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Abstract

The additivity assumption underlying Giddings’ coupling model for the eddy-dispersion in laminar flows through heterogeneous media is critically analyzed and a potential solution for its non-additivity in the high velocity limit is presented. Whereas the unit cell in Giddings’ model only consists of a single velocity bias step, the unit dispersion cell of the newly proposed model comprises two consecutive velocity bias steps. Consequently, the unit cell of this new model allows to account for the occurrence of an internal velocity bias rectification at high reduced velocities and is therefore additive in both the low and high velocity limit.

First, a mathematical expression for the velocity- and diffusion-dependency of the model’s dispersion characteristics has been established. Subsequently, the physical behavior of the model is discussed. It is shown the relation between the eddy-dispersion plate height \( h \) and the reduced velocity \( v \) can be expected to display a local maximum in systems where the transversal dispersion purely occurs by molecular diffusion, as is the case in perfectly ordered flow-through media. In disordered media, where the transversal dispersion also contains a significant advective component, the model predicts a velocity-dependency that is qualitatively similar to that described by Giddings’ coupling model but, all other conditions being equal, converges to a significantly smaller horizontal asymptote at high reduced velocity. The latter might shed new light on earlier eddy-dispersion studies pursuing a quantitative agreement between experimental data and the Giddings model.

1. Introduction

The modeling of the axial dispersion or band broadening in packed bed columns for liquid chromatography is a difficult problem, due to the inevitable heterogeneity of the packing, the laminar nature of the flow and the occurrence of a phase equilibrium between the particles and the surrounding mobile phase [1-5]. Because of this complexity, the initial attempts [6-7] to establish an analytical expression for the relation between the band broadening and the velocity of the mobile phase and the diffusivity and retention factor of the analytes were based on the (strongly) simplifying assumption that the bed can be represented by a system of two adjacent parallel plug flow zones, both remaining in contact with each other over the entire length of the bed, with one zone representing the particle zone and the other zone representing the mobile phase in the flow-through pores between the particles [8].

This geometrical representation is simple enough to be amenable to an analytical solution, as was demonstrated by Lapidus & Amundson, van Deemter, Kucera, Huber, and others [1,3,6,7,9]. This analytical solution, and its dependency on the retention coefficient and the mobile phase velocity, corresponds to what is today known as the B- and C-term appearing in the general rate model for packed bed columns [10].

To account for the effect of the bed heterogeneity on the multi-particle scale, the general rate model has been extended with a so-called eddy-dispersion term, a term whose contribution and modelling is as of today still the focus of a considerable debate [11-13]. The eddy-dispersion term was originally also
referred to as the mechanical dispersion \[2\] term, to express that this was a term calculated by
neglecting the occurrence of transversal diffusion or dispersion. This approach was first adopted by van
Deemter \[7\], leading to his famous A,B,C-term equation. Later, van Deemter’s approach was corrected
by Giddings \[1,14\], who showed in a very elegant way that the band broadening contribution of the
resistance to transversal mass transfer and the mechanical dispersion originating from a given velocity
bias (VB) should be combined harmonically, leading to his famous coupling equation \[1,15-16\]:

\[ h_{\text{Gidd}} = \left( \frac{1}{A} + \frac{1}{C \cdot \nu} \right)^{-1} \]  \hspace{1cm} (1)

with \( \nu = u \cdot d_p / D_{\text{mol}} \) in engineering literature generally referred as the Peclet-number \( \text{Pe} \) \[17\].

In \[18\], it was shown that it is mathematically more exact and physically more sound to replace the
harmonic coupling proposed by Giddings by an exponential decay coupling, because the latter
automatically emerges as a factor when solving the dispersion in a velocity bias zone with finite length
using the Taylor-Aris theory. The core solution to this problem, describing the local plate height, can be
written as \[18\]:

\[ h_{\text{FPZ,loc}} = h_\infty \cdot \left[ 1 - e^{-\ell / (t_{\text{diff}} u)} \right] \]  \hspace{1cm} (2)

wherein \( h_\infty \) is the solution for the infinite parallel zone model (see \[8\] for general and explicit
expressions for \( h_\infty \)) and wherein the factor between brackets represents the exponential decay coupling
function. Further, \( \ell \) is the axial length of the velocity bias zone and \( t_{\text{diff}} \) is the characteristic time for
lateral diffusion across the lateral width of the velocity bias zone. General and explicit expressions for
\( t_{\text{diff}} \) are respectively given by Eq. (7) of \[18\] as well as in the supporting material of the same reference.

This model has been termed the “finite parallel zone (FPZ)"-model, to emphasize that it relates to a
model assuming velocity biases (VB) with finite length, in contrast with the (infinite) parallel zone model
\[8\] leading up to the \( C_m \)- and \( C_s \)-term in the general plate height model. Advantages of the FPZ-model
over the Giddings model are: \( i \) it more accurately accounts for the diffusive nature of the coupling
between the A- and C-constant mechanisms, \( ii \) it produces expressions for the A- and C-constants that
contain an explicit dependency on the differences in packing density and phase ratio between the
different VB-zones and \( iii \) the same general expression holds for all possible VB scales, while Giddings’
model becomes a too crude approximation for VBs spanning the entire trans-column scale.

