high degrees of spatial discretization. Furthermore, all conditions and analyte properties are exactly known as they are user-defined.

The dispersion in ordered 2D pillar array columns has been extensively studied both experimentally [3,19] and numerically [20-21] by our group and many others [22-24] and is generally considered as a perfectly ordered system. Although this qualification certainly applies to the arrangement of the pillars, the microscopic velocity distribution clearly displays some heterogeneities. Although these are perfectly repetitive, they anyhow lead to some degree of eddy-dispersion, which already became apparent when it was observed in [20] and [26] that at a small \( A \)-term constant was needed to fit the plate height curves obtained by CFD. Compared to the simulations shown in these studies, the simulations performed in the present study have been computed with a considerably higher degree of spatial resolution to produce more accurate results.

2. Numerical methods

All numerical data were obtained using the computational fluid dynamic (CFD) software package Ansys Fluent® 16.2. This package has been extensively validated for the high accuracy with which the band broadening in chromatographic systems can be calculated [20,21]. The different considered flow geometries were designed using the Design Modeler and Meshing-module of the same software package. Subsequently, the geometries were spatially discretized (=meshed) to calculate the velocity
field and the species dispersion. The mesh cell size was chosen such that the finally obtained plate height values were independent of this size to within 0.5%. For the 2D pillar array geometry (20 unit cells long), meshing density was at 16,000/\(\mu m^2\). For the ordered checkerboard geometry (46 unit cells long) considered in Section 3.2 while the meshing density was at 9500 cells/100 \(\mu m^2\) in the random checkerboard geometry (70 unit cells long) in Section 3.3.

The CFD Fluent® software was first used to calculate the steady-state velocity field by solving the incompressible Navier-Stokes equations for a Newtonian fluid using the segregated pressure-based steady state solver with a Least-Squares Cell-Based gradient evaluation and a second order upwind interpolation scheme for the momentum equations. All velocity profiles were calculated by imposing a uniform velocity profile at the inlet, and a fixed pressure at the outlet. Subsequently, a rectangular band of tracer species was patched into the considered flow domain (injection width was in all cases taken equal to \(\frac{1}{2}\) of a single unit cell). The evolution of this initial species distribution was subsequently calculated in a time-resolved way by solving the general advection-diffusion mass balance using the previously computed velocity fields as the input for the velocity terms. The equations were solved using a first-order upwind spatial discretization and second order implicit temporal discretization. Spatial gradients were again evaluated using the Least-Squares Cell-Based method.

All simulations were performed on Dell Power Edge R210 Rack Servers, with IntelXeon x3460 processors (clock speed 2.8 GHz, 4 cores) and 16 Gb,1333 MHz ram memory running Windows server edition 2008 R2(64-bit) as an operating system.

Post-processing was done by computing the spatial moment integrals of the species distribution registered at a given time \(t\), using:

\[
M_k = \int_{-\infty}^{+\infty} C(x, t) x^k \, dx \quad \text{with } k=0,1,2
\]

From these moments, the spatial variance was calculated using:

\[
\sigma_x^2 = \frac{M_2}{M_0} - \left( \frac{M_1}{M_0} \right)^2
\]

Subsequently, the local plate height was determined as:

\[
H = \frac{\sigma_x^2(t + \Delta t) - \sigma_x^2(t)}{\Delta t}
\]

In most calculations, \(\Delta t\) was on the order of \(5 \times 10^{-6}\)s.

In the checkerboard geometries, a final validation check for the employed computation schemes was made by calculating \(H\) for the special case wherein the permeability in all zones is equal. This induced a pure plug flow velocity field, for which it is theoretically expected that \(H=2.D_{mol}/u\). It was found that the maximal deviation between the computed value of \(H.u/2\) and \(D_{mol}\) was maximally equal to 0.8% over the entire range of investigated velocities. In the 2D-pillar array case, it was verified that the computed plate
height approximated the theoretically expected B-term contribution ($h_B = 1.242/v$ for the considered case of $\varepsilon=0.40$ [27]) to within 0.3% over the entire range of investigated velocities.