Eq. (2) is however not the required eddy-dispersion solution yet, as it only describes the local or
instantaneous degree of band broadening, whereas the pursued expression should be the total band
broadening accumulated at the end of a given VB. This is obtained by averaging Eq. (2) over the total
axial length \( \ell \) of the VB:

\[ h_{\text{FPZ}} = h_\infty \cdot \left[ 1 - \frac{t_{\text{diff}} \cdot u}{\ell} \cdot (1 - e^{-\ell / (t_{\text{diff}} u)}) \right] \]  \hspace{1cm} (3)
As shown in [18], Eq. (3) can also be rewritten in terms of the same type of A- and C-constants as used in
the Giddings model:

$$h_{FPZ} = C v \left[ 1 - \frac{C v}{2A} \left( 1 - e^{-2A/(C v)} \right) \right]$$  (4)

wherein $A$ is the limiting value of $h_{FPZ}$ for large $v$ (i.e., for $v \gg \lambda_{ax}/\tau_{diff}$):

$$h_{FPZ}(v \to \infty) = A = 2\alpha \Delta v^2 \lambda_{ax}$$  (5)

and wherein $C.v$ is the limiting value of $h_{FPZ}$ for small $v$ (i.e., $v << \lambda_{ax}/\tau_{diff}$):

$$h_{FPZ}(v \to 0) = C.v = \alpha \Delta v^2 \tau_{diff}$$  (6)

In these expressions, $\alpha$ is a geometrical constant (cf. [18]), $\lambda_{ax}$ is the dimensionless axial length of the VB
zones ($\lambda_{ax} = \theta/d_p$) and $\tau_{diff}$ is the dimensionless characteristic time for lateral diffusion across the VB
zones, defined as $\tau_{diff} = \tau_{diff} D_{mol}/d_p^2$ (see [18] for more detailed expression for $\tau_{diff}$).

When using the same A- and C-constants, the Giddings and FPZ-models perfectly overlap in the low and
high $v$-asymptote, while the main difference between the two models is situated around the $v=2A/C$-
point [18]. The model in Eq. (3) bears a clear resemblance with the Gunn-model traditionally used in
chemical engineering [17], so that it can be concluded the FPZ-model makes the bridge between the
Giddings model used in chromatography and the Gunn-model used to describe packed bed reactors
[16].

Explicit expressions for A and C for the different possible velocity bias levels are given in [18] and in part
II. Adopting Giddings’ classification [1], these levels involve the single through-pore and particle level
(level=1), the transcolumn-level (to capture radial velocity differences spanning the entire column cross-
section) as well as one or more multi-particle levels (often referred to as short-range and long-range
levels). Finally, there is also the transcolumn velocity-level (level N) accounting for the fact that some
radial packing density differences (cf. the side-wall effect) persist over the entire column length [12]
[19]. In sum, these different contributions make up the overall eddy-dispersion plate height $h_{eddy}$ [1]:

$$h_{eddy} = \sum_{j=1}^{N} h_{eddy,j} = \sum_{j=1}^{N} h_{FPZ,j}$$  (7)

wherein $N$ is the number of levels to be taken into account (Giddings suggested that typically $N=5$) and
wherein each $h_{eddy,j}$-term is given by an expression of the form of Eq. (1) or (4).

The problem addressed in the present study (cf. Section 2), i.e., the additivity of the variances of the
individual velocity bias steps underlying the calculation of the $h_{eddy,j}$-values pertains to all levels, except
for the transcolumn level. The velocity bias at this level generally covers the entire column length, such
that a summation over several zones is not needed.

2. The axial additivity problem

It is a well-established fact that the total dispersion variance generated in a flow system consisting of a
series connection of different sub-systems can only be obtained by summing the variances of the
individual sub-systems, if, and only if, the dispersion in these sub-systems is independent of each other [1,2,20]. In a packed bed, this requires that the velocity bias (VB) experienced by a group of species in a particular zone should be independent of the VB they experienced in the preceding zone. In turbulent flows, this condition is easily satisfied, because the random temporal fluctuations of the velocity field make the species to very rapidly "forget" completely about their past velocity history. In steady-state laminar flows, however, the velocity streamlines are fixed in time and the species are bound to stay on these streamlines, at least in the absence of any significant diffusion. In the latter case, species flowing through a given velocity zone do so because they were already on that streamline in the preceding VB zone. This implies that, in this case, the velocity experienced by the species in the given zone depends on velocity experienced in the preceding zone, thus violating the aforementioned condition.

The consequence of this dependence is that the band broadening variance experienced in the different zones cannot just simply be added, implying that the most important premise in the Giddings or FPZ-model is not satisfied at high \( \nu \) under the laminar flow conditions that prevail in liquid chromatography. A simple way to demonstrate this is by considering the simple binary VB distribution shown in Fig. 1a. Whereas this distribution is certainly hypothetical and highly idealized, it can nevertheless be considered as a relevant first-order approximation of the physical reality, as a real column packing anyhow consists of a patchwork of zones with alternating high and low packing density, and hence also with an alternating low and high velocity.

The representative axial unit cell in this flow geometry is delineated by the red dashed box added to Fig. 1a. This unit cell covers the total length of the bed and determines the total eddy-dispersion contribution of the entire bed, because this will behave as a parallel bundle of these unit cells. The symmetry condition \( \partial C/\partial y = 0 \) applies on both axially-oriented side walls of the unit cell). Note that, as a consequence of this symmetry, the representative unit cell only occupies half the height of a VB zone.

Let us now first consider the dispersion in this axial unit cell for the case of a strong lateral diffusive exchange. This situation, represented in Fig. 1b, prevails in the case of sufficiently narrow and long VB zones and/or a low average velocity and/or high transversal dispersion, i.e., for \( \tau_{\text{diff}} \gg \lambda_{ax} \). Because of the intense lateral equilibration, there is in this case no difference in average migration speed between the high and low velocity zones. It is hence irrelevant whether a molecule is leaving a high or a low velocity zone when starting its journey through the next VB zone. I.e., the dispersion that will be experienced in this next zone is completely independent from the velocity history experienced in the previous zone. Under these conditions, the dispersion variance \( (\sigma_{1VB-UC}^2) \) acquired in each of the subsequent zones can be directly added, as is assumed in the Giddings and FPZ-model:

\[
\sigma_{tot}^2 = \sigma_{1VB-UC}^2 (\ell) + \sigma_{1VB-UC}^2 (\ell) + \ldots + \sigma_{1VB-UC}^2 (\ell) = \sum_{i=1}^{n} \sigma_{1VB-UC}^2 (\ell) = n \sigma_{1VB-UC}^2 (\ell) \tag{8}
\]

wherein \( \ell \) is the length of a single VB-zone, depicted by the black rectangular box denoted "1VB-Unit Cell" in Fig. 1a, and wherein further \( n = L/\ell \) and:

\[
\sigma^2 (\ell) = H_{1VB-UC} \cdot \ell, \tag{9}
\]
wherein $H_{1\text{VB-UC}}$ is in turn the plate height obtained when using a single VB step as the unit cell for the eddy-dispersion. Expressions for $H_{1\text{VB-UC}}$ are obtained by equating it to either $H_{\text{Gidd}}=h_{\text{Gidd}}d_p$ or $H_{\text{FPZ}}=h_{\text{FPZ}}d_p$, using the expressions given in Eq. (1) and (4).

Next, let us consider the case of a very low degree of transversal dispersion, occurring when the VB zones are very wide, or in case of a low degree of transversal dispersion and/or a high average velocity. In these cases, $\tau_{\text{diff}} \gg \lambda_{\text{ax}}$, and there is ample or no time for a radial diffusive exchange between the two zones of the VB. As such, the species are likely to stay on the same side of the axial VB division line (cf. white dashed line added to Fig. 1a and black dashed line added to Figs. 1b-c) and will continue to do so over a very long distance (extending to infinity when $v$ tends to infinity). In this case, as is represented in Fig. 1c, species starting on the same line at $x=0$ will have undergone a clear separation in two groups when reaching the end of the first velocity bias zone (i.e., at $x=\ell$) because the species in the upper half move slower than those in the bottom half (note the assumption of a high $v$ in combination with the assumption that the velocity in each zone is radially uniform also implies the longitudinal dispersion is minimal, hence the absence of any increase in axial width of the band segments represented in Fig. 1c). However, in the next VB step, the species above the axial split line will move faster and are therefore able to catch up with the species below the axial split line by the time they have reached the end of the second velocity bias zone (i.e., at $x=2\ell$). This shuffling process continues in the subsequent VB-zones, with the even numbered zones perfectly countering the dispersion created in the odd numbered zones, such that the total variance obtained at the end of the column can be written as:

$$\sigma_{\text{tot}}^2=\sigma_{1\text{VB-UC}}^2(\ell)-\sigma_{1\text{VB-UC}}^2(\ell)+\sigma_{1\text{VB-UC}}^2(\ell)-\sigma_{1\text{VB-UC}}^2(\ell)+\cdots+\sigma_{1\text{VB-UC}}^2(\ell)-\sigma_{1\text{VB-UC}}^2(\ell)=0$$

(10)

Eq. (10) obviously does not represent an addition, but an alternating series of additions and subtractions, leading to a zero sum.

As such, this simple example shows that the dispersion in the individual VB zones is not additive, at least not in the high $v$-limit, i.e., for $v\gg\lambda_{\text{ax}}/\tau_{\text{diff}}$. As a side note, it can be remarked that this sum is not strictly equal to zero in case of an uneven number of VB-zones, given the presence of one residual $\sigma^2(\ell)$-value that is not compensated for in an ensuing VB-zone. However, this value remains negligible compared to the overall variance that would be obtained when simply adding the variances of the different zones as is assumed in Eq. (8) and can hence still be approximated as being equal to zero.

The fact that $\sigma_{\text{tot}}^2=0$ for the situation in Fig. 1c also implies the additivity underlying the Giddings or FPZ-model (cf. Eq. 8) is clearly invalid in the high $v$-limit of laminar flows through media with fluctuating VB zones. The reason for this invalidity is that these models are based on a dispersion unit cell that only consists of a single velocity bias zone (cf. the “1VB-Unit Cell” in Fig. 1a) and that the dispersion in this type of unit cells is clearly not additive at large $v$. 

3. Double velocity-bias unit cell for dispersion (checkerboard unit cell)

3.1 Physical description

One of the simplest conceivable solutions to construct a model where the dispersion in the subsequent unit cells would be additive, at least in the two asymptotic v-ranges, consists of defining a unit cell consisting of two consecutive velocity bias zones instead of only one. This double velocity bias cell is represented by the black rectangular box denoted “2VB-Unit Cell” in Fig. 1a. In the low v-range, the velocity history is anyhow already forgotten within the span of the first of the two VB zones by virtue of the strong lateral diffusion and/or long residence times, such that the “forgetting” condition will automatically also be satisfied at the end of the double VB-zone. In the high v-range, lateral diffusion and/or the residence time are so small that species do not have the time to cross the axial VB split line. Given the opposite signs of the VB in the first and second half of the 2VB-cell, species entering the unit cell via a low velocity zone can make up their delay in the second half of the unit cell and will again perfectly align with the species moving on the other side of the axial VB split line after having reached the end of the double VB-unit cell (cf. Fig. 1c). This realignment is equivalent to stating that the species have forgotten about their dispersion history, which is exactly the condition required for the dispersion in the different unit cells to be additive.