3. Results and discussion

3.1 Dispersion in 2D pillar array columns (non-porous, non-retentive pillars)

Fig. 1 shows the velocity contour plots in a pressure-driven flow through a 2D pillar array with no-slip conditions at the wall of the pillars. As a consequence of the latter, the velocity drops to zero close to the pillar walls (cf. blue colored areas). Note the dashed black horizontal line represents the inner symmetry line of the represented unit cell. Given this symmetry, only the upper (or the bottom) half of the represented geometry needs to be considered to compute the effective band broadening for any given array width (save the side-wall effects at the extremities of the bed [21], which have been excluded in the present study).

As indicated, the velocity field is marked by a repetitive alternation of identical velocity bias zones with alternating sign (cf. regions marked by “fast” and “slow” in Fig. 1). As such, the system fits the description of the checkerboard pattern considered in part I. The represented geometry in fact covers two consecutive double-velocity bias unit cells (2VB-cells in the nomenclature of part I), separated by the vertical dashed line running through the middle of the represented geometry. Another correspondence with the checkerboard model is that there is also a persisting preferential flow path (cf. black arrowed curve), composed of the streamlines that are on average most remote from the pillar walls and their flow arresting effect. Consequently, the velocity along this central flow path is larger than in the streamlines running on average closest to the pillar walls. A difference with the checkerboard model as depicted in Fig. 1 of part I is that the VB-zones in the present case are not immediately connected but are interspersed by a zone where the average velocity on each side of the preferential flow path is equal, and hence do not display a velocity bias. These zones are indicated by the letters A and B in Fig. 1 and correspond to the zones where both sides of the representative flow-through pore are bound by a solid pillar wall.

Fig. 2 shows the evolution of the $h-h_B$-values as a function of the reduced velocity $v$ as computed in a 2D-pillar array with the same pillar arrangement as in Fig. 1, but in a flow domain that was 50 times longer than the unit cell shown there. The $h$-values were calculated using $h=H/d_p$ with $d_p=2\mu m$. The $h_B$-values were taken from the theoretically known B-term plate height for 2D-pillar arrays. An analytical expression for these values is given by Eq. (14) in [27] with $\zeta_2 = 8.07 \times 10^{-3}$, an expression that has been confirmed by CFD-simulations in the same study. Note the data are plotted as $h-h_B$, rather than in the more commonly $h$-format, to maximize the view on the dispersion sources coming from the velocity field as well as to point out the high accuracy of the data, as the $h-h_B$-curve clearly tends to zero as theoretically expected and this is only possible if $h$ is known with a very high accuracy [28].
Around $\nu=5$, the data clearly reveal a distinct local dispersion maximum. As argued in part I, this points at a system where the unit dispersion cell comprises two VB zones, with a significant band broadening compensation in the second half of the unit cell. Considering the velocity field in Fig. 1, this indeed agrees with the actual physical situation. This local maximum was not observed in our earlier CFD work [20,25,29], but became apparent here due to the much higher degree of discretization (factor of 5 higher density of grid cells) that can be afforded with the computational power that is nowadays available.

As can be noted from the good fit in Fig. 2, Eq. (3) allows to closely represent the observed complex eddy-dispersion behavior, especially considering the fit runs over a very large range of $\nu$-values (up to $\nu=250$). Please note that, given the dispersion system is limited to a single flow-through pore, we have in this case $D_{\text{trans}}=D_{\text{mol}}$, such that $\gamma_{\text{eff}}=1$ and $\beta=0$ in Eq. (4), which also implies that here $\nu_r=\nu$ in Eq. (3).