It further seems a plausible hypothesis that, given the independency in both asymptotes, the additivity of the different two-VB unit cell dispersion cells will at least also be a good approximation in the intermediate range of v-values, such that we can now write for the general case:

\[ \sigma^2_{\text{tot}} = \sum_{i=1}^{\frac{n}{2}} \sigma^2_{\text{2VB-UC}} = \frac{n}{2} \sigma^2_{\text{2VB-UC}} \]  

(11)

wherein \( \sigma^2_{\text{2VB-UC}} \) is the variance acquired over the distance of a unit dispersion cell that is two VBs long.

3.2 Mathematical expression for dispersion in double VB (2VB-)cell

The next problem to be faced is to find a suitable expression for the \( \sigma^2_{\text{2VB-UC}} \) term appearing in Eq. (11). This can be done as follows. With reference to Fig. 2a, it can be inferred a given fraction f of the species will not have had the time to diffuse to the other side of the VB when having reached the end of the 1st half of the unit cell. This species fraction will hence follow the straight running red arrows added to Fig. 2a and as such will enter a velocity zone with opposing velocity when moving to the 2nd half of the dispersion cell. In other words, a fraction f of the species experiences the velocity pattern depicted in Fig. 2b, for which the resulting variance is, following Eq. (10), given by:

\[ \sigma^2_{\text{2VB-UC}} = 0 \]  

(12)

The other part of the species (fraction 1-f) will have had the time to diffuse to the other side of the VB (cf. bended red arrows added to Fig. 2a) and will hence enter a velocity zone with opposing velocity when entering the second half of the dispersion cell. This fraction will hence experience the velocity
pattern depicted in Fig. 2c, i.e., it will experience the same degree of dispersion as typical for a single VB-
cell, albeit one with length $2\ell$ in this case:

$$\sigma_{2\text{VB-UC}}^2 = \sigma_{1\text{VB-UC}}^2(2\ell) \quad (13)$$

To calculate the right-hand side of Eq. (13), we can write:

$$\sigma_{1\text{VB-UC}}^2(2\ell) = H_{1\text{VB-UC}}(2\ell).2\ell, \quad (14)$$

wherein $2\ell$ is the length of the dispersion unit cell and wherein the notation $H_{1\text{VB-UC}}(2\ell)$ is used to point
out that the A appearing in the expressions for $H_{1\text{VB-UC}}$ (cf. Eqs. (1 and 4) should be replaced by $2A$, given
that now the unit dispersion cell is twice as long as in the single VB-unit cell, and given that A is
proportional to the length of the unit cell (cf. Eq. (5) where now $\lambda_{ax}=2\ell/d_p$ instead of $\lambda_{ax}=\ell/d_p$ in the
1VB-cell models).

Adding the contributions from both fractions using Eqs. (12-13), the final variance gained by the
dispersion in a single 2VB-cell can now be written as:

$$\sigma_{2\text{VB-UC}}^2 = \sigma_{1\text{VB-UC}}^2(2\ell).(1-f) + 0.f = \sigma_{1\text{VB-UC}}^2(2\ell).(1-f) \quad (15)$$

To establish an expression for $f$, it should be considered that the fractions $f$ and $1-f$ are fully controlled
by the degree of lateral diffusion. A good estimate for the fraction $(1-f)$ that has had the time to move
sides is therefore the exponential decay function appearing in the single-VB cell FPZ-model (Eq. 2):

$$1 - f = 1 - e^{-f/(t_{\text{diff-u}})} = 1 - e^{-\lambda_{ax}/(t_{\text{diff-u}})} = 1 - e^{-A/(C,v)} \quad (16)$$

Note that the last equality is obtained by using the expressions in Eq. (5) and (6).

Finally combining Eqs. (4), (14), (15) and (16), and inserting the result into Eq. (11), we obtain:

$$\sigma_{\text{tot}}^2 = \frac{n}{2} 2\ell \cdot d_p \cdot C_v \left[ 1 - \frac{C_v}{4A} \cdot \left( 1 - e^{-\frac{4A}{C_v}} \right) \right] \cdot \left( 1 - e^{-\frac{A}{C_v}} \right) \quad (17)$$

which finally reduces to:

$$h_{\text{checker}} = C_v \left[ 1 - \frac{C_v}{4A} \cdot \left( 1 - e^{-\frac{4A}{C_v}} \right) \right] \cdot \left( 1 - e^{-\frac{A}{C_v}} \right) \quad (18)$$

wherein $h_{\text{checker}}$ is the reduced plate height contribution originating from a pure checkerboard velocity
distribution such as the one depicted in Fig. 1a.