For what concerns the terminology of the different contributions, it seems appropriate to identify the degree of eddy-dispersion in the cylindrical pillar array exclusively with the $h_{\text{checker}}$-part of Eq. (3) because the $h_{\text{pref}}$-part of this expression (=second term on r.h.s.) can be considered as a classical C-term contribution, originating from the parabolic flow that is established in the through-pores. Although some might argue that the pillar array is a perfectly ordered system, and should hence not produce any eddy-dispersion, it cannot be negated that the velocity field displays a clear spatial heterogeneity, even though this is a repetitive one. And this local heterogeneity obviously induces an extra dispersion, displaying the unusual property of going through a sharp maximum before returning to zero at large $\nu$ as accounted for by the $h_{\text{checker}}$-part of the checkerboard-model.

3.2 Dispersion in 2D ordered checkerboard medium

Fig. 3 shows images of a species band progressing through the representative axial unit cell of a perfectly ordered checkerboard flow-through medium. Conditions are given in the figure caption. Important to remark is that a significant part of the observed band broadening is due to the longitudinal diffusion, partly obscuring the eddy-dispersion effects. Nevertheless, the first frame in Fig. 3a clearly show how first the bottom half of the injected band is pulled forward, as this part resides in a high velocity zone, whereas the upper half of the band passes through a low velocity zone and is hence retarded with respect to its lower half. Next (Fig. 3b), the retarded fraction in the top half of the geometry has nearly perfectly caught up with the bottom part of the band, after both band parts have passed through a new VB zone with opposite sign. This process is then repeated in the next parts of the geometry. The species contour plots in Fig. 3 also clearly reveal the parabolic flow profile of the preferential flow path meandering back and forth across the axial VB split line (cf. white tilted arrows added to Fig. 3c). The dashed meandering line in Fig. 3d has been added to accentuate this preferential flow path and its meandering movement.
Fig. 4 shows how the local plate height (corrected for the contribution of longitudinal diffusion) typically varies with the distance along the x-axis for a variety of different fluid velocities. In case of the highest velocities (black and red curves), the H-Hₚ-curve displays the most pronounced oscillation, decaying only rather slowly as it persists over a length of about 10 VB zones. The period of the oscillation is 80μm, which corresponds to the length of 2 consecutive VB zones. This reflects the fact that, over a period of two consecutive VB zones, the band first stretches (going from point A to B in Fig. 4a) in the first VB zone and then compresses again (going from point B to C) in the second VB zone as in this zone the VB has an opposite sign. The fact that this compensating effect is so strongly apparent in the black and red curves in Fig. 4 is because the majority of the species stays on the same side of the axial VB split line at the high velocities for which these curves have been recorded (residence time in given VB zone is too short to allow for a significant degree of transversal diffusion or dispersion). In case of the smaller velocities (cf. blue and green curves in Fig. 4), the species have more time to move across the axial VB split line such that only a fraction of the species is subjected to the compensating effect experienced by the band when moving from one VB zone to a next zone with opposing sign. Consequently, the oscillations fade out more rapidly.

At first sight there appears no direct correlation between the fluid velocity and the vertical position of the curves in Fig. 4 but this changes when the long-time limit H-Hₚ-values results are plotted as a function of the reduced velocity (see Fig. 5). This plot reveals the eddy dispersion again clearly goes through a local maximum, as was the case in the ordered pillar array and as was predicted in part I for a system with a distinct checkerboard velocity distribution.

The dashed line added to Fig. 5 represents the (v,h)-relationship predicted by Eq. (3), using the A- and C-constant values predicted by Eqs. (7-8). For the considered permeability distribution, it was already found in part I that, in case of the presently considered geometry and permeability pattern (cf. Fig. 3), the average velocity in the low and the high permeability region respectively equal \( u_1 = 0.958u_{av} \) and \( u_2 = 1.042u_{av} \). This implies the relative velocity difference to be used in Eqs. (7-8) is given by \( \Delta v/v = 0.084 \).