Although its underlying assumptions are still very crude, Eq. (18) at least displays the desired behavior in
the two velocity asymptotes. When $v$ tends to zero, corresponding to $f=0$, we mathematically find that
the factors between the straight and round brackets in Eq. (18) both tend to unity, such that Eq. (18)
tends to the same $h=C.v$-limit as the single VB-unit cell models (cf. Eq. 6). This hence also implies that
Eq. (18) predicts the eddy-dispersion turns to zero when $v$ goes to zero, in agreement with physical
expectations. When $v$ tends to infinity, Eq. (18) tends to zero as well. Mathematically, this can be
understood from the fact that $f=1$ in this case (no time for lateral diffusion, all species remain on their
original side). As a consequence, the factor between the round brackets in Eq. (18) tends to zero.
Physically this makes sense as well, because, in the absence of any significant transversal exchange, both the species in the top zone and the bottom zone will each have travelled with an average velocity \((u_1 + u_2)/2\) at the end of the (double) unit dispersion cell. Since the velocity profile inside the VB-zones is that of a pure plug flow, there is no other contribution to dispersion, such that it is indeed obvious to see that \(h_{2\text{VB-UC}}\) tends to zero in the high \(v\)-limit.

Tending to zero at both velocity extremes, and thus going through an intermediate maximum, Eq. (18) is clearly differentiated from the current literature models for the eddy-dispersion (all based on a single-VB unit cell), monotonously increasing from \(h=0\) at \(v\) to saturate at \(v=A\.

Obviously more complex addition schemes (involving more than two unit cells) and more complex species transition schemes can be conceived (i.e., accounting for the fact that species can cross the axial VB split line more than once within the span of a single VB step), but it is believed this would only provide a marginal increase in accuracy, at the expense of a large increase in complexity.

3.3 Numerical velocity field calculations: formation of a preferential flow path

Before proceeding, it is instructive to investigate the fine details of the velocity distribution in a bed where the local packing density, and hence also the local permeability, displays a checkerboard distribution pattern. This was done using the computational fluid dynamics data (CFD) methods described in part II.

Fig. 3a shows the resulting velocity magnitude distribution. As expected, this displays the same general checkerboard pattern as the underlying packing density and flow permeability pattern. However, there is a distinct difference with the schematic representation given in Fig. 1a, as the coloring of the different fields is not uniform but displays a distinct pattern. Whereas the central region of each VB zone is marked by strong lateral gradients (with the strongest gradient occurring around the axial VB-division line), these gradients are totally absent at the beginning and end of each VB zones (cf. green regions with transversally uniform coloring).

Computing the average velocity in each individual packing density zone for the case considered in Fig. 3 (permeability ratio of the two different zones=1.2 with \(K_{v1}=1.43 \times 10^{-14} \text{ m}^2\); \(K_{v2}=1.19 \times 10^{-14} \text{ m}^2\), where ‘1” and “2” respectively refer to the zones with a high and a low packing density), it was found that \(u_1=0.958u_{av}\) and \(u_2=1.042u_{av}\) corresponding to a ratio \(u_2/u_1=1.09\). In other words, the ratio of the effective average velocities is not linearly proportional to the ratio of the permeability, but rather corresponds to its square-root value.

Next, it is important to remark not everything is as symmetrical as may appear from Fig. 3a. The corresponding streamline pattern shown in Fig. 3b clearly shows that streamlines starting in a given permeability zone do not run perfectly straight and parallel but are grouped in bundles that expand when reaching a zone with low permeability and contract when reaching a zone with high permeability. This is caused by the fact that the fluid always follows the path of the least resistance, such that a
streamline situated sufficiently close to the axial VB division line of the different permeability zones will have the tendency to cross this division line and move to the adjacent high permeability zone when approaching a low permeability zone. This pattern emerges because the extra distance to be covered by following a tortuous instead of a straight path is more than compensated by the reduction of the overall permeability gained by following the tortuous path. Continuously switching to the most advantageous side of the VB-split line, the species following this path permanently reside in a high velocity zone and hence have a higher average velocity than the species on streamlines that are too far from the VB division line to transfer to the adjacent high permeability zone. These streamlines have a lower average velocity than the centrally positioned streamlines meandering back and forth across the axial VB division line, which hence form a persisting preferential flow path.

The occurrence of this preferential flow path was further demonstrated using so-called particle trajectory analysis, wherein the position and speed of a set of hypothetical zero mass, zero size and zero diffusivity particles is tracked at every time step. Tracking five such tracer particles, all starting on the same vertical line (see blue dots added to Fig. 3b), with the central starting point lying exactly on the VB-division line, Fig. 4 clearly shows that the particle released in this central point has a consistently higher velocity than the four other particles which all tend to the same average velocity after having passed the first few cells. Note that the particles are only released in the inner half of the geometry because of the transversal symmetry of the velocity pattern.

It should also be noted that the above discussed type of preferential flow path should not be confused with a preferential flow path being created when a stream of liquid enters an axially extended region with low packing density. The latter type of preferential flow paths is already accounted for via the checkerboard permeability distribution. The preferential flow path referred to in the present section relates to a pure velocity redistribution phenomenon of a fluid flow spontaneously seeking the path of least resistance by meandering over adjacent zones with different packing densities.

### 3.4 Contribution of the preferential flow path and final expression for $h_{\text{eddy}}$

As numerically demonstrated in the previous section, the alternating pattern of high and low permeability regions leads to the creation of an uninterrupted preferential flow path slowly meandering over the axial VB division line (cf. position of horizontal dashed black line in Figs. 1b-c). The simplest conceivable physical representation of the band broadening effect of this preferential flow path is by overlaying the checkerboard pattern in Fig 1b with an additional high velocity region, axially oriented and centered around the axial VB split line (cf. Fig. 5a). As this high velocity-region persists over the entire column length, and therefore has an infinitely larger wavelength than the checkerboard velocity pattern, the effect of this high velocity zone can be represented with an infinite parallel zone model, consisting of one zone with a velocity equaling that of the high preferential flow path (dark blue region in Fig. 5b) and one with a velocity equaling the average of the two velocities of the checkerboard pattern far away from the interface (lighter blue region in Fig. 5b). The symmetry around the axial VB split line
further makes that only half of the original axial unit cell width needs to be considered when calculating the overall effect (cf. transition from Fig. 5a to 5b).