Inserting this value in Eq. (7) together with \( \lambda_{av} = \gamma_{av}/d_p = 10 \), we get \( A = 0.0176 \). For the C-term constant, inserting the given \( \Delta v/v \)-value together with \( \gamma_{trans} = 1 \) and \( \lambda_{trans} = \delta_{trans}/d_p = 10 \) into Eq. (8) predicts a value of \( C = 0.0586 \). Note also that that the zone retention factor \( k'' \) in the \( (1+k'') \)-factor appearing in Eq. (8) is taken as \( k'' = 0 \) because our simulations relate to non-retained species. This however does not affect the general applicability of the work, because the simulation occurs at a zoomed-out level (multi-particle scale) such that the velocity we observe is anyhow the actual velocity of the species, independently whether the species is retained or not at the microscopic level.

Considering the prediction of \( C_{pref} \), it is unfortunate that it is very difficult to accurately determine the relative velocity difference between the preferential flow path and the rest of the bed. This requires a more elaborate and in-depth study covering a broad variety of geometries. At present, we can only
make some crude estimates. Estimating from Fig. 3 that the preferential flow path takes up about 10% of the VB-region ($\alpha_{\text{pref}}=0.1$) and assuming that $\Delta v_{\text{pref}}=0.05$, Eq. (b3) returns a value of $C_{\text{pref}}=3.8 \times 10^{-4}$.

As can be noted from the dashed line curve in Fig. 5, the above generated a priori calculations of $A$, $C$ and $C_{\text{pref}}$ generate a model prediction that is qualitatively already of the right form, clearly predicting the occurrence of a local dispersion maximum, and already providing a relatively close prediction of the order of magnitude of the height and the position of this maximum, albeit that the height of the maximum is about a factor of 2 off.

Using Excel’s solver function to obtain the best fit between the CFD data and Eq. (3) leads to: $A=0.010$, $C=0.016$ and $C_{\text{pref}}=3.55 \times 10^{-4}$. With these values, a very good agreement with the computed data is obtained (cf. full model line in Fig. 5). Apparently, the A-value predicted by Eq. (7) is off by some 70%, while the C-constant predicted by Eq. (8) is off by a factor of about 4. The value for $C_{\text{pref}}$ predicted by Eq. (9) on the other hand was already close to the best-fit value ($3.8 \times 10^{-4}$ versus $3.55 \times 10^{-4}$). Finding the origin of these deviations and ways to improve the a priori prediction for the model constants will be the subject of a broader follow-up study, involving a broader range of geometries.

### 3.3 Dispersion in 2D random checkerboard medium

It is obviously highly unlikely the permeability distribution in real packed bed or an in-situ synthesized monolithic packing will display a perfectly repetitive checkerboard pattern as considered in the previous Section. Instead, it is much more straightforward to expect a random distribution of the permeabilities.

To investigate the effect of such a random distribution, we also performed a series of simulations at different velocities in the same type of rectangular grid as shown in Fig. 3, but now with a randomly assigned permeability in each of the different zones. The assignment was done using Excel’s uniform probability random number generator, drawing permeabilities in an interval of $\pm 10\%$ around the average of the permeability values taken for zones 1 and zone 2 in the ordered checkerboard case considered in Fig. 5 (see caption for average $K_v$-values). An example of the resulting velocity field is represented in Fig. 6. Note that only a fraction (about $1/3^\text{rd}$) of the total flow domain is shown. In total, this was 70 VB units long.

Fig. 7 shows the variation of the local eddy-dispersion plate height ($H-H_B$) with the distance in the random checkerboard medium is again strongly oscillatory (especially at high $v$), similar to the ordered checkerboard case in Fig. 4. Instead of having a clear periodicity, the pattern is now erratic and random, as a direct reflection of the underlying random permeability distribution.

The fact that the curves for the different $v$ in Fig. 7 do not have the same length and have different starting and ending points is because the starting position of the band in our computations was optimized to avoid diffusion leakage of the “injected” species through the inlet plane of the flow geometry. The higher $v$, the faster the peak leaves the region close to the inlet boundary and hence the
closer to this inlet the band can be “injected” without risking to lose a significant part of the species diffusing out of the flow domain through the inlet. A similar consideration was made at the outlet boundary.