Given the velocity zones in Fig. 5b extend over an infinite length (in practice over the entire length of the bed), there will generally always be enough time for a sufficient diffusional exchange such that their band broadening contribution can be expected to be a purely linear C-term contribution:

$$h_{\text{pref}} = C_{\text{pref}} \cdot v$$  \hspace{1cm} (19)

Finally, adding the contributions originating from the checkerboard velocity distribution and that from the preferential flow path (resp. given by Eqs. 18 and 19), we obtain for the overall eddy-dispersion band broadening in a flow-through medium with a checkerboard distribution of the packing density:

$$h_{\text{eddy}} = h_{\text{checker}} + h_{\text{pref}} = C_v \left[ 1 - \frac{C_v}{4A} \cdot \left( 1 - e^{-4A/(C_v)} \right) \right] \cdot \left( 1 - e^{-A/C_v} \right) + C_{\text{pref}} \cdot v$$  \hspace{1cm} (20)

4. Properties of the solution and inclusion of velocity-dependence of the transversal dispersion

In a more general approach, the reduced velocity appearing in the equations in Eqs. (18)-(20) should be replaced by the more general:

$$v_t = \frac{u \cdot d_p}{D_{\text{trans}}}$$  \hspace{1cm} (21)

with $D_{\text{trans}}$ the transversal dispersion coefficient.

This generalization is needed because, as soon as the eddy-dispersion problem relates to VBs with a lateral width covering multiple parallel through-pores or particle rows, the transversal transport (which is responsible for the relaxation of the lateral velocity differences) no longer occurs by pure molecular diffusion but also has an important convective component. In its most commonly written form [21-23], $D_{\text{trans}}$ is assumed to consist of two terms: a pure diffusion term ($D_{\text{eff}}$), and a term that accounts for the advective contribution of the lateral transport:

$$D_{\text{trans}} = D_{\text{eff}} + \beta \cdot u \cdot d_p$$  \hspace{1cm} (22)

with $D_{\text{eff}}$ the effective molecular diffusion, having a value that typically only makes up some 30 to 60% of the $D_{\text{mol}}$-value because of the tortuosity and obstruction experienced by molecules diffusing through a porous medium [24]. In principle, the $D_{\text{eff}}$-contribution can be assessed directly from the longitudinal contribution to band broadening (using $H_B = 2 \cdot D_{\text{eff}} \cdot (1+k)/u$ [24]), as it is common to assume diffusion in packed chromatographic media is isotropic. Many literature values exist for the $\beta$-value appearing in the advection-dominated term of Eq. (22). Depending on the literature source, $\beta$ can vary between 1/12 and 7/16 [21]. Whereas other, more complex expressions have been proposed for the second term of Eq. (22) [12,23,25], we can, for the sake of the present argument, suffice with the simple linear form.

From Eqs. (21) and (22), it follows directly that the relation between $v$ and $v_t$ can be written as:

$$v_t = \frac{u \cdot d_p}{D_{\text{trans}}} = \frac{v}{\gamma_{\text{eff}} + \beta \cdot v}$$  \hspace{1cm} (23)
with $\gamma_{\text{eff}}$ the reduced effective diffusion ($\gamma_{\text{eff}}=D_{\text{eff}}/D_{\text{mol}}$).

When the lateral transport remains restricted to the width of a flow tube or inside a single through-pore, $D_{\text{trans}}$ simply remains given by [23]:

$$D_{\text{trans}} = D_{\text{mol}}$$  (24)

In this case, $\gamma_{\text{eff}}=1$ and $\beta=0$ such that Eq. (23) reduces to $v_T = v$.

After the above generalization, Eq. (20) can be finally written as:

$$h_{\text{eddy}} = C v_t \left[ 1 - \frac{C v_t}{4A} \left( 1 - e^{-4A/(C v_t)} \right) \right] \left( 1 - e^{-\frac{A}{C v_t}} \right) + C_{\text{pref}} v_t$$  (25)

### 4.1 Case 1: transversal dispersion via pure molecular diffusion

Fig. 6a shows the course of the $h_{\text{eddy}}$-curve, and its two constituent contributions ($h_{\text{checker}}$ and $h_{\text{pref}}$) as represented by Eq. (25) for the case where $D_{\text{trans}} = D_{\text{mol}}$ and for some typical values of $A$, $C$ and $C_{\text{pref}}$. As can be noted, the band broadening contribution associated with the checkerboard velocity distribution ($h_{\text{checker}}$, red curve) displays a clear maximum, as the curve tends to 0 at both ends of the $v$-range. Taking the derivative of Eq. (18) with respect to $v$ and equating it to zero, it is found that the curve reaches its maximum when:

$$v = v_{\text{max}} = 0.830 \frac{A}{C}$$  (26a)

regardless of the value of $A$ and $C$. Reintroducing this result into Eq. (18) shows that the height of the $h_{\text{checker}}$-curve maximum is always given by:

$$h_{\text{checker}} = 0.482 A$$  (26b)

This implies the maximum height of the $h_{\text{checker}}$-contribution only depends on $A$, i.e., on the relative velocity difference and the axial length of the VB-zones (cf. Eq. 5) and is independent of $C$, i.e., independent of the diffusion coefficient or the width of the VB zones.

Fig. 6a also shows that the composite $h_{\text{eddy}}$-curve (Eq. 25) can generally be expected to display three distinct regimes. At very low $v$, the curve rises with a slope equal to $C$. Then, in some intermediate region, the curve goes through a local maximum before eventually increasing again linearly with $v$, but now with $C_{\text{pref}}$ as the slope.

Since the maximum of the $h_{\text{checker}}$-contribution is independent of $C$, the $C$-term contribution has, next to its effect on the horizontal position of the maximum (cf. Eq. 26a), essentially an effect on the slope of the curve left and right of the optimum: the higher $C$, the steeper the slopes. This can be readily assessed when comparing the $h_{\text{checker}}$-contribution in Fig. 6b with that in Fig. 6a, considering the $C$-constant was taken 5 times higher in the case in Fig. 6b, hence producing a sharper maximum. This is also reflected in the aggregate curve for $h_{\text{eddy}}$, displaying a sharper local dispersion maximum than in the
former case. On the other hand, when the C-constant is smaller, the optimum becomes broader. This can be assessed by comparing Fig. 6c with Fig. 6a, also showing that a low enough C-value can lead to a situation where the local dispersion maximum is no longer visible in the overall h_{eddy}-curve.

Finally, Fig. 6d illustrates the essence of Eq. (26b), showing that halving A indeed leads to a halving of the maximum of the h_{checker}-contribution (h_{checker,max} = 0.482 compared to h_{checker,max} = 0.964 in Figs. 6a-c).

4.2 Case 2: transversal dispersion with advective contribution

Fig. 7a shows the course of the h_{eddy}-curve predicted by Eq. (25) for the case of a velocity-dependent transversal dispersion (i.e., for D_{trans} given by Eq. 22). Comparing with Fig. 6a (having exactly the same A, C en C_{pref}, only the v-dependency of D_{trans} is different), it can clearly be noted that the existence of a linear velocity-dependence term in D_{trans} completely changes the course of the curves for both constituent contributions (h_{checker}, red curve and h_{pref}, gray curve) as well as for the aggregate effect (h_{eddy}, black curve). The h_{eddy}-curve no longer goes through a local dispersion and clearly levels off to a finite value in the high v-range. Looking more in detail, it is observed that, for large v, the h_{pref} and the h_{checker}-values are respectively much higher and much lower than in the D_{trans} = D_{mol}-case in Fig. 6. The former obviously is the consequence of the fact that h_{pref} in the present case tends to C_{pref}/β at high v, which is generally much smaller than the h_{pref}C_{pref}.v-values that prevail in the large v-limit in the D_{trans} = D_{mol}-case. The latter (higher h_{checker}-values compared to D_{trans} = D_{mol}-case for same A and C in Fig. 6) is caused by the fact that D_{trans} = β v.D_{mol} in the high v-range in the present case, which inevitably is much larger than the D_{trans} = D_{mol}-values in the case considered in in Fig. 6. This strongly increased transversal dispersion strongly diminishes the possibility for a velocity bias rectification within the same unit dispersion cell, for the latter requires the species to stay on the same side of the axial VB-line, hence the larger h_{checker}-contribution at large v. Mathematically, this is represented by the fact that, as soon as D_{trans} contains a convective term, the part between straight brackets in Eq. (18) no longer tends to zero in the v→∞-limit but tends to a finite value, given by 1-exp(-A.β/C).

Fig. 7b shows that, at least qualitatively, the curve predicted by the checkerboard model (black curve) appear very similar to the curves predicted by the Giddings or the FPZ-model (resp. blue and red curves in Fig. 7b). However, they clearly level off to a completely different asymptotical value. Whereas it is well known that the 1VB-cell models (assuming D_{trans} = D_{mol}) in their v→∞-limit tend to:

\[ h_{Gidd}(v \rightarrow \infty) = h_{FPZ}(v \rightarrow \infty) = A, \]  

\[ (27) \]

it can be mathematically shown that for the 2VB-cell model this limit goes to:

\[ h_{eddy}(v \rightarrow \infty) = \frac{C}{\beta} \left[ 1 - \frac{C}{4A\beta} \cdot (1 - e^{-4A\beta/C}) \right] \cdot (1 - e^{-A\beta/C}) + \frac{C_{pref}}{\beta} \]  

\[ (28) \]

In the low v-limit on the other hand, all models reduce to the same limiting form:

\[ h_{eddy}(v \rightarrow 0) = C.v \]  

\[ (29) \]
hence explaining why all $h_{\text{eddy}}$-models coincide in the low $v$-range of Fig. 7b.

The fact that Eq. (27) and (28) are fundamentally different implies that, for the same velocity bias, i.e., for the same $A$ and $C$, the 2VB-model leads to a significantly lower $h_{\text{eddy}}$-value in the large $v$-range than the 1VB-cell models used up to now in literature. This even holds when $C_{\text{pref}}=0$, whose occurrence in the expression for $h$ is another differentiating factor between the checkerboard model and the 1VB-cell models.