Just as for the ordered checkerboard case, it can again be clearly observed how the amplitude of the oscillations increases with increasing $v$, i.e., with increasing fluid velocity and/or decreasing diffusion. This concurs with one’s physical expectations, as these conditions imply a reduced lateral equilibration between the species travelling on each side of the axial VB split line, hence allowing for a more pronounced contribution of the VB effects. It can also be noted the global average of the local $H-H_B$ values for the $v=6.4$-case is slightly lower than that for the $v=1.2$-case (an exact readout-out of the corresponds to $H-H_B=0.0179\mu m$ at $v=6.4$ and $H-H_B=0.0184\mu m$ at $v=1.2$). This again points at a (slight) reduction of the dispersion at higher $v$, as was observed in the perfectly ordered case in Section 3.2. A more complete set of plate height data is shown in Fig. 8, now plotted as a function of the different considered $v$-values. Again, this reduced plate height curve goes through a maximum, albeit it a very weak one and much less pronounced than in the perfectly ordered case in Section 3.2. However, it is preferred here not to overinterpret this finding as this still needs to be confirmed for other permeability patterns and in longer flow domains, comprising a larger number of VBs.

What is irrefutably clear from Fig. 8 is that the eddy-dispersion in the random checkerboard medium is much stronger than in the perfectly ordered case. This seems in agreement with the fact that the possibility for an immediate and perfect VB rectification is inevitably lost in case of a random VB distribution. Consequently, the VB rectification step will either be under- or over-compensating the preceding VB, and both cases can be expected to lead to an increase in dispersion.

4. Conclusions

The new eddy-dispersion model presented in part I of the present study is capable of representing the occurrence of a local maximum in the $(v,h_{eddy})$-curve. This maximum appears to be characteristic for ordered 2-D chromatographic media and has been observed for the first time in the present study. Combining this capability of the checkerboard eddy-dispersion model with the fact that the model can also represent the typical Giddings-like behavior in highly disordered media (monotonous increase of $h_{eddy}$ with $v$ to level off to $h_{eddy}=A$ at high $v$, cf. Section 4.2 in part I), it can be concluded the newly proposed checkerboard eddy-dispersion model is capable of representing the eddy-dispersion in both ordered as well as in disordered systems. To the best of our knowledge, this is the first time such a comprehensive model has been established and validated against high-accuracy dispersion data. In the future, it will be interesting to investigate whether the checkerboard model can describe the transition between the different degrees of disorder by just varying the model constants.
More research is also needed to obtain better estimates for the A- and C-term constant, or to introduce
other or more elaborate coupling and transition schemes between the different VB steps. For example,
there is no proof the expression for the (1-f)-factor given in Section 3.2 of part I does not require an
additional geometrical factor in the argument of the exponential function, nor can it be excluded a more
correct model could be obtained when accounting for the possibility the species can change VB zone
more than just once during their passage through the checkerboard model unit cell. To better
understand these aspects, a more elaborate study on a broader variety of different, and more complex
random checkerboard geometries is needed. In addition, the study also absolutely needs to be extended
to 3-D flow geometries to gain more relevance. Nevertheless, it can be expected the general notion of a
VB-rectifying effect between consecutive VB zones will also be present in 3D. And again, the effect will
be most pronounced in systems with a high structural repetitiveness.

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**Figure Captions**

**Figure 1.** CFD-computed velocity distribution in a perfectly ordered 2D pillar array bed (non-porous, non-retentive pillars). External porosity $\varepsilon=0.4$, $d_p=5\mu m$, $u=3mm/s$. Colour scale varies linearly with local velocity magnitude (highest=red). See text for discussion of dashed black lines and meaning of A and B. Black tortuous line with arrows represent the course of the preferential flow path.