This is a new finding and might shed new light on earlier studies where often a lower $h_{\text{eddy}}$ is observed than what was expected based on the $A$- and $C$-values estimated from the details of the velocity field. For example, Gritti and Guiochon found in [16] a $h_{\text{eddy}}$ that was only half of what was expected based on the velocity biases and could only obtain agreement with the dispersion data computed in [26] after lowering the $A$-value. Another example is the numerical computation in [27], where most values for the $A$-constant of the short-range interactions fall well below the theoretically expected 0.5. With the 2VB-cell model, there is now a model explaining how a given set of $A$- and $C$-values can lead to significantly lower $h_{\text{eddy}}$ than expected based on the Giddings or the FPZ-model.

5. Conclusions

The present study invalidates the assumption underlying Giddings' random walk model that the individual dispersion steps in flows through heterogeneous media such as the packed bed and monolithic columns used in liquid chromatography are additive. However, it has also been demonstrated an eddy-dispersion model can be constructed that does not suffer from this problem but is fully additive in the upper as well as in the lower end of the reduced velocity range. To achieve this, it is important that the different individual velocity bias (VB) steps are not treated as isolated steps as is done in the single VB models in literature (Giddings model, FPZ-model), but to recognize that each VB zone is connected to a next VB zone carrying an opposite sign, such that a (partial) rectification of the band broadening experienced in the preceding VB step may occur.

The newly proposed model therefore uses a double VB-zone as its unit dispersion cell. In addition, the model also recognizes that the alternation of high and low permeability zones leads to a persisting preferential flow path producing an extra C-term type contribution. In systems where the transversal transport occurs by pure molecular diffusion, the model predicts the potential occurrence of a local dispersion maximum. When the transversal transport also contains a convective component, the model predicts a $h_{\text{eddy}}$-curve with a velocity-dependence that is qualitatively similar to the Giddings and FPZ-models, such that the new model can be expected to fit equally well to the existing experimental data. However, the $h_{\text{eddy}}$-values predicted by the new model are, for a given velocity bias, i.e., for a given set of $A$- and $C$-constants, considerably lower (up to 50%) than those predicted by the Giddings and FPZ-models, which do not incorporate a VB rectification mechanism. This implies the new model may
provide an explanation for the fact that the Giddings model tends to overestimate the observed eddy-
dispersion, as was observed in a number of recent literature reports.

References

Figure Captions

**Figure 1.** (a) Checkerboard model representation of an idealized distribution of low and high velocity regions in a heterogeneous flow-through medium. Light blue=low velocity region (dense packing, low permeability); Light blue=low velocity region (dense packing, low permeability). Red rectangular dashed box represents the axial unit cell determining the eddy-dispersion in the entire bed. White dashed line in the middle represents the axial division line of the velocity bias zones. (b,c) Sequential images of a hypothetical narrow band of tracer moving through the axial unit cell for the case of (b) a very low reduced velocity $v$ and (c) a very high reduced velocity $v$.

**Figure 2.** (a) Double velocity bias (2VB) unit dispersion cell with red arrows indicating the fraction ($f$) of tracer species still on the same side of the axial division line at the end of the first half of the unit dispersion cell and the fraction (1-$f$) that already has been exchanged with the opposite side of the axial division line. (b) Effective velocity patterned experienced by species of fraction $f$. (c) Effective velocity patterned experienced by species of fraction 1-$f$.

**Figure 3.** (a) CFD-computed velocity distribution in flow-through medium with checkerboard distribution of packing density and ensuing local permeability. Permeability ratio $K_{v1}/K_{v2}=1.2$ and true zone aspect ratio $\lambda_{ax}=1/2.\lambda_{trans}$. (b) Corresponding streamline pattern. See text for description of numbered dots. System parameters: $K_{v1}=1.43 \times 10^{-10} \text{m}^2$, $\lambda_{ax}=20 \mu\text{m}$, $u=1\text{mm/s}$. Colour scale varies linearly with local velocity magnitude (highest=red). White tortuous line added to (a) to emphasize meandering nature of preferential flow path.

**Figure 4.** Particle tracking analysis showing particle speed as a function of the elapsed time. See Fig. 3b and text for definition of tracking particle numbers.

**Figure 5.** (a) Overlay of checkerboard with high velocity region representing the existence of a preferential flow path automatically establishing in a system with a checkerboard distribution of packing densities and bed permeabilities. (b) Simplified effective velocity pattern induced by presence of preferential flow path.

**Figure 6.** Course of $h_{\text{eddy}}$ (black curve) and its two constituent contributions ($h_{\text{checker}}$ (red curve) and $h_{\text{pref}}$ (gray curve)) as predicted by Eqs. (18-20) for the case where $D_{\text{trans}}=D_{\text{mol}}$, with (a) $A=2$ and $C=1$; (b) $A=2$ and $C=5$; (c) $A=2$ and $C=0.2$; (d) $A=1$ and $C=1$. $C_{\text{pref}}=0.05$ in all cases.

**Figure 7.** (a) Course of $h_{\text{eddy}}$ (black curve) and its two constituent contributions ($h_{\text{checker}}$ (red curve) and $h_{\text{pref}}$ (gray curve)) as predicted by Eqs. (18-20) for the case where $D_{\text{trans}}=D_{\text{eff}}+\beta u d_p$ and with $A=2$, $C=1$, $C_{\text{pref}}=0.05$ and $\beta=0.3$. (b) Comparison of $h_{\text{eddy}}$-curves predicted by the checkerboard model (black) and the two 1VB-cell models: Giddings- (blue) and FPZ-model (red). Same $A$, $C$ and $C_{\text{persist}}$ as in (a).
Figure 5

(a) 

(b)