**Figure 2.** Variation of reduced plate height $h-h_B$ (=representing band broadening after correction for longitudinal diffusion) with reduced velocity for a flow through a perfectly ordered 2D pillar array bed (non-porous, non-retentive pillars). Full symbols: data points computed via CFD. Full line: curve represented by checkerboard model (Eq. 3), with $A=0.21$; $C=0.042$; $C_{pref}=1.07 \times 10^{-3}$.

**Figure 3.** Species contour plots of a species band progressing through the representative axial unit cell of a perfectly ordered checkerboard flow-through medium taken at (a) $t=0.9ms$, (b) $t=2.6ms$ (c), $t=5.0ms$, (d) $t=7.5ms$, (e) $t=10.9ms$. Size of velocity bias zones=20$\mu m \times 20\mu m$ (transversal width). Zone permeability ratio=1.2 ($K_{v1}=1.43 \times 10^{-14} m^2$; $K_{v2}=1.19 \times 10^{-14} m^2$). Peclet number $Pe=16$ based on $d_p=2\mu m$. Total domain length= xxx m (only xxx m represented). Dashed meandering line: see text. Tilted arrows added to (c) to point at tip of parabolic velocity profile across preferential flow path.

**Figure 4.** Variation of local plate height $H-H_B$ (=eddy-dispersion band broadening) as a function of the elapsed distance for 4 different velocities: $u=3.0 mm/s$ ($v=6$, black curve), $u=1.5 mm/s$ ($v=3$, red curve), $u=0.35 mm/s$ ($v=0.7$, blue curve) $u=0.1 mm/s$ ($v=0.2$, green curve). $D_{mol}=1.10 \times 10^{-9} m^2/s$. Same geometry and permeability pattern as in Fig. 3. Zone permeability ratio=2. See text for discussion of points A, B, C.

**Figure 5.** Variation of plate height $h-h_B$ (=eddy-dispersion band broadening) as a function of the reduced velocity for a laminar flow through a perfectly ordered checkerboard flow-through medium. Full symbols: data points computed via CFD. Dashed line: curve represented by checkerboard model (Eq. 3), with $A=0.0175$; $C=0.0234$; $C_{pref}=3.8 \times 10^{-3}$. Full line: model curve with $A=0.0175$; $C=0.0234$; $C_{pref}=3.55 \times 10^{-3}$. Same geometry as in Fig. 3. Zone permeability ratio=1.2 ($K_{v1}=1.43 \times 10^{-14} m^2$; $K_{v2}=1.19 \times 10^{-14} m^2$).

**Figure 6.** Velocity distribution in random checkerboard produced with random porosity fluctuation. Average in low permeability zone: $K_{v1}=1.19 \times 10^{-14} m^2$; average in high permeability zone: $K_{v2}=1.43 \times 10^{-14} m^2$. Color scale varies linearly with local velocity magnitude (highest=red).

**Figure 7.** Variation of local plate height $H-H_B$ (=eddy-dispersion band broadening) as a function of the elapsed distance for 3 values of the $D_{mol}$-based reduced velocity: $u=0.2mm/s$ ($v=0.4$, red curve), $u=0.6mm/s$ ($v=1.2$, black curve), $u=3.2mm/s$ ($v=6.4$, blue curve). Data obtained on same geometry and permeability pattern as in Fig. 6. $D_{mol}=1.10 \times 10^{-9} m^2/s$. 


Figure 8. Variation of reduced plate height $h-h_b$ (=representing eddy-dispersion band broadening after correction for longitudinal diffusion) as a function of the reduced velocity $v$ for a laminar flow through a checkerboard medium with random porosity fluctuation (red circles). Data obtained on same geometry and permeability pattern and for same conditions as in Figs. 6-7. Full line: model curve with $A=0.0175$; $C=0.0234$; $C_{\text{pref}}=3.55 \times 10^{-3}$. Blue data points and dashed lines taken from Fig. 5 for comparison purposes.
Figure 